Progress and status of radioanalytical chemistry of radionuclides

Hou, Xiaolin

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Verbal presentations

PLE-I00, (Id: 450)

ADVENTURES IN ACTINIDE NUCLEAR AND RADIOCHEMISTRY

Heino Nitsche

UC Berkeley and Lawrence Berkeley National Laboratory
hnitsche@berkeley.edu

In the spirit of the Hevesy Award, this talk will cover selected examples of my research during the last four decades. My work has been focused on the chemistry of the actinides and the superheavy elements. I will discuss research within actinide chemistry related to solution thermodynamics of uranium, neptunium, plutonium, and americium, as well as their sorption and biological interactions with geologic matrices, for the performance assessment of potential high-level nuclear waste repositories and environmental remediation. Additionally, I will present my work on the physics and chemistry of the heaviest elements, including the confirmation of new elements, discovery of new isotopes, and one-atom-at-a-time chemistry.

PLE-I01, (Id: 446)

FUKUSHIMA ACCIDENT: RADIOACTIVITY IMPACT ON ENVIRONMENT, LAND AND OCEAN

Michio Aoyama

Institute of Environmental Radioactivity, Fukushima University
r706@ipc.fukushima-u.ac.jp

Radioactive materials were released to the environment from the Tokyo Electric Power Company Fukushima Dai-ichi Nuclear Power Plant (FNPP1) as a result of reactor accidents caused by a total loss of electric power (black out) after the Tohoku earthquake and tsunami on 11 March 2011. Radioactive materials were emitted into the atmosphere and transferred to the land and ocean through wet and dry deposition. In addition, highly contaminated water was directly released to the ocean. Therefore radioactive materials were released to the ocean by two major pathways, atmospheric deposition and direct release from the site.

Regarding with ^{137}Cs, ca. 2% of ^{137}Cs (15 PBq) of total inventory of the three melt down cores of which total inventory was 700 PBq, were released into the atmosphere then 80 % of atmospheric release were deposited in the ocean. Twenty percent of ^{137}Cs (141 PBq) were dissolved in the stagnant water in turbine buildings and surrounding areas by the accident. 0.5 % of ^{137}Cs (3.5 +- 0.7 PBq) were directly released in the ocean. Since the ^{134}Cs to ^{137}Cs activity ratio was almost 1 at the time of the accident, same amount of ^{134}Cs were injected in the environment as well as that of ^{137}Cs stated above. The total amount of deposited ^{137}Cs in Japan was estimated to be 2.9 PBq based on aerial monitoring in Fukushima prefecture and daily deposition monitoring at 50 stations in each prefecture.

The oceans are important sinks of anthropogenic pollutants, such as radionuclides, heavy metals and organic compounds, that are mainly atmospherically derived and/or directly discharged, but there is little information on their overall transport process during several decades after their injection. The bulk of the anthropogenic radionuclide ^{137}Cs present in the oceans today was injected about five decades ago from atmospheric nuclear weapons tests and total inventory of ^{137}Cs in the North Pacific Ocean was 69 PBq just before the FNPP1 accident. Until the end of 2011, a main body of Fukushima derived radiocaesium were existed at surface layer, however, after winter cooling 2011/2012 we found subsurface maximums of Fukushima derived ^{134}Cs and ^{137}Cs due to subduction in the subtropical gyre in the North Pacific Ocean. The subsurface maximums corresponded wiith SubTropical Mode Water (STMW) and Central Mode Water (CMW). The water column inventory shallower than 200 meters depth in November 2011 at 40 deg. N, 165 deg. E was 80 % of total, while it decreased 20 % in June 2012.

In winter 2013/2014, ^{137}Cs activity in surface water close to the FNPP1 site is still around 1000 Bq m-3 while a maximum of Fukushima derived ^{137}Cs in surface water were observed at the eastern part of the North Pacific Ocean and the ^{137}Cs activity was a few Bq m^{-3} which is already close to pre-Fukushima level and ^{134}Cs activity in surface water was less than 1 Bq m^{-3}.

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PLE-I02, (Id: 181)

PROGRESS AND STATUS OF RADIOANALYTICAL CHEMISTRY OF RADIONUCLIDES

Xiaolin Hou

Technical University of Denmark, Center for Nuclear Technologies
xiho@dtu.dk

In the studies of radioecology, investigation of environmental radioactivity and environmental processes using radionuclide tracer, as well as characterisation of nuclear waste for decommissioning of nuclear facilities and depository of radioactive waste, nuclear forensics and geological dating using radioisotopes, the key issue is to accurate determination of concentration of various radionuclides and their speciation in different environmental, biological and geological materials. Radioanalytical chemistry therefore plays a central and critical role in these works. Since the discovery of radioactivity a century ago, many separation and detection methods have been developed and successfully applied in the determination of various radionuclides. With the development of new separation and detection techniques, significant improvement of the traditional analytical techniques, as well as the increased requirement for the knowledge and information on the speciation of radionuclides, a significant development on radioanalytical chemistry has been achieved in the past decade, this mainly focus on three aspects including the synthesis and commercialization of various extraction chromatographic resins and application of them in the separation of specific radionuclide or groups of radionuclides; sensitive detection of long-lived radionuclides using mass spectrometric techniques including ICP-MS and accelerator mass spectrometry; development of various approaches for rapid determination of radionuclides of difficult to measure in order to quick responses in the emergency preparedness and analysis of large numbers of samples for decommissioning of nuclear facilities.

In the past years, our laboratory has developed a series of radiochemical analytical methods aiming at characterization of various decommissioning waste; improved our traditional analytical methods for determination long-lived radionuclides in the environment focusing on improving the detection limit, automation of analytical operation, and rapid determination; developed many analytical methods for speciation analysis of various radionuclides in environmental and biological samples for radioecology researches, and developed and applied mass spectrometric methods for rapid and sensitive determination of long-lived radionuclides. This presentation gives an overview of these analytical methods, mainly on the present status, progress and perspectives.

PLE-I03, (Id: 422)

POSITIONING THE NEW ELEMENTS IN THE PERIODIC TABLE

Andreas Türler

Paul Scherrer Institute and Bern University
andreas.tuerler@psi.ch

With the discovery of six new elements in the past decade an extraordinary expansion of the Periodic Table took place, so that now all elements of the 7th period have been synthesized. This success was possible by exploiting the concept of “warm” fusion using the available, neutron-rich actinide target materials and the tightly bound, doubly magic projectile ^{48}Ca [1]. Most of these discovery experiments were conducted by the Dubna-Livermore collaboration at the Flerov Laboratory in Dubna, Russia and a number of independent experiments have been able to confirm these findings [2-4], most recently for element 117 [5]. Due to the discovery of relatively long-lived isotopes of copernicium (element 112) and flerovium (element 114) first chemical experiments have successfully been conducted, revealing the special chemical properties of these elements, which can be attributed to the influence of strong relativistic effects [6,7]. Substantial progress has also been achieved in investigating the lighter heavy actinide and transactinide elements, where new properties of heavy actinide elements and new classes of tansactinide containing compounds have been synthesized. In my lecture I will review these recent developments and give an outlook on upcoming opportunities for chemical investigations of heavy and superheavy elements.

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PLE-I04, (Id: 433)

COMPARISON OF EIGHT POSSIBLE 99-MOLYBDENUM PRODUCTION ROUTES

Bert Wolterbeek, Jan-Leen Kloosterman, Martin Rohde, Danny Lathouwers, August Winkelman, Lodewijk Frima, Frank Wols

Delft University of Technology
h.t.wolterbeek@tudelft.nl

The present paper addresses eight possible routes of producing ^{99}Mo, and discusses both yield and ^{99}Mo specific activities (SA) in the context of future anticipated worldwide demand. The dimensions of the targets are modelled by considering both the limits set by cooling and those by inside-target radiation attenuation characteristics. Energy deposition profiles are modelled by MCNP6, the reaction probabilities are taken from TALYS/TENDL and JANIS codes, and both are used in calculating produced ^{99}Mo.

The results suggest that U neutron-fission may remain one of the most relevant and efficient means of producing ^{99}o, but that new developments may surface, such as ADSR or AHR production modes. Accelerator- based ^{99}Mo production is discussed as asking for developments in both the cooling of targets and new concepts in post-EOB upgrading of ^{99}Mo SA, and/or new concepts for ^{99}Mo/^{99m}Tc-generators, the latter possibly in both volumes (mass) and ^{99}Mo capacities.

PLE-I05, (Id: 441)

CHEMISTRY FOR THE FUTURE NUCLEAR FUEL CYCLES

Stéphane Bourg

CEA, Nuclear Energy Division, RadioChemistry & Processes Department
stephane.bourg@cea.fr

Actinide chemistry is at the centre of key issues to be faced by nuclear energy. Indeed, in addition to an increased safety of the reactors themselves, the acceptance of the nuclear energy is still closely associated to our capability to reduce the lifetime of the nuclear waste, to manage them safely in a long term disposal and to propose options for a better use of the natural resources. Before implementing a process at the industrial level, it is of primary importance to increase our fundamental knowledge in actinide sciences in terms of safety, fabrication and performance of fuels, reprocessing and long term waste management.

Among FP7-EURATOM Framework Program, a few projects work closely to address the challenges of future fuel cycles. Among them, SACSESS (Safety of ACtinide SEparation proceSSes) and TALISMAN work to improve our knowledge in actinides chemistry in order to develop advanced separation processes. SACSESS is focused on the development of safe advanced separation processes, both aqueous and pyrochemical. Head-end steps, fuel refabrication, solvent treatment, waste management are also taken into account.

TALISMAN (Transnational Access to Large Infrastructures for a Safe Management of ActiNides) gives European researchers the opportunity to come and work in unique facilities. By offering transnational access to the main European nuclear research facilities, TALISMAN aims at increasing the knowledge in actinide sciences by gathering all the expertise available in nuclear research institutes or university in Europe and giving them the opportunity to come and work in hot-labs or beamlines.

Exchanges and complementarities are also established with other Euratom initiative (ASGARD, CINCH-II…) to cover broadly the nuclear fuel cycle challenges.

In all projects, efforts have been made to increase collaborations, mutualize and homogenize procedures and share good practices. Training and education initiatives including seminars, workshops, brainstorming meeting but also student exchanges and support to post-doctorate fellowships is a key point for maintaining and increasing a high expertise level in actinide separation sciences in Europe.

PLE-I06, (Id: 73)

TARGETED ALPHA THERAPY RESEARCH - A RADIOCHEMISTRY PERSPECTIVE

Emma Aneheim[a], Sture Lindegren[a], Holger Jensen[b]

[a]Sahlgrenska Academy at Gothenburg University
[b]Copenhagen University Hospital
emma.aneheim@radfys.gu.se

One of the greatest challenges in the treatment of different types of cancers is an efficient therapy of occult metastasis. Today chemotherapy is generally employed as an adjuvant treatment to eradicate the minimal residual disease. However, despite that chemotherapy often is a very aggressive method the cancer cells can transform and become resistant towards the chemicals used. This means that the quality of life of the patient is affected in a negative way without resulting in a therapeutic effect. Therefore, new types of treatment for disseminated cancer are of vital importance. One such method is targeted alpha therapy.

Targeted alpha therapy utilizes the high energy and short tissue range (50-100 μm) of the alpha particles. This range is orders of magnitude shorter than the beta particle range from other radionuclides widely used within nuclear medicine, such as iodine-131 or yttrium-90, resulting in a significantly higher LET for the alpha particles. This means that if administered to the cancer cells by a tumor specific carrier agent, e.g. an antibody, the alpha emitting nuclide efficiently kills the tumor cell by causing irreparable double strand breaks of the DNA, while sparing the surrounding healthy tissue. This makes the method suitable for treatment of disseminated occult cancers in the form of micro tumors and even single cancer cells. A radioactive nuclide with suitable properties is, however, needed to conduct this type of treatment. The half-life should be relatively short to be able to achieve a high dose and avoid prolonged irradiation in the body but still long enough to be able to perform the radio synthesis and allow for distribution to the target cells. In the same way the daughter nuclides must have a suitable decay pattern. The production route should also be fairly straight forward to ensure availability of the nuclide. One nuclide that fulfils these demands is astatine-211.

Astatine-211 is produced using a cyclotron by circa 30MeV alpha particle activation of bismuth-209 through the reaction $^{209}\mathrm{Bi}(\alpha, 2n)^{211}\mathrm{At}$. The half-life is 7.2 hours and the mode of decay is 100 % alpha emission along two different routes. Astatine-211 is therefore a promising nuclide for targeted alpha therapy. At Sahlgrenska Academy in Gothenburg, Sweden, radiolabelling research of monoclonal antibodies and polypeptides using astatine-211 has been on-going for almost 20 years. The research is performed within the targeted alpha therapy (TAT)-group that are moving towards phase II/III clinical trials using astatine labelled monoclonal antibodies for patients with disseminated ovarian cancer. This after a successful phase I trial conducted in 2009. The TAT-group is an interdisciplinary group consisting of chemists, physicists, biologists and clinicians from different research centers.

Today efforts concerning radiochemistry within the group are directed towards increasing the specific activity of the immunoconjugates, investigating the shelf-life of the prefabricated conjugates before labelling and designing new linker-molecules. There is also a focus on simplifying the chemical production route by automating the radio synthesis.

Radionuclides in the Environment, Radioecology (RER)

Verbal presentations

RER-I01, (Id: 119)

MOBILITY OF RADIOCAESIUM IN BOREAL FOREST ECOSYSTEMS: INFLUENCE OF PRECIPITATION CHEMISTRY

Eiliv Steinnes

Norwegian University of Science and Technology
eiliv.steinnes@chem.ntnu.no

Mobility of radiocaesium in boreal forest ecosystems: Influence of precipitation chemistry Steinnes E1, Gjelsvik R2, Skuterud L2, Thørring H2 1. Department of Chemistry, Norwegian University of Science and Technology, No-7491 Trondheim, Norway 2. Norwegian Radiation Protection Authority, NO-1332 Østerås, Norway Mobility and plant uptake of Cs in soils is generally limited by the presence of clay minerals in the soil. However, cations supplied by precipitation may substantially influence the mobility of radiocaesium in natural surface soil and subsequent transfer to food chains. The chemical composition of precipitation shows substantial variation among different areas in Norway for two main reasons. At sites close to the coast the atmospheric supply of marine cations and anions is many-fold greater than in regions shielded from marine influence by mountains. The southernmost part of the country has been, and still is, substantially affected by soil acidification due to long-range atmospheric transport of acidifying substances from areas elsewhere in Europe. This may explain a much higher greater uptake of ^{137}Cs from the Chernobyl accident in moose in this region than elsewhere (Steinnes et al., 2009), in spite of the fact that some areas farther north received substantially greater fallout. Similarly a much greater transfer of ^{137}Cs to natural birch forest vegetation is evident from the more acidified soils in the south than in comparable ecosystems elsewhere in the country (Thørring et al., 2012). Repeated recordings of activity levels in natural surface soils showed faster leaching of Chernobyl ^{137}Cs relative to inland areas not only in the south but also in coastal areas farther north (Gjelsvik and Steinnes, 2013), indicating that the amounts of marine cations in precipitation also has an appreciable effect on the Cs leaching. The geographical leaching differences still became less prominent with time. Recent lysimeter experiments with undisturbed soil columns obtained from an area receiving high radiocaesium deposition from the Chernobyl accident, applying precipitation with ionic composition characteristic of the different regions mentioned above, did not change the current depth distribution of ^{137}Cs. However, acidic precipitation increased the mobility of Cs added during the experiment. All in all the mobility in boreal soils of freshly added radiocaesium may be considerably affected by the chemical composition of precipitation.

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RER-I02, (Id: 182)

STUDY OF ^{137}Cs, ^{241}Am AND PU ISOTOPES SORPTION BEHAVIOR IN THE ENVIRONMENT: PRAGUE – VILNIUS COLLABORATION*

Galina Lujaniene

SRI CENTER FOR PHYSICAL SCIENCES AND TECHNOLOGY
lujaniene@ar.fi.lt

Results of long-term collaboration with the Czech Technical University in Prague are reported. Sorption behavior of ^{137}Cs, ^{241}Am and Pu isotopes was studied with the aim of better understanding their migration mechanisms in the Triassic clay selected for engineered barrier of the near surface low and intermediate level radioactive waste repository, as well in soil and bottom sediments from the natural environment.

The Baltic Sea bottom sediments and well characterized clay samples with different amounts and compositions of iron oxides as well as synthetic magnetite, goethite and hematite were used in equilibrium and kinetic sorption experiments. Sorption was studied as a function of pH, a composition of solutions, and a contact time. The character of Cs, Pu and Am bonding was analyzed by sequential extraction (SE). Solvent extraction techniques, ultrafiltration and alpha spectrometry as well as ICP-MS were employed to characterize the oxidation states of the formed plutonium species. Two Chernobyl soil cores were also analyzed on the vertical distribution of radionuclides, their bonding to soil components, as well as on Pu oxidation state distribution. Experimental data obtained from the laboratory and field observations were used in modeling.

Despite their similar sorption kinetics, Pu(IV), Pu(V) and Am(III) showed different bonding to soil, clay and bottom sediment coatings. Pu was predominantly associated with amorphous Fe-oxides and natural organic matter sites, whereas in the case of Am(III), the exchangeable and carbonate sites played the principal role. It has been shown that Pu(V) sorption mechanism includes a very fast Pu(V) reduction (reaction rate $\leq 2.33\times10^{-3}s^{-1}$) to Pu(IV) and partly to Pu(III). Following reduction Pu isotopes were bound to various components of bottom sediments via ion exchange and surface complexation reactions and a slow incorporation into the crystalline structure of Fe minerals. Kinetics experiments showed that the sorption of Cs(I), Pu(V), Pu(IV) and Am(III) to bottom sediments from natural seawater was controlled by the inert layer diffusion process.

The analyses of data obtained from sorption experiments, field observations and speciation of radionuclides have indicated a slightly higher migration potential for Am both in the Chernobyl soil and the natural clay minerals. The exchangeable and carbonate bound Am(III) should display faster migration rate and greater bioavailability in the environment.

*) Dedicated to the memory of Prof. Petr Beneš

RER-V03, (Id: 305)

JOINT BRATISLAVA-PRAGUE AMS/IBA STUDIES USING TANDEM ACCELERATOR

Pavel Povinec[a], **Ivo Světlík**[b], **Jan John**[c], **Miroslav Ješkovský**[a], **Mojmír Němec**[c], **Jan Kučera**[b]

[a]*Faculty of Mathematics, Physics and Informatics, Comenius University, Bratislava, Slovakia*
[b]*Institute of Nuclear Physics, Czech Academy of Sciences, Řež near Prague, Czech Republic*
[c]*Faculty of Nuclear and Physical Engineering, Czech Technical University, Prague, Czech Republic*
povinec@fmph.uniba.sk

A joint research programme has been established to study anthropogenic radionuclides in the environment using Accelerator Mass Spectrometry (AMS), namely ^{14}C variations in the atmosphere and biosphere, and content of plutonium isotopes in the atmosphere and hydrosphere. Specifically, observations of ^{14}C variations in the atmosphere and biosphere around the Czech and Slovak nuclear power plants wil be presented and discussed in detail. Ion Beam Analysis (IBA) techniques have ben applied for radiation damage studies of construction materials of nuclear reactors, and of electronics components working in high radiation fields, e.g. at nuclear reactors and in space instruments.

*) Dedicated to the memory of Prof. Petr Beneš

RER-I04, (Id: 51)

NATURAL RADIONUCLIDES IN DRINKING WATER FROM THE SURROUNDINGS OF THE FORMER ŽIROVSKI VRH URANIUM MINE

Ljudmila Benedik[a], **Hiacinta Klemenčič**[b], **Janja Smrke**[a]

[a]*Jožef Stefan Institute*
[b]*Žirovski vrh mine*
ljudmila.benedik@ijs.si

Under articles 35 and 36 of the European Atomic Energy Community (EURATOM) Treaty, the Member States of the European Union are obliged to inform the European Commission on a regular basis of the radioactivity levels in their environment. The Council directive 2013/51/EURATOM of 22 October 2013 laying down requirements for the protection of the health of the general public with regard to radioactive substances in water intended for human consumption, defines the maximum values for individual radionuclides to be monitored in drinking water. In the present study, the concentrations of the natural radionuclides Po-210, Ra-226, U-238 and U-234 were determined in surface, well and drinking water by alpha-particle spectrometry, while Pb-^{210} and Ra-228 were determined by beta counting and gamma-ray spectrometry. The tap water samples were collected on target areas and villages in the surroundings of the former uranium mine at Žirovski vrh, Slovenia to assess the effective exposure of the public. Many small springs used for water supply were included in this study. For determination of Po-210, Pb-210 and uranium radioisotopes, a sequential method was used. After addition of U-232 and Po-209 tracers and Pb^{2+} carrier, the radionuclides were coprecipitated with MnO_2. Separation was carried out by selective separation of lead and polonium on a Sr resin column. Uranium was not retained and was determined in the effluent by separation on UTEVA resin. The procedure for Ra-226 was based on coprecipitation of $Pb(Ra)(Ba)SO_4$, followed by alpha-particle spectrometry and determination of the recovery with Ba-133. For determination of Ra-228 coprecipitation with $Ra(Ba)SO_4$ was performed and measured via its daughter Ac-228 by gamma-ray spectrometry. The results obtained show that values of natural radionuclides in drinking water from a private well in the surroundings of the former uranium mine were below values defined in the Directive.

RER-V05, (Id: 116)

SEPARATION OF URANIUM FROM DRINKING WATER IN THE CZECH REPUBLIC

Jan Krmela

ÚJV Řež, a.s.
jan.krmela@ujv.cz

Natural ground water used for the preparation of drinking water contains a number of cations, anions, elements and other substances depending on the bedrock composition (Ca, Mg, Fe, Mn, heavy metals, radioactive elements, arsenic, chromium, carbonates, sulfates, phosphates, silicates, fulvic and humic acids etc.). Information about composition of drinking water is important to comply with all the requirements on sanitary of drinking water.

The elements that affect the quality of drinking water mainly from groundwater, also includes radioactive elements contained in bedrock sections where water is extracted. These are the elements with long half-lives, mainly alpha emitters (U, Ra, Rn, Th, and elements of the decay series). Uranium and its decay products are found in all environmental compartments. Radionuclides come to the environment both naturally - weathering and leaching of the rocks, and as a consequence of human activities in connection with the use of raw materials.

Uranium occurs naturally in four oxidation states. The most mobility has hexa-valent state (uranyl ion). Uranyl is highly soluble form of uranium in water. Mobility of uranium in soil and water is affected by many factors. Complex processes in soil and rock lead to redox reactions forming both insoluble compounds (lower valence forms of uranium) and soluble form of U (VI) (forming by reoxidation), which is again leachable into groundwater. The content of uranium in groundwater depends on the geological composition of the ground, and can reach up to hundreds of μg/L.

At present the issue associated with removing uranium from drinking water is solved in the Czech Republic. New limit for the concentration of natural uranium (^{234}U, ^{235}U and ^{238}U) was recommended at a level of 15 μg/L as the highest limit based on the World Health Organization (WHO). Advice of the Chief Health Officer of the Czech Republic came into force on 1st January 2010, which decreased the limit for uranium in drinking water from original 30 μg/L to new 15 μg/L recommended by WHO. However, the WHO reported a new limit value of 30 μg/L in 2011 based on a new studies, which proved that 30 μg/L uranium in drinking water has not negative effect on the human organism (chemical toxicity). Limit in the Czech Republic remained at the same level 15 μg/L.

Change the limit leaded to solving the issue on the waterworks in the Czech Republic, which had not any experiences with radioactivity. Some waterworks installed a new device from Germany (ion exchanges), but did not solve what they do with saturated ion exchanges. Ion exchanges as the most suitable material for removing of uranium from drinking water is not reused (without regeneration), but it is used in the uranium industry, where is putted to start of processing of uranium ore. Ion exchanges are replaced with a new one in the waterworks and saturated ion exchanges are discarded in the uranium industry.

Regeneration of ion exchanges could be cheaper, because ion exchanges could be reused and processing of ion exchangers could be cheaper, because it is possible to put the regenerant before the process of precipitation of “yellow cake” in the processing of uranium ore. This project TA02010044 was supported by TA CR.

RER-V06, (Id: 113)

SORPTION BEHAVIOR OF Sr(II) AND Am(III) IONS FROM INDUSTRIAL WASTE WATER BY LOW COST NATURAL MATERIALS OF THE BIOLOGICAL ORIGIN

Leon Fuks, Agata Oszczak

Institute of Nuclear Chemistry and Technology
leon.ichtj@gmail.com

Waste waters that contain radioactive metal ions like Sr(II) or Am(III) are dangerous for the environment. There are several methods to remove them from waste water using ion exchange resins, chemical precipitation or reverse osmosis. Very often sorption, precipitation or complexation is combined with ultrafiltration in one hybrid process of enhanced ultrafiltration. Small ions bound by macromolecular agents form complexes, which can be retained by UF membrane. The hybrid complexation-UF method is effectively applied in several plants processing α-bearing radioactive waste streams. Multiple installations are under operation in nuclear centers and much effort was done to implement ultrafiltration for radioactive wastes processing. All these methods, however, are highly energy consuming thus expensive.

Alternative method of eliminating the radioactive metals from waste water is sorption by low cost natural materials of the biological origin. The major advantages of sorption over conventional treatment methods include: (i) low cost, (ii) high efficiency, (iii) minimization of chemical and/or biological sludge, (iv) no additional nutrient requirement; (v) easy regeneration of biosorbent, and (vi) possibility of metal recovery [1,2].

Chitosan is derived from an inexpensive material: chitin. The latter is the second most abundant polymer in nature and can be found in the skeletons of insects and shellfish. Calcium alginate is a water-insoluble, gelatinous substance that can be produced through the addition of aqueous calcium chloride to aqueous sodium alginate. The parental substance - alginic acid - is a naturally occurring hydrophilic polysaccharide obtained from various kinds of brown seaweeds. In presented studies, sorption of americium(III) or strontium(II) was studied as a function of contact time, initial pH of water and mass of the sorbent, respectively. Water was collected in the Institute of Nuclear Chemistry and Technology (Warsaw). Post-decontamination liquids were simulated by dissolving citric acid in the water to obtain 1 M solution prior to the radionuclide addition.

Decontamination Factor - the ratio of specific activity prior to and after decontamination [3] has been found above 95 % for Sr(II) on calcium alginate, while ca. 50 % on polyamino polysaccharide - chitosan. An attempt to revitalize of the Am(III) - and Sr-loaded sorbents was done by shaking the material at room temperature with different types of desorbing agents.

Thermogravimetric analyzes of the materials show that commercially available products decompose at about 600 °C (calcium alginate) and 700 °C (chitosan) and the residue after ignition as mass is about 5-10 % of the initial material. In contrast, the sorbents obtained in our laboratory decompose at only ca. 200 °C. This means that energy necessary to reduce the mass of the potential solid wastes formed from the latter calcium alginate may be considerably smaller than from the commercial sorbents.

Conclusions:
Laboratory obtained beads of calcium alginate seem to be a better sorbent than the materials commercially available.

Calcium alginate is more effective than chitosan in binding strontium(II) potentially present in the aqueous solutions.

Studies were performed in frame of the Strategic Project Technologies Supporting Development of Safe Nuclear Power Engineering Domain 4 Development of spent nuclear fuel and radioactive waste management techniques and technologies.

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RER-V07, (Id: 319)

EXCESS OF POLONIUM-210 ACTIVITY IN THE SURFACE URBAN ATMOSPHERE

Magdalena Długosz-Lisiecka

Technical University of Lodz, Faculty of Chemistry
mdlugosz@mitr.p.lodz.pl

The concentrations of ^{210}Pb, ^{210}Bi and ^{210}Po were measured from February 2010 to May 2010 and from May 2011 to April 2012. The seasonal change of ^{210}Po/^{210}Pb and ^{210}Bi/^{210}Pb activity ratios indicate on independent fluctuations of tropospheric ^{210}Pb and its decay products, particularly ^{210}Po. A simple calculation method for the estimation of the excess of ^{210}Po, in relation to its activity formed from ^{210}Pb, during the residence time of the urban aerosols in Lodz city, Central Poland is proposed. Most of ^{210}Po in urban air is not a decay product of ^{222}Rn but is result of input of artificial origins. The highest levels of ^{210}Po were observed in winter period. It suggests that the substantial source of ^{210}Po in this region is an anthropogenic emission from domestic and power plant combustion of coal, rather than other usually suggested sources such as soil resuspension, or stratospheric air intrusion.

The comparison of date with ^{210}Po/ ^{210}Pb ratios allows to determinate the excess of the unsupported ^{210}Po activity in the aerosol samples. Additional influx of unsupported ΔAPo, can be calculated. The main aim of this work was to check the seasonal fluctuations of the Δ^{210}Po activity on the base of aerosol residence time determinations in the urban area.

The activity concentration fluctuation during the period of whole year: from 3548 to 133.5 µBq/m^3, from 1025.8 to 54.6 µBq/m^3 and from 136.9 to 9.44 µBq/m^3 for ^{210}Pb, ^{210}Bi and ^{210}Po, respectively. In all cases the highest concentration was measured in a winter period. The results of activity ratio were divided for 4 seasons spring (March-May), summer (June-August), autumn (September-November) and winter (December-February).

In urban air ^{210}Po coming from additional source is adsorbed on the surface of particles. Specific activity strongly dependents on the aerodynamic diameter of the solid particles of aerosol. Generally, fine particulate matter carries more ^{210}Po than the coarser fractions. Anthropogenic source of Polonium is strongly connected with not only heating (power plant and domestic coal burning) typical for winter season but also with electricity generation and technical activity during the whole year.Polonium as more volatile element than Pb or Bi can be emitted with flue gases. In high temperatutre processes average about 50 % of the total activity of ^{210}Po is discharged in gaseous form or ultra-fine particles to the atmosphere.

RER-V08, (Id: 245)

NEW TITANATE MATRICES FOR IMMOBILIZATION OF ACTINIDE HIGH-LEVEL WASTE

Tatiana Livshits[a], **Jiaming Zhang**[b]

[a]*Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry*
[b]*Stanford University, USA*
lita_232@yahoo.com

Uranium and plutonium extraction from spent nuclear fuel leads to formation of high-level waste (HLW) with complex composition. Actinides (An) from HLW due to their long half-lives (10^3-10^6 years) are the most dangerous elements for biosphere in long-term perspective. To enhance the effectiveness of waste handling it is expedient to extract from HLW An and rare earth elements (REE) in separate fraction. These elements can be incorporated in durable crystalline phases (matrices) and then disposed in geological repositories. Compounds with pyrochlore structure are considered as suitable An host phases [1,2]. Whereas in the system REE_2O_3-TiO_2 pyrochlores are formedonly for REE with ionic radius smaller than Pm^{3+}[3]. Titanates of large rare earths (La,Ce,Nd,Sm), which are dominated in HLW, crystallize in the monoclinic perovskite-type structure. Substitution of Ti^{4+} to Zr^{4+} stabilizes pyrochlore lattice. Therefore zirconate pyrochlores are one of the most well studied candidates for An host phases [4]. However the rate of phase formation in Zr systems during the process of synthesis is very slow even at high temperatures (1500 °C)[5]. This results in presence of residual oxides in ceramics based on zirconate pyrochlores which deteriorates their matrix properties, e.g. corrosion stability in solutions. Phases with monoclinic and orthorombic structures are also formed in the system REE_2O_3-TiO_2-ZrO_2. These compounds are characterized by high REE concentrations [6].

The goal of our investigations was to prove the suitableness of monoclinic $REE_2(Ti,Zr)_2O_7$ and orthorombic $REE_4Ti_9O_{24}$ for use as An-REE host phases. The series of samples were prepared by cold pressing and sintering and inductive melting in cold crucible (IMCC) and studied by different analytical methods: X-ray difraction, scanning and transperent electron microscopy. One sample of monoclinic titanate was irradiated by 1 MeV Kr^+.

Data obtained show that structures of $REE_2(Ti,Zr)_2O_7$ and $REE_4Ti_9O_{24}$ are characterized by high isomorphic capacity in respect to rare earth imitators of An-REE waste. Contents of REE_2O_3 in these phases reach 50 wt. %. There were not any additianal phases with REE in ceramics. All rare earths are occured only in. Thus ceramics based on target monoclinic and orthorombic titanates can be produced by two of the most suitable methods of matrices fabrication: cold pressing and sintering and IMCC. Irradiation of monoclinic $REE_2Ti_2O_7$ by Kr^+ leads to gradual destruction of its structure. And full amorphization takes place at 2.5×10^{14} ion/cm^2. Radiation resistance of $REE_2Ti_2O_7$ with the monoclinic structure is close to titanate pyrochlore and ferrite garntes.

The future investigations will be aimed to the determination of Ce oxidation state in different phases by EXAFS and XANES. Irradiation experiments with $REE_4Ti_9O_{24}$ and studying of chemical durability of monoclinic and orthorombic titanates will be also carried out.

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RER-I09, (Id: 77)

RADIOACTIVITY IN MINERAL WATERS FROM IBERIAN PENINSULA

Fernando P. Carvalho, João M. Oliveira

Instituto Superior Técnico/ LPSR
carvalho@itn.pt

Bottled mineral and spring waters in a total of 38 commercial brands from Portugal and Spain, all available from shelf in supermarkets, were analyzed for natural occurring radionuclides such as uranium and thorium isotopes, radium (^{226}Ra), ^{210}Pb, ^{210}Po and tritium (3H). Radionuclide concentrations vary widely depending on the geological formation of the water source and the chemical characteristics of water. Uranium (^{238}U) activity concentrations ranged from 0.2 to 297 mBq/L, ^{226}Ra varied from 0.5 to 949 mBq/L, radioactive lead (^{210}Pb) from 1.7 to 78 mBq/L and ^{210}Po from 1.2 to 75 mBq/L. Radionuclide activity concentrations particularly those of uranium, thorium, and radium are assessed in conjunction with dissolved salts and major ions present in water. Isotopic ratios of uranium are analyzed and discussed in relationship with characteristics of water sources. Radioactivity intake through consumption of these waters was assessed and concluded that daily consumption of of these waters may give rise to internal radiation doses above the recommended dose limit of 0.1 mSv/y for water consumption. Results are compared with data on other bottled waters in the European Union market , and discussed in the perspective of radiation protection of members of the public and current EU Directives.

RER-V10, (Id: 85)

A COMPARATIVE STUDY FOR THE DETERMINATION OF URANIUM AND URANIUM ISOTOPES IN GRANITIC GROUNDWATER

Min Hoon Baik[a], Mun Ja Kang[a], Soo Young Cho[b], Jonmgtae Jeong[a]

[a]*Korea Atomic Energy Research Institute*
[b]*Korea Institute of Geoscience and Resources*
mhbaik@kaeri.re.kr

The determination of uranium and uranium isotopes in groundwater is very important in the context of the safety of the deep geological disposal of radioactive wastes. The effects of groundwater-rock interaction on the migration of radionuclides can be evaluated using naturally occurring radionuclides as analogues of radioactive waste disposal in a deep geological repository. In this study, the uranium concentration was determined using different analytical methods such as alpha-spectrometry, a liquid scintillation counter (LSC), and inductively coupled plasma mass spectrometry (ICP-MS). The groundwater was sampled from a small underground research facility called KURT (KAERI Underground Research Tunnel) located in Daejeon city, in the center of Korea. Groundwater samples were taken from 6 different depths down to 300 m from a borehole where a multi-packer system is installed. The dissolved U concentrations in the 6 groundwater samples determined by 3 different methods widely ranged from 0.3 to 854 μg/L. The results from the 3 different methods showed a good agreement with each other. An anomaly showing a high U concentration was observed at a relatively shallow region (92 ~ 200 m depth). The ARs of U-234/U^{-238} analyzed by alpha-spectrometry and LSC showed AR values between 1.149 and 2.384 depending on the depth and analytical method. These ARs indicate that the uranium isotopes are out of secular equilibrium owing to an increased water-rock interaction and different origins of the sampled groundwaters.

RER-V11, (Id: 183)

APPLICATIONS OF ^{137}Cs AND PU ISOTOPES IN TRACER STUDIES

Galina Lujaniene, Darius Valiulis, Jonas Šakalys, Nijolė Remeikaitė –Nikienė, Algirdas Stankevičius, Sergej Šemčuk

SRI Center for Physical Sciences and Technology, EPA, Vilnius, Lithuania
lujaniene@ar.fi.lt

This study was performed to assess activity concentrations of radionuclides and characteristic Pu activity and atom ratios in the atmosphere, soil, suspended particulate matter and bottom sediments with the aim of their possible application to trace the pollutants in the environment. Analyses of airborne radioactive aerosols were carried out in daily samples collected in Vilnius as well as in 10-day samples at the background station in Preila (at the Baltic Sea shore, Lithuania). ^{137}Cs, ^{241}Am and Pu isotopes were also analyzed in soil, seawater, bottom sediments (BS) and suspended particulate matter (SPM) samples collected in the Baltic Sea and the Curonian Lagoon during 1997–2013.

The observed ^{238}Pu/^{239,240}Pu activity ratios ranged from 0.44 to 0.50, while the ^{240}Pu/^{239}Pu atom ratio varied after the Chernobyl accident. The ^{240}Pu/^{239}Pu ratio in aerosol in 1995 – 1999 varied from 0.14 to 0.40 whereas in Preila the ^{240}Pu/^{239}Pu ratio varied from 0.135 to 0.247. The exponential decrease in the ^{240}Pu/ ^{239}Pu atom ratio from 0.30 to 0.19 observed from 1995 to 2003 was explained by a decrease in the amount of the Chernobyl derived plutonium in the environment. The analyses of frequency count of the Pu atom ratio (N = 74) indicated that Pu originated from at least two different sources. Activity ^{238}Pu/^{239,240}Pu and atom ^{240}Pu/^{239}Pu ratios indicated a different contribution of the Chernobyl-originated Pu to the suspended particulate matter (SPM) and bottom sediments. The largest amount of the Chernobyl-derived Pu was found in the smallest suspended matter particles of 0.2 – 1 µm in size collected in the Klaipeda Strait in 2011 – 2012. The decrease of characteristic activity ^{238}Pu/^{239,240}Pu and atom ^{240}Pu/^{239}Pu ratios towards the global fallout ones in surface soil and the corresponding increase of plutonium ratios in the suspended particulate matter and bottom sediments have indicated that the Chernobyl-derived Pu, primarily deposited on the soil surface, was washed out and transported to the Baltic Sea.

The obtained results indicated that although the main source of Pu in the Baltic Sea environment was considered to originate from the global fallout after atmospheric nuclear weapons tests, the recently observed inflow of the Chernobyl-derived Pu to the Baltic Sea is linked to the contamination of soil surface after the accident. This secondary source of Pu was attributed to the dissolution of particles deposited on the soil surface and transport of Pu isotopes by water flow. Contrary to Pu isotopes data on activity concentrations of ^{137}Cs in the bottom sediments indicated its redistribution in the Curonian Lagoon – the Baltic Sea system that points to certain limitations in the application of ^{137}Cs in the tracer studies. The Financial support provided by the Research Council of Lithuania (contract No. MIP-080/2012) is acknowledged.

RER-V12, (Id: 165)

INFLUENCE OF THE REDOX STATE ON THE ACTINIDE SORPTION UNDER HIGHLY ALKALINE CONDITIONS: BATCH SORPTION STUDIES ON TITANIUM DIOXIDE AND CALCIUM SILICATE HYDRATES

Jan Tits[a], Xavier Gaona[b], Andreas Laube[a], Erich Wieland[a]

[a]Paul Scherrer Institute, CH-5232 Villigen-PSI, Switzerland
[b]Karlsruhe Institute of Technology, D-76021 Karlsruhe, Germany
jan.tits@psi.ch

Cementitious materials are an important component in the multi-barrier concepts developed in many countries for the safe storage of low and intermediate level radioactive waste (L/ILW) in deep geological repositories. Reliable thermodynamic models able to predict the interaction between radionuclides and cementitious materials in the long term are important for the performance assessment of such repositories. Development of these models requires a sufficiently detailed macroscopic and molecular-level understanding of the uptake processes involved. Studies on the retention of radionuclides by cementitious materials have focused predominantly on adsorption as the relevant uptake process. However, recent spectroscopic studies performed in our laboratory, suggest that incorporation in calcium silicate hydrates (C-S-H) may contribute significantly to the radionuclide immobilization. C-S-H phases, the major constituent of hardened cement paste, are characterized by high recrystallisation rates making them an ideal system for the incorporation of radionuclides present in cement-based repositories. In the present study, batch sorption experiments have been performed to investigate the effect of the redox state (+IV, +V, +VI) and aqueous speciation on the uptake of neptunium in cementitious systems under high pH conditions. Batch sorption experiments were carried out with C-S-H phases and titanium dioxide (TiO_2), a solid phase stable under high pH conditions and often used as a model sorbent in surface complexation studies. Comparison of the sorption of the actinides on these two solids may allow the influence of incorporation processes on the immobilisation of actinides by C-S-H phases to be assessed.

Neptunium uptake was found to be fast and sorption distribution ratios (Rd values) were high, indicating strong retention by all solids. The experimental data further indicate that the sorption of the Np(IV,V,VI) on both types of solids strongly depends on the degree of hydrolysis. On TiO_2, Rd values for Np(IV), Np(V) and Np(VI) are identical at pH = 10 and decrease with progressing hydrolysis in case of Np(V) and Np(VI). On C-S-H phases, Rd values for the three redox states are also identical at pH = 10. While the Rd values for Np(VI) sorption on C-S-H phases decrease with progressing hydrolysis, the Rd values for Np(IV) and Np(V) sorption are not affected by the pH. In addition to the effect of hydrolysis, the presence of Ca is found to promote Np(V) and Np(VI) sorption on TiO_2 whereas on C-S-H phases, the present wet chemistry data do not give unambiguous evidence. Thus, the aqueous speciation appears to have a similar influence on the sorption of Np(IV,V,VI) on both types of solids. Batch sorption tests with Th(IV) and U(VI) on C-S-H phases confirmed the sorption behavior observed for Np(IV) and Np(VI). Desorption tests finally showed that the actinides sorption on C-S-H phases is reversible. The observed sorption behavior of the actinides on TiO2 and C-S-H phases is qualitatively explained by invoking inter-ligand electrostatic repulsion between OH groups in the coordination sphere of Np(V) and Np(VI). This mechanism was proposed earlier in the literature for the prediction of actinide complexation constants with inorganic ligands.

We conclude that the present actinide sorption data on C-S-H phases can be interpreted in line with a reversible sorption mechanism. The degree of hydrolysis of the actinide cations and the presence of Ca play a key role in the sorption process. Wet chemistry studies of the actinides uptake by C-S-H phases cannot provide clear evidences for incorporation processes.

RER-V13, (Id: 247)

DETERMINATION OF SORPTION CHARACTERISTICS OF ARTIFICIAL RADIONUCLIDES IN THE HYDROSPHERE

Eva Juranová, Eduard Hanslík

[a]*Department of Radioecology, T. G. Masaryk Water Research Institute, Public Research Institution; Faculty of Science, Institute for Environmental Studies, Charles University in Prague*
eva_juranova@vuv.cz

Adsorption onto solid particles plays an important role in behaviour and transport of radioactive contaminants in hydrosphere. Sorption is usually described with distribution coefficient; a ratio of radioactivity fixed on solid phase and dissolved in water in equilibrium. In this study, distribution coefficients of sediment-water and suspended solids-water were determined using a method, developed in our laboratory.

For sorption characteristics determination, series of batch experiments were used. To prepare the experimental batch, assortment of artificial radionuclides, representing an accidental source term, was added to surface water containing suspended solids or to a mixture of sediment and water. After that, prepared test series were blended for 24 hours. Then, the solid phase was separated from the water and analysed using gammaspectrometry.

Using this method, distribution coefficients were determined for sediment-surface water and suspended solids-surface water systems, sampled along the Vltava River. This data was used for the method verifying – determination of its repeatability. The determined distribution coefficients show that most radionuclides are readily fixed on the solid phase, although moderate variations were observed among the radionuclides and the sediments. Evaluating sorption on suspended solids, slight differences were found compared to sediments, as a consequence of markedly lower solid-liquid ratio of suspended solids in the experimental mixture.

In summary, the method was developed to be able to obtain representative and comparable data on sorption characteristics of artificial radionuclides in hydrosphere. The results, show that sorption onto solid phase is an important factor influencing fate of radioactive substances in hydrosphere. Indeed, in the case of radioactive contamination of hydrosphere, we can expect a strong contamination of bottom sediments caused not only by the direct sorption but also by the sedimentation of contaminated suspended solids. On the other hand, consequently, certain decrease of radioactivity dissolved in water can be estimated. Acknowledgement

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RER-I14, (Id: 154)

ISOTOPIC-RATIO STUDIES ON THE REDOX CHEMISTRY AND MOBILITY OF URANIUM IN A PHOSPHOGYPSUM DISPOSAL SITE

Ioannis Pashalidis[a], Juhani Suksi[b]

[a]*Department of Chemistry, University of Cyprus*
[b]*Laboratory of Radiochemistry, Department of Chemistry, University of Helsinki*
pspasch@ucy.ac.cy

The present study aims to assess the effect of redox conditions existing within a phosphogypsum disposal site on the redox stability and mobility of uranium in the disposed material. Phosphogypsum sampling and in-situ measurements were carried out at a coastal stack in Vasiliko, Cyprus. pH, EH and solubility experiments were performed in-situ and in laboratory systems. Generally, in the open stack oxidizing conditions predominate stabilizing uranium in its hexavalent oxidation state. On the other hand, after the application of a soil/vegetative cover and in the presence of natural organic matter, anoxic conditions prevail (EH < -70 mV) enabling U(VI) reduction to U(IV). Uranium concentration measurements as well as $^{230}Th/^{238}U$ ratios show higher uranium retention under anoxic conditions, which could be ascribed to the lower solubility and mobility of U(IV).

RER-V15, (Id: 343)

PARTITIONING AND SPECIATION OF Pu IN THE SEDIMENTARY ROCKS AQUIFER FROM THE DEEP LNW DISPOSAL

Irina Vlasova[a], Elena Zakharova[b], Anna Volkova[b], Anna Romanchuk[a], Igor Presnyakov[a], Alexey Sobolev[a], Stepan Kalmykov[a]

[a]Lomonosov Moscow State Univercity
[b]Frumkin IPCE RAS
irinaeng@gmail.com

The sedimentary rocks aquifers are used as the reservoir beds for the deep injection of liquid nuclear waste (LNW) in Russia. The reservoir beds are located at the depth of 290-370 m and are limited from above and from below by the impermeable clayey strata. LNW injections vary in composition including acidic technological wastes, which consist of sodium nitrate, acetic acid, corrosion products and radionuclides. Safety of the LNW disposal depends on the migration properties of radionuclides as well as on the ability of the bearing stratum to localize radionuclides within the nearest zone of the repository.

Sorption of Pu onto the components of the different types of sandy rocks of the LNW disposal under the hydrothermal (100-150 °C) acidic (pH 1.8 - 2.5) conditions have been studied. It was established that the presence of corrosion products (Fe, Cr) in the LNW solutions causes formation of Fe(III)-Cr(III) oxides-hydroxides that stimulates sorption of Pu on the solid phase. In the presence of Fe, Cr, Mn, Ni in the LNW composition Pu was bound to the solid phase almost quantitavely while without corrosion products only 30-60 % of Pu was sorbed onto the sands. Sequential extraction of Pu from sandy rocks has demonstrated the influence of corrosion products in the binding of Pu to the solid phase. In the presence of Fe, Cr, Mn, Ni about 70 % of Pu was fixed in the hardly-leachable phase (acid-soluble and residue fractions). The content of initial sandy rocks influenced the partitioning of Pu. Organic rich sands (with coaly minerals) contain higher fraction of Pu bound to organic phase while sands rich in Fe-containing dark minerals have larger Pu fraction bound to Fe-Mn oxides.

Mössbauer spectroscopy and XRD identified the Fe-Cr-containing phases as hematite and goethite. HR-TEM reveals the morphology of the Fe-Cr-containing colloids which have been responsible for Pu sorption under hydrothermal conditions in acid media (pH 1.8 – 2.5).

The Pourbaix diagrams for Pu in the presence and in the absence of hematite were calculated to describe the sorption equilibrium in the system. Equilibrium constants for Pu sorption reactions were calculated using linear free-energy relationship (LFER) that is based on the analogy of hydrolysis in solution and sorption onto surface hydroxyl groups of hematite. It was established using Pourbaix diagram that the mixture of Pu(3+), $PuO_2(+)$ and some $PuO_2(2+)$ could be expected in the absence of corrosion products under acid conditions of LNW deep injection. In the presence of hematite Pu in the sorbed form, mainly presents in tetravalent form as ≡FeOPu(3+).

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RER-V16, (Id: 347)

SORPTION OF Cs (I), Eu (III) AND U(VI) ONTO ROCK SAMPLES FROM NIZHNEKANSKY MASSIVE (RUSSIA)

Vladimir Petrov[a], Natalia Kuzmenkova[b], Vladislav Petrov[c], Valery Poluektov[c], Artem Kashtanov[a], Anna Shiryaeva[a], Stepan Kalmykov[a], Irina Vlasova[a]

[a]*Lomonosov Moscow State University*
[b]*Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences*
[c]*Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Academy of Sciences*
vladimir.g.petrov@gmail.com

The repository for high level wastes (HLW) and spent nuclear fuel (SNF) in Russia is planned to be constructed in the deep underground crystalline rock formations near the Krasnoyarsk. Three areas of the Nizhnekansky Granite Massive, namely “Kamenny”, “Itatsky” and especially “Eniseysky”, are supposed as the most perspective locations for the future HLW and SNF disposal site. Physical and chemical properties of rock minerals (especially sorption towards radionuclides) are essential for the modeling of their long-term behavior and radionuclides migration through the granite body of the repository and, thus, for the Safety Assessment. Previously core materials from the specified areas have been studied in terms of petrographic and mineralogical characterization; definition of filtration, elastic, petro-physical and strength properties; estimation of hydrothermal-metasomatic transformation of rocks. In this work sorption of Cs(I), Eu(III) and U(VI) onto granite samples from aforementioned areas is studied.

Batch sorption experiments were performed both in glove box with inert atmosphere (N_2) and at open-air conditions. Sodium perchlorate was used as a background non-complexing electrolyte (0.01 M). Initial concentration of each cation was $1E^{-7}$ mol/L and isotopes (U-233, Cs-137, Eu-152) were used for liquid-scintillation or gamma counting. The solid to liquid ratio was kept at 1:4. Rock samples were crushed and sieved with 1-2 mm grain size. Additionally, four undisturbed rock slices were used to reveal the minerals responsible for cation sorption.

The spatial distribution of cesium, europium and uranium(VI) onto surface of the undisturbed rock slices was investigated by digital radiography using imaging plate technique. Comparison of radiography and optical images of samples allowed us to reveal that dark minerals presented in the investigated rock samples (biotite, chlorite) are mostly responsible for Cs and Eu sorption. According to the results of digital radiography about 70 % of radionuclides were sorbed onto these minerals whereas biotite and chlorite content is about 20 %, means that dark minerals ca. ten times more effectively sorb Cs and Eu than other minerals. The distribution of U among different rock minerals is much more homogeneous. The results of time-dependence study of radionuclide sorption showed that steady-state conditions of cations sorption onto investigated rock samples are reached within 15-20 days both in inert and air atmosphere. Thus, metal concentrations in solutions in other sorption studies were analyzed in three weeks after beginning of experiment. It was shown that in case of cesium sorption has no clear dependence on the pH values typical for ion-exchange mechanism. Thus, observed increase on Cs uptake with increasing of biotite content in rock samples is consistent. The pH-dependence of sorbed uranium fraction has typical hump-shape: increase of sorption percentage with increasing pH values to 6, plateau (90-98 % of uranium sorbed), decrease of sorption percentage with increasing pH values from 8 due to U(VI) hydrolysis and/or carbonate complex formation.

RER-V17, (Id: 237)

INTERACTIONS INVOLVING STRONTIUM AND VARIOUS ORGANIC ACIDS ON THE SURFACE OF BENTONITE (MX80)

Timothy Payne[a], Tsing-Hai Wang[b], Jennifer Harrison[a], Shi-Ping Teng[b]

[a]*Australian Nuclear Science and Technology Organisation*
[b]*Institute of Nuclear Engineering and Science, National Tsing-Hua University, Taiwan*
tep@ansto.gov.au

The adsorption of strontium and organic acids on MX80 bentonite in NaCl solutions was investigated in batch experiments. The organic acids included five dicarboxylic acids ($HOOC(CH_2)_nCOOH$) of various alkyl chain lengths (n = 0, 2, 4, 7 and 18) and three aromatic acids (benzoic, salyclic and gallic acids). The objective of the work was to study the interactions occurring in bentonite systems containing both strontium and organic acids. X-ray diffraction and FTIR were used to probe the adsorption mechanism. The sorption of strontium on the bentonite was influenced by pH and ionic strength, but not strongly affected by the presence of the organic acids. However, the presence of adsorbed strontium significantly affected the binding of the organic acids. In the experimental systems studied, structural sites contribute the majority of strontium adsorption to MX80. Although the FTIR did not provide conclusive evidence regarding how the organics were bound by the bentonite in these mixed systems, they suggested the binding was dissimilar to that found in strontium-free systems. The XRD results indicated that the presence of organic acids and strontium affect the interlayer chemistry and layer spacing of MX80 bentonite.

RER-V18, (Id: 189)

TREATMENT OF WASHING SOLUTION OF URANIUM-CONTAMINATE WASTES

Seung Soo KIM, Gye Nam Kim, Jei Kwon Moon

Korea Atomic Energy Research Institute
nsskim@kaeri.re.kr

A large quantity of acidic waste solution containing uranium is generated when U-contaminated soil and concrete are decontaminated using nitric or sulfuric acid in the electrokinetic equipment. If the uranium in the solution selectively sorbed on an ion exchange resin or extracted by a proper reagent, the acid would be recycled, and a very small amount of sludge would be generated. Two strong anion exchangers, IRA 910 and Ag1x8, were examined to capture uranyl sulfate anion complexes such as $UO_2(SO_4)_2^{2-}$ and $UO_2(SO_4)_3^{4-}$ from sulfuric waste solution. Tri-n-butyl phosphate was used to extract uranyl ions from the nitric waste solution, and the interference of iron ions in the waste solution was also considered. When pH of the solution was adjusted to around 9.0 by adding CaO to precipitate uranium ions in an acidic washing solution, high concentration of calcium created several problems in the electrokinetic equipment. The addition of sulfuric acid reduced the concentration of calcium from 3.8 % to 0.08 % by precipitation of $CaSO_4$.

RER-I19, (Id: 123)

PROPERTIES AND APPLICATIONS OF NANOSCALE ACTINIDE CAGE CLUSTERS

Peter Burns

University of Notre Dame
pburns@nd.edu

Uranyl peroxide cage clusters self-assemble from aqueous solution under ambient conditions. To date, we have isolated more than 80 distinct clusters that differ in the number of uranyl ions, size, and topology. These clusters contain from 18 to 124 uranyl ions, and are from 1.5 to 4 nm in diameter. Most are readily soluble in aqueous solution. Although peroxide bridges between uranyl ions are thought to be essential for cage cluster formation, other bridges are also incorporated into the clusters, including phosphate, oxalate, pyrophosphate, nitrate, hydroxyl, tungstate, and phosphite.

The topologies of uranyl peroxide cage clusters vary dramatically. Several have fullerene topologies consisting of 12 pentagons as well as hexagons, whereas others consist of combinations of topological squares and hexagons. Several, including U^{60}, are topologically analogous to C fullerenes. The largest cluster, containing 124 uranyl ions, consists of four cages in a tetrahedral arrangement, and an additional cage at the center of the tetrahedron. The properties of the cage clusters, including stability and aqueous solubility, appear to be related to the details of the topologies.

Uranyl peroxide cage clusters are crystallized for structural characterization, and characterized in solution using a combination of small-angle X-ray scattering (SAXS), electrospray ionization mass spectrometry (ESI-MS), dynamic light scattering (DLS), static light scattering (SLS), transmission electron microscopy (TEM), and nuclear magnetic resonance spectroscopy (NMR). At low concentrations these clusters persist as monomers in solution for months or longer, and undergo dynamic interchange between conformations in some cases. At higher concentrations, aggregation occurs to form "blackberries" that have well defined shapes and sizes.

One potential application of uranyl peroxide cage clusters is for recovery of uranium from nuclear materials, such as irradiated nuclear fuels. Specifically, uranium oxide fuel can be dissolved under alkaline aqueous conditions in the presence of peroxide, which both oxidizes the U(IV) to U(VI) and bridges the uranyl ions, forming cage clusters. These clusters may then be recovered from solution by filtration through a porous membrane. Complicating factors include blackberry formation and association of counterions with the anionic cage clusters.

RER-V20, (Id: 313)

NANOMATERIALS FOR SORPTION OF CRITICAL RADIONUCLIDES

Vojtěch Brynych[a], Lórant Szatmáry[a], Jana Pospěchová[a], Václav Štengl[b]

[a]ÚJV Řež, a. s.
[b]Institute of Inorganic Chemistry AS CR, v.v.i.
vojtech.brynych@ujv.cz

Any activity that produces or uses radioactive materials generates radioactive waste. Disposal of radioactive waste is a complex issue, not only because of the nature of the waste, but also because the need to solve the problem not to burden future generations. Retention processes of key important radionuclides were studied within this study.

Cesium is one of the most important nuclides. The reasons for this are following: the isotope ^{137}Cs has high gamma radiation and half life 30.08 years. The isotope ^{135}Cs has very long half life of about 2.3 million years. The isotope belongs to group of isotopes in nuclear waste that are present for the very long time scales and can be conveyed far from the containment. Another important radioisotope in nuclear waste is strontium. The isotope ^{90}Sr belong to mid-lifed isotopes with the half life of 29 years. Europium is a typical member of the lanthanide series and can be utilized as a homologue for the prediction of other lanthanide behavior. Cesium is chemically very similar to potassium as strontium is similar to calcium. They both can then penetrate into the living organism and get it exposed to internal irradiation. Therefore it is necessary to prevent migration leaking of these radionuclides to the biosphere and develop progressive retention techniques.

In the presented work, new composite nanomaterials, based on graphene, graphene oxide and cellulose, are developed for the retention purpose. The nanomaterials (graphene and graphene oxide) used were prepared from natural graphite using high intensity cavitation field [1] in a pressurized (6 bar) batch-ultrasonic reactor (UIP1000hd, 20 kHz, 2000 W, Hielscher Ultrasonics GmbH). The graphite was exfoliated with the effect of high intensity ultrasound and delaminated graphene nanosheets were used for graphene oxide [2] preparation improved by Hummers method [3]. Graphene oxide polystyrene composite was synthesized using direct emulsion polymerization of styrene in the presence of graphene oxide at 90 °C. Hydrothermal conditions were maintained in stainless steel stirred autoclave. The metal Ni0 nanoparticles modified cellulose was prepared by reduction of nickel (II) nitrate with sodium borohydride at 25 °C or hydrazine hydrate under refluxing for 24 h. The method used for evaluation of nanomaterial retention properties was batch sorption experiment, being based on contact of solid material with tracer solution under defined boundary conditions (solid/solution ratio, solution composition etc.). The experiment results were then evaluated, using sorption distribution coefficient (KD) and Cation Exchange Capacity (CEC). Acknowledgements: We thank for support from Ministry of the Interior of the Czech Republic (Project No. VG20132015132).

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RER-V21, (Id: 87)

SELECTIVE REMOVAL OF METALS FROM AQUEOUS SOLUTIONS USING SILICA ATTACHED LIGANDS

James Holt

Department of Chemistry, Loughborough University, Loughborough, Leicestershire
j.d.holt@lboro.ac.uk

In order to facilitate the selective sequestration of important radionuclides and contaminants, a surface attached ligand, (3-Aminopropyl)triethoxysilane (APTES) has been attached to 2 types of silica with very different surface areas. ZEOprep 60 HYD Silica gel, 40-63 µm and fumed silica, 0.007 µm were used as the solid support for APTES attachment. A further 14 ligands attached to silica substrates by PhosphonicS Ltd have also been tested for their selectivity of sequestration in a solution containing cobalt, nickel, copper, zinc, cadmium, europium and uranium at a concentration of ca. 20 ppm.

Following successful attachment of polymer to the silica surface, our focus moved to the attachment of ligands to silica and the testing of their selectivity. By utilising two different silica types, we have been able to investigate the differences in the amount of ligand we can attach but then also the ability for each of these to sequester metal. Following successful sequestration of some transition metals, our research has been extended by using radionuclides including ^{57}Co, ^{63}Ni, ^{109}Cd, ^{152}Eu and ^{238}U. These concentrations ranged from 2.5 ppm up to 160 ppm in some cases. To make the investigation more relevant to real case scenarios, a great excess of potentially competitive groundwater cations, such as Na^+ and Ca^{2+} were added to further the study. It has been shown that the metal sequestration is not significantly affected by the addition of these ions.

Rd's for the sequestration of ^{63}Ni from deionised water range from 4×10^4 to 1.2×10^7 ml/g compared to 5.3×10^4 to 7.9×10^5 ml/g for potentially competitive calcium in solution and 1.2×10^5 ml/g to 7.3×10^6 ml/g for potentially competitive sodium sequestration. Isotherms have also been produced across a pH range from 5.01 to 6.80 before addition of the material, to a final pH of 6.90 to 9.49 depending on the original concentration and competitive ions in solution. Similar Rd values or better have been recorded for other metals including ^{57}Co, ^{109}Cd, ^{152}Eu and ^{238}U.

Uranium was found to be highly selectively removed by the APTES ligand with copper being the next favourable. These results were obtained by measuring the metal concentration before and after the modified silica had been added to the aqueous solution using ICP-OES. A minor difference between the ZEOprep and fumed silica materials was also noticed in terms of quantity of metal removed. Investigations with the PhosphonicS Ltd. samples have shown a range of selectivity with the molecules attached to the silica which include a range of sulphur, nitrogen, carbonyl and phosphonate ligands. With many nitrogen containing ligands, uranium was found to be removed from a concentration of 21.5 to 1.5 ppm over a four week period, whilst in the same solution, copper was only reduced to 8.5 ppm from an original concentration of 19.8 ppm. The remaining metals in solution did not see a noticeable change. The other tested ligands have been found, in this seven metal system to be selective for europium and copper whilst none of the other metals have seen a noticeable change.

RER-V22, (Id: 36)

INFLUENCE OF THE ALPHA RADIATION ON THE UO_2 DISSOLUTION AT HIGH PH CEMENTITIOUS WATER

Thierry Mennecart, Christelle Cachoir, Karel Lemmens

SCK-CEN
thierry.mennecart@sckcen.be

Since 2004, the supercontainer design has been selected by the Belgian authority for the management of the nuclear waste (NIRAS/ONDRAF) as the preferred new reference design for disposal of High Level Waste and Spent Fuel. This design is based on a buffer and backfill materials of Ordinary Portland Cement (OPC).

In this supercontainer, the spent fuel will be surrounded by a 30 mm thick carbon steel overpack and a 540 mm thick OPC concrete buffer. The supercontainer will contribute to the containment of radionuclides within the waste matrix but will also have an effect on the retardation of radionuclide release from the waste and will retard the migration of radionuclides. Because the supercontainer design (alkaline cementitious environment) differs significantly from designs for HLW and spent fuel used in other national programs, a specific evaluation of the behaviour of spent fuel in such high-pH conditions has been started at SCK•CEN in collaboration with NIRAS/ONDRAF. An experimental programme has been initiated to study the behaviour of UO_2 as an analogue of real spent fuel in the cementitious environment of the supercontainer design, more specifically to determine the UO_2 stability (dissolution rate), the UO_2 solubility and the influence of alpha radiation on the behaviour of the UO_2.

The experiments are carried out at 25-30 °C in glove box under anoxic conditions in static (SA/V ratio of 6, 17 or 257 m^{-1}) or dynamic set-up at pH of 13.5, 12.5 or 11.7, representative of the ageing steps of cement. The influence of the alpha radiation is investigated using Pu doped UO_2. The activity of the doped UO_2 batches is in the range 244 to 1.4 MBq/g of UO_2, representative of the ageing of the spent fuel from 150 years to 89000 years after discharge. The results are compared with those obtained with depleted UO_2, which simulates very old spent fuel. In an additional series of experiments, a H_2 overpressure was imposed (0.5 or 5 bar).

The experiments in hyperalkaline conditions confirm the behaviour generally observed with UO2 at neutral pH. In most tests, the uranium concentration is close to 10^{-8} $mol.L^{-1}$, which could correspond to thermodynamic equilibrium. The experiments with Pu doped UO_2 indicate that the dissolution rate and the solubility of UO_2 increases with increasing alpha activity. Due to the radiolysis of water, the produced oxidizing species, oxidise the U(IV) to U(VI), leading to an increase of the uranium concentration. In the tests at high SA/V, equilibrium with U(VI) phases may be reached. Based on the results, we estimated a dissolution rate from 0.01 $\mu g.m^{-2}.d^{-}1$ for the least active (depleted) UO_2 to 40 $\mu g.m^{-2}.d^{-1}$ for to the most active doped UO_2. Imposing a H2 overpressure had no significant effect on the UO_2 behaviour, probably because the used UO_2 did not contain epsilon particles, which are known to catalyse the H_2 reduction processes on the UO_2 surface.

RER-V23, (Id: 307)

DIGITAL COINCIDENCE SPECTROMETER WITH TWO HPGE DETECTORS CONSTRUCTED AT IFJ PAN – DESIGN, CONSTRUCTION AND EARLY RESULTS

Jerzy-Wojciech Mietelski, Janowski Janowski, Renata Kierepko

The Henryk Niewodniczanski Institute of Nuclear Physics, Polish Academy of Sciences (IFJ PAN), AGH Technical University Krakow
jerzy.mietelski@ifj.edu.pl

The use of digital coincidence opens new perspectives for low background gamma rays measurements. The basic idea is that two detectors are collecting independently gamma spectra, but spectrum is not stored as one dimensioned array of counts but two-dimensional array where data on each registered photon energy is registered together with information on its arrival with several nanoseconds precision. During off-line analyses of such spectrum different numeric filters can be applied to search for coincidences between different parts of each spectra, for example annihilation line at one spectrometer with certain gamma line of a beta plus emitter registered on another detector. The coincidences between any gamma ray line of certain radionuclide and X-ray line of daughter are also possible. The constructed by us system uses two HPGe detectors: coaxial in vertical cryostat and planar in L shape cryostat. They are shielded by one 5 cm thick standard lead shield. Spectra are collected using CAEN digitizerand they are registered using build-in software. The off-line analyses are made by means of purposely written our own code. At moment of writing abstract the system is not operating yet. First it will be applied for attempt of ^{85}Kr determination on environmental levels (collected in a cryogenic charcoal trap) using gamma-X ray coincidences and ^{22}Na in air using 511 keV/1275 keV coincidences. The first results will be presented during Conference.

Work was carried out under the strategic research project “Technologies supporting the development of safe nuclear power” financed by the National Centre for Research and Development (NCBiR). Research Task “Development of methods to assure nuclear safety and radiation protection for current and future needs of nuclear power plants”, contract No. SP/J/6/143339/11.

RER-V24, (Id: 40)

HUMIC ACID AS A SORBENT MODIFIER: HUMIC ACID INDUCED SYNERGETIC SORPTION BEHAVIOR OF PRUSSIAN BLUE

Evgeny Polyakov[a], Ilya Volkov[a], Victor Remez[b]

[a]*Institute of Solid State Chemistry, UB RAS*
[b]*Ecsorb, the Compamy*
polyakov@ihim.uran.ru

Recent investigations show that sorption properties of solids in natural or synthetic humic acid (HA) solutions strongly depend on the ability of HA to form complexes with ions of sorbate and to interact with the surface of solids. In general, both factors are negative for the sorption technologies due to the known dramatic diminution of sorption processes in HA solutions. We found that industrially produced samples of Fe(II) cyanoferrate(II) (Prussian blue, PB) drastically change their sorption behavior in HA aqueous solutions in comparison with inorganic electrolyte solutions. Numerous experimental data showed that the revealed synergetic sorption of the couple “PB – HA” may be connected with two groups of factors: firstly, an effect of partial HA complex formation by cations in HA-solution which suppresses the known stereoselective sorption properties of d-metals cyanoferrates(II), and secondly, the growth of sorption affinity of some HA complexes of p-, d- and f-metal cations toward PB in the conditions when HA macromolecules don not interact with PB surface due to the same sign of electrostatic charge of interacting particles. In this presentation we show the results of investigation of the system “PB – HA” and discuss the reasons of the revealed enhancement of the sorption affinity of PB toward HA-complexes of ions of I-VI groups of D.I. Mendeleev Periodic System in the framework of the problem of chemical and radiochemical protection of the environment..

Radionuclides in the Environment, Radioecology (RER)

Posters

RER-P01, (Id: 5)

EXTRACTION OF RARE EARTH ELEMENTS FROM THE NATURAL AND MAN-MADE RAW BY USING SUPERCRITICAL CARBON DIOXIDE

Maxim Samsonov, Trofim Trofimov, Yury Kulyako, Sergey Vinokurov, Olga Mokhodoeva, Boris Myasoedov

Vernadsky Institute of Geochemistry and Analytical Chemistry of Russian Academy of Sciences
max_samsonov@mail.ru

In connection with the development of modern high-tech industries and changing market conditions in the last few years have seen a growing interest in rare-earth elements (REE). This necessitates the creation of new technologies for processing of mineral raw materials, as well as various industrial wastes and secondary resources. Virtually all fields of REE are part of complex ores, incorporating a wide range of components. In this context a crucial role in the development of deposits, processing of ores and other sources play an extraction and sorption methods are widely used for the extraction, separation and purification of individual REE.

In this paper proposed the use of supercritical fluid extraction method for the isolation and separation of REE, uranium and thorium in the processing of mineral raw materials and industrial waste such as monazite concentrate and phosphogypsum. On the example of organophosphorus reagents such as TBP, CMPO, TOPO, and nitrogen-containing ligands DMDOGEMA and TODGA, as well as TBP-HNO3 adduct we studied the possibility of sorption of REE by the previously synthesized solid phase extractants, based on carbon nanotubes and polystyrene Taunit media.

There was a fundamental possibility of separation of REE, uranium and thorium, the above extractants and their allocation to individual phases using supercritical carbon dioxide. A scheme for the processing of monazite concentrate and phosphogypsum.

RER-P02, (Id: 18)

DECREASING OF TRANSFER OF CAESIUM AND STRONTIUM RADIONUCLIDES FROM SOIL TO VEGETATION

Marina Blinova, Anna Voronina, Vladimir Semenishchev

Ural Federal University
smo.ural.russia@gmail.com

Decreasing of transfer of radionuclides from soil to vegetation is the main purpose of remediation of radioactively contaminated lands with the aim of their returning to farming industry. The method of addition of sorbents to soils is seemed to be the most afficient in these cases. Using sorbents should possess affinity to natural systems, high specificity and selectivity and also irreversibility of sorption of radionuclides for effective retention of radionuclides as wel as to prevent their migration into vegetation and further movement through food chains. A number of publications suggest to use natural and modified aluminosilicates for remediation of territories but there were no comparative studies of use of various materials, questions of selectivity and reversibility of sorption of radionuclides have not taken into an account.

Comparative study of specificity, selectivity and reversibility of sorption of caesium and strontium radionuclides by natural aluminosilicates (glauconite from Karinskoe deposit (Russia) and clinoptilolite from Shivyrtooinsky deposit (Russia)) and modified ferrocyanide sorbents based on them is presented in this work.

The natural glauconite sorbs caesium from tap water with distribution coefficient Kd = 10(3.5±0.1) mL/g, static exchange capasity of Cs is 11.0 mg/g; it shows lower specificity to strontium: Kd = 10(2.5±0.1) mL/g, static exchange capasity = 9 mg/g. For clinoptilolite these parameters are for caesium Kd = 10(4.4±0.5) mL/g, static exchange capasity ^{210} mg/g; for strontium Kd = 10(3.5±0.1) mL/g, capasity = 12 mg/g. Ferrocyanide sorbents concentrate caesium radionuclides more effectively: distribution coefficient of Cs from tap water by mixed nickel-potassium ferrocyanide based on glauconite is 10(5.9±1.6) mL/g, static exchange capasity of Cs is (63.0±2.0) mg/g; for mixed nickel-potassium ferrocyanide based on clinoptilolite these characteristics are respectively 10(7.4±1.3) mL/g, 500 mg/g. In case of modified sorbents specificity to strontium remains the same as for natural aluminosilicates. Reversibility of sorption of caesium by natural glauconite and ferrocyanide sorbent was determined as caesium leaching degree from saturated samples. High caesium leaching rates and degrees are typical for natural glauconite irrespective of leachant salinity: total degree of leaching after 35 days of leaching was: mineral water = 63.4 %, tap water = 41.6 % and rain water = 28.8 %. For flauconite modified by ferrocyanides total degrees of leaching under the same conditions were: mineral water = 1.5 %, tap water = 14.6 % and rain water = 6.6 %. Thus, it could be expected, that there will not be reliable retention of caesium by solid phase after addition of natural aluminosilicates into soil. Surface-modified glauconite and clinoptilolite provide rather lower caesium leaching degrees, so it can be successfully used for remediation of lands contaminated by radiocaesium.

Also the assessment of efficiency of extraction of caesium from soil solutions (solutions after leaching from various types of soils). It is shown that using of modified sorbent is more economically feasible, because it is needed 500 mg of ferrocyanide sorbent vs. 25000 mg of natural glauconite per 1 L of oil solution to achieve the same decontamination degree. The quantity of sorbent to introduce as well as its efficiency will depend on type of soil at contaminated lands. Results of experiments have shown that decreasing of transfer of caesium radionuclides from tested soils to vegetation after addition of mixed nickel-potassium ferrocyanide based on glauconite was 20 times.

Thus, it is shown that modification of natural aluminosilicates by ferrocyanides allows to increase their sorption and mechanical features and to make sorption of caesium more selective and almost irreversible. These features allow to recommend modified aluminosilicates for remediation of radioactively contaminated lands

RER-P03, (Id: 25)

SURVEY OF RADIOACTIVITY ALONG THE BOSNA RIVER

Gabriela Wallova, Elena Rajczykova, Jarmila Makovinska, Zuzana Kulichova, Alena Belanova

Water Research Institute Bratislava
gabriela.wallova@gmail.com

The Bosna River is a tributary of the Sava River. It flows through the central part of Bosnia and Herzegovina. Along the Bosna River course, high density of settlements, agricultural areas, industries, not existing or not properly functioning urban and industrial wastewater treatment plants contribute largely to the rivers excessive pollution. The main objective of the project “Development of a Decision Support System for Reducing Risk from Environmental Pollution in the Bosna River” is identification of major risks related to environmental pollution in the Bosna basin and formulation of recommendations for technical solutions for the pollution reduction (removal). The project has been financed by the North Atlantic Treaty Organization (NATO) the Science for Peace and Security Programme and has been implemented as a partnership between two water research institutes: the Slovak National Water Reference Laboratory from Bratislava and the Hydro Engineering Institute Sarajevo, Bosnia and Herzegovina. In the frame of this Project an assessment of general radiological conditions in the Bosna River has been carried out. This work presents the results of natural and anthropogenic radioactivity in water and sediment samples collected along the Bosna River to assess the possible impacts of radionuclides on the surface water quality.

RER-P04, (Id: 32)

USE OF Rn-222 AS A TRACER FOR GROUNDWATER SURFACE WATER INTERACTION IN RIVER BASIN

Yoon Yeol Yoon, Yong Chul Kim, Kil Yong Lee, Soo Young Cho

Korea Institute of Geoscience and Mineral Resources
yyyoon@kigam.re.kr

The properties of radon (half-life 3.8 days, chemically inert) and high activities in groundwater make it a powerful and potentially useful tracer of hydrological processes at the interface between surface and sub-surface water bodies. The groundwater-surface water interface is a dynamic system that plays an important role in the hydrogeological functioning of many catchments. The physical properties of this interface can influence the discharge and recharge of aquifers, while chemical attenuation processes that take place during water transfer can affect the quality of both groundwater and river water. Study area is used groundwater as a water curtain greenhouse in winter, so shortage of groundwater problem is occurred and groundwater-river water interaction was severely varied at this time. This variation was studied with ^{222}Rn and ^{3}H during water curtain greenhouse operation period. To understand groundwater surface water interaction, multi-depth well sample were collected and groundwater and river water samples were analysed for radon and stable isotopes between May 2012 and Nov 2013. The concentration of radon was different with the distance of the river and innerside groundwater radon contents was more than 20 % lower than riverside groundwater at the rainy season. Rn-222 concentration was varied with groundwater depth and groundwater using time at the multi-depth well. It was decreased when high groundwater using winter time due to river water intrusion and shallow(5 m depth) and deep groundwater(30 m depth) was nearly river water intrusion region. And H-3 concentration was ranged 2.45- 3.98 TU with sampling time and depth.

RER-P05, (Id: 33)

NATURAL RADIONUCLIDE AS A TRACER IN GROUNDWATER-SURFACE WATER INTERACTIONS AT THE ARTIFICIAL RECHARGE SYSTEM

Yoon Yeol Yoon, Yong Chul Kim, Youn Young Jung, Kyu Chul Ha, Kil Yong Lee, Soo Young Cho

Korea Institute of Geoscience and Mineral Resources
yyyoon@kigam.re.kr

Determining the relationship between surface water and groundwater systems is critical to understanding hydrogeological systems, protecting riverine ecosystems, and managing water resources. Due to its high activities in groundwater, the radionuclide ^{222}Rn is a sensitive natural tracer to detect and quantify groundwater. In this study ^{222}Rn and stable isotope were used as a tracer in groundwater and river water interaction. The short half-life(3.8 days) and chemically inert properties of radon make it a powerful and potentially useful tracer of hydrological processes at the fast interface interaction between surface and sub-surface water bodies.

Study area is pilot artificial groundwater recharge system near Nakdong river in Korea. Rn-222 and stable isotope were used natural tracer to understand surface water recharge effect. Artificial recharge system was consist of four input and one pumping well. Rn-222 and stable isotope samples were collected during recharge operation time. For one day recharge operation period, Rn-222 concentration was decreased at the observation well groundwater. OBS-1 and 5 were decrease about 35 % due to surface water dilution effect but OBS-6 was 4 time increased due to surround groundwater input effect. The stable isotopes were similar trend with radon concentration but OBS-4 sample was different with other samples. This means different groundwater was introduced during recharge operation time. To understand surface water-groundwater interaction, 14 days artificial recharge experiment was performed and groundwater samples were collected during the operation time. This long-term experiment result showed radon concentration was not varied at the OBS-1 and 2. However, OBS-3 was increased and OBS-4 was decreased with time and about 200 hours passed radon concentration was not varied severely.

RER-P06, (Id: 46)

POROSITY OF INORGANIC ION-EXCHANGERS AND THEIR SORPTION SELECTIVITY TOWARDS THE IONS OF HEAVY METALS AND RADIONUCLIDES

Volodymyr Strelko[a], Tetjana Psarova[a], Igor Zhuravlov[a], Oltg Zakutevskyy[a], Vitalii Milyutin[b]

[a]*Institute for Sorption and Problems of Endoecology of National Academy of Sciences of Ukraine*
[b]*Institute of physical chemistry and electrochemistry of Rusian Academy of Sciences.*
vstrelko@ispe.kiev.ua

The report presents data about the new method of synthesis of inorganic ion-exchangers in continuous mode of sol-gel process, which provides the possibility of obtaining the spherically granulated hydrogels and xerogels of highly porous oxides, silicates and phosphates of polyvalent metals. The basis of the process – the reactions of templating competitive interactions between Fe and Al salts and the basic components in the reaction mixture, namely, with Ti and Zr salts, as well as phosphoric and silicic acids and sodium, potassium, ammonium hydroxides etc. [1,2].

Using the washing procedure of gel spherical particles (d = 0,2 ~ 1,2 mm) by water with different pH values and organic solvents, it is possible, after drying, to obtain the inorganic ion-exchangers with bimodal nanoporosity, in particular, with transport ultramicro- and meso-pores and with the specific surface area values around 200 - 600 mg/g It was shown that due to the factors of structural compliance (between the size of ultramicropores and diameter of sorbed ions) and also complex formation with functional and hydroxyl groups in the matrix of ion-exchangers, the selective sorption of cations of d- metals and trace amount of radionuclides ^{137}Cs, ^{90}Sr, ^{239}Pu, ^{241}Am, and uranium is carried out from solutions with complex composition. It was also found that in case of the uranium sorption from the model solutions of uranyl acetate on the highly porous titanium phosphates is occured the formation of a separate phase of uranyl phosphate in mesopores at pH range ~ 5-7, wherein the sorption equilibrium is reached only during ~ 3000 hours. In the report is also presented data that demonstrate the effect of various factors on the sorption selectivity of radionuclides Cs and Sr, and also uranium and transuranic elements by powdered forms of ion-exchangers on the basis of amorphous titanium silicates. It was found that this inorganic ion-exchanger has, in some way, the properties of universal sorbent, capable to selective sorption of the most long-lived radionuclides from solutions with complex composition. Finally, it was shown that the combined use of some inorganic coagulants, based on titanium compounds, and the inorganic ion-exchangers investigated in this project enables to purify, almost completely, the liquid radioactive waste of destroyed 4th block of the Chernobyl nuclear power plant from the entire spectrum of radionuclides. In the report is also presented the field data of our investigations at the Chernobyl nuclear power plant.

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RER-P07, (Id: 52)

SEMI-AUTOMATED PROCEDURE FOR RAPID DETERMINATION OF ^{90}Sr IN WATER SAMPLES BY CHERENKOV COUNTING

Ivana Milanović, Željko Grahek

Rudjer Boskovic Institute, Laboratory for Radioecology
imilanov@irb.hr Rudjer

Radiostrontium as a high yield fission product with long physical (28.8 years) and biological half-life (~49 years), is one of the most hazardous radiocontaminants in the environment. Therefore, almost all environmental radioactivity monitoring programs include its quantitative determination. Due to its radiochemical properties standard procedure for its determination is complicated and time consuming. Consequently, so called rapid methods for its separation and determination are being rapidly developed [1-4]. However, there is a lack of prompt and reliable methods for determination of low level activities in the environmental samples. Hence, in this paper, method for rapid low level activity determination which includes simultaneous selective binding of ^{90}Sr and ^{90}Y on chromatographic column filed with mixture of DGA-SuperLig resins and subsequent on column Cherenkov detection will be presented. Highly selective strontium binding on SuperLig 620 and yttrium on DGA resin are based on molecular recognition [5,6] and enable their selective and quatitative binding with almost 100 % recovery. If one assume that in the sample ^{90}Sr is in equilibrium with its daughter ^{90}Y, mixture of SuperLig 620 and DGA resin might enable rapid selective separation of ^{90}Sr and ^{90}Y from matrices and direct on column Cherenkov counting. Therefore, method consist of automated sample delivery to the column filled with DGA/SuperLig resins and ^{90}Sr-^{90}Y Cherenkov counting on low level counter, TriCarb 3180 TR/SL. Sample is delivered to the column at constant flow rate until the breakthrough point and ^{90}Sr via ^{90}Y was determined by counting column in PE vial surrounded with 5 M HNO_3 to achieve higher efficiency determination. Thereby, to develop this method, best mixing options using different media were examined as well as breakthrough curves for strontium and yttrium in 0.5 M HNO_3 were determined. The new method significantly reduces time and human labor for determination of radioactive strontium in water samples. It was validated with proficiency testing water samples as well as natural water samples.

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RER-P08, (Id: 65)

DEVELOPING OF A METHOD OF DETERMINATION OF CONCENTRATION AND ISOTOPIC COMPOSITION OF THORIUM IN NATURAL WATERS IN RADIATION MONITORING

Anna Paliga, Tatyana Nedobuh

ФГАОУ ВПО «УрФУ имени первого Президента России Б.Н.Ельцина»
paliga_anna@mail.ru

Determination of the isotopic composition of natural radionuclides in natural waters is an integral part of radioecological monitoring. A full analysis of thorium radionuclides should solve two problems: determination of analytical concentration and isotopic composition. The main problem in the analysis of fresh water with low thorium content is preconcentration step; for samples with a high salt content and the complex composition it is removal of the most non-radioactive contaminants and alpha-emitters, e.g. uranium, preventing the preparation of high-quality source for alpha spectrometry. The aim of this work is to develop a thorium preconcentration step for large volumes of natural water. Th-234 was used as tracer in all experiments.

Coprecipitation with iron hydroxide (III) followed by precipitation on cellulose in frontal chromatography condition was choosed for preconcentration of thorium. Theoretical and experimental modeling of thorium coprecipitation with iron hydroxide was performed. Calculations of solubility of thorium hydroxide have shown that its own hydroxide phase is not formed in range of concentrations typical for natural waters. Therefore, coprecipitation with carrier (iron hydroxide) is the only possible way for thorium preconcentration. Processes of iron hydroxide precipitation and thorium coprecipitation with iron hydroxide from freshwater were studied by ultrafiltration method in dependence on pH, concentration of the thorium and iron (III). To isolate the precipitate of iron hydroxide, which contains thorium, we proposed filtration through a nozzle in frontal chromatography condition. Cellulose was used as a nozzle. The study allowed to determine conditions thorium preconcentration that provide thorium yield (98 ± 8) %: the concentration of the iron (III) is 100 mg/l; pH 6.5-7.5; sediment formation time - 1 hour , the flow rate through column with filtration nozzle ~ 130 ml/min×cm^2 . Weight of nozzle depends on volume of the sample. The ratio of height to diameter of the column is not less than 1:10. Extraction of thorium from filter nozzle by ammonium oxalate solution was performed under dynamic conditions. The method of coprecipitation with cerium fluoride was used for preparation of samples for alpha-spectrometric determination of thorium isotopes. Coprecipitation method with further separation of the precipitate by ultrafiltration was selected due to the fact that uranium(VI) remains in solution under these conditions. By fluoride precipitation the quality of the sample depends on presence of calcium in the sample, forming a crystalline precipitate. Therefore, solubility of cerium, thorium and calcium fluorides with taking into account hydroxycomplexes was calculated to optimize the conditions for sample preparation for α-spectrometric determination of thorium isotopes. The results have shown that precipitation of calcium fluoride does not occur, while thorium and cerium fluoride will be precipitated when concentration of fluoride ions was $1{,}8\times10^{-5}$ mol/l $\leq$ CF- $\leq 5{,}0\times10^{-3}$ mol/l. Optimal concentrations of cerium nitrate and hydrofluoric acid, providing a quantitative release of thorium and good quality of sample for α-spectrometry were determined. Thorium yield in fluoride precipitation step was (98 ± 9) %. Total yield of thorium in the whole method, defined by thorium-234 was (98 ± 11) %. Decontamination factor of uranium for samples containing up to 500 g/l of uranium according to the methods was ~ $10^2 \div 10^3$.

Thus, the proposed method make it possible to perform a thorium preconcentration from large volumes of natural waters, providing its quantitative extraction and good separation from uranium. This method can be recommended for determination of total analytical concentration of thorium and its isotopic composition by alpha-spectrometry.

RER-P09, (Id: 66)

AN AIR-WATER EQUILIBRATOR FOR CONTINUOUS RADON MONITORING IN GROUNDWATER AND SURFACE WATER INTERFACE

Kil Yong Lee

Korea Institute of Geoscience and Mineral Resources
kylee@kigam.re.kr

Radon is useful as a tracer of certain groundwater discharge processes in marine and aquatic environments. A continuous monitoring system with an equilibrator has used to monitor radon in the fields. However, air-water equilibration time of the equilibrators was longer than 30 min. In the present work, we tried to reduce the equilibration time by a new equilibrator. The proposed equilibrator consists of an acrylic body, an impeller connected with a DC motor, water and air loops. Radon activity of the air loop has measured by a radon-in-air detector. The equilibration time can be reduced to 20 min by the equilibrator. It can be used to monitor radon activity continuously in groundwater and surface water interface.

RER-P10, (Id: 67)

NATURAL RADIOACTIVITY LEVELS IN THE AREA AROUND THE URANIUM DEPOSIT OF THE BAHI DISTRICT IN DODOMA REGION, TANZANIA

Najat Kassim Mohammed

University of Dar es Salaam
njkassim@yahoo.com

Economically viable uranium deposit has been discovered at Bahi district in Dodoma Region of Tanzania. The uranium deposit in Bahi is reported to be shallow therefore the activity concentration of the area is expected to be high. Exploration which is still going on in Bahi might also result into radioactive contamination into the environment. The radioactivity might then be transferred to the food chains in the area which may pose a health problem to a big population within the Dodoma region and the nearby places. Moreover, the expectations of uranium mining in the near future pose another concern on the environmental contamination of radionuclides. This is because uranium mining normally leave behind a huge volume of radioactive waste. Hence, there is a need to implement routine radiological surveillance during mining, whereby surveillance is best carried out when the pre-mining data are available for comparison purposes. In this study samples of soil from different areas in the Bahi district were analysed for radioactivity using gamma ray spectrometry of the Tanzania Atomic Energy Commission in Arusha Tanzania. The selection of sampling locations was based on the accessibility of the sampling station to the public, as well as their proximity to the centre of the deposit and the exploration sites. The aim of this work was to dertermine the radioactivity levels in the Bahi district to assess the current radiological status of the area. The information will also play an important role on the estimation of any change on the environmental radiation due to the expected uranium mining activities.

RER-P11, (Id: 78)

NATURALLY-OCCURRING RADIOACTIVITY IN TABLE WINES

Fernando P. Carvalho, João M. Oliveira

[a]*Instituto Superior Tecnico/LPSR*
carvalho@itn.pt

Table wines are part of the Mediterranean diet and a common component of the adults' diet in many countries. Wines are produced from vineyards grown in soils of different types from loam soils to granitic soils and in regions with different natural radioactivity levels. Twenty table wines, red and white, from large producers in several regions of Portugal, encompassing uranium provinces, were analyzed for naturally occurring radionuclides including uranium isotopes, ^{226}Ra, ^{210}Po and ^{232}Th. Four other bottled table wines imported from Spain, France, USA, and Chile were analyzed for comparison. Uranium activity concentrations (^{238}U) in Portuguese wines ranged from 1.1 to 12.9 mBq/L, ^{226}Ra ranged from 2.0 to 22.0 mBq/L and ^{210}Po from 14.8 to 74.4 mq/L. These ranges are nearly comparable to the activity concentration ranges determined in imported wines. Concentration of radionuclides in Portuguese wines were assessed by regions and it was observed that ^{238}U concentrations were in average slighter higher only in wines from granitic regions of the Centre-North than from sedimentary regions of the south of the country. Radium (^{226}Ra) concentrations in the wines were generally higher (by a factor of 2) than those of uranium, reflecting enhanced root uptake of radium from soils into grapes, such as commonly observed in many agriculture products. Polonium (^{210}Po) concentrations in wines were in the average higher (by a factor of 4) than ^{226}Ra concentrations, indicating that most ^{210}Po in wine was probably from atmospheric depositions on vines and grapes rather than from root uptake. Radionuclide concentrations in table wines are comparable to concentrations of the same radionuclides in drinking water, and the radioactivity exposure through this ingestion pathway is minor. Results suggest that natural radionuclide levels in wine from several continents and latitudes may be very similar.

RER-P12, (Id: 86)

RADIOCARBON CALIBRATION CURVE INTCAL AND ATMOSPHERIC $^{14}CO_2$*

Ivo Světlík[a], Pavel Povinec[b], Lenka Tomaskova[a]

[a]*Nuclear Physics Institute AS CR*
[b]*Department of Nuclear Physics and Biophysics, Faculty of Mathematics, Physics and Informatics, Comenius University, SK-842 48 Bratislava, Slovakia*
svetlik@ujf.cas.cz

A calibration curve IntCal has been applied for radiocarbon dating of terrestrial samples to correct fine variations of ^{14}C activity in the environment. The calibration curve has been constructed from precise determinations of ^{14}C levels in sample sequences (e.g. tree rings, lake varves, coral layers, etc.). The age determinations of these samples have been carried out using other dating methods (e.g. dendrochronology, varve chronology, U/Th dating). The resulting calibration curve is a relation between years of calibrated age (real age) and ^{14}C activity (usually reported in years BP of Conventional Radiocarbon Age, following generally accepted Stuiver-Polach convention). For this purpose, the IntCal13 (2013) curve has been constructed, a more precise version of previously published IntCal09. The headway of this curve seems to be close to the linear relation in millennia scales. Nevertheless, the time course of the curve can be complicated considerably, if the scale expands on centuries or decades. Four characteristic shapes of the IntCal13 substructures, and implying limitations and possibilities of radiocarbon dating will be described in our presentation. Likewise, responsible mechanisms, connected with changes of environmental carbon (CO_2) and ^{14}C ($^{14}CO_2$) transport, will also be discussed.

RER-P13, (Id: 106)

COLLIDERS AND THEIR POSSIBLE GEORADIOCHEMICAL EFFECTS ON THE ENVIRONMENT

George Ryazantsev, Daria Minyaeva

anis-mgu@mail.ru

A dangerous factor is considered, which may precede the formation of black microholes, strangelets, magnetic monopoles and other objects in colliders, – the probability of turning the Earth into the "iron planet" or the flow of iron asteroids and meteorites. Proceeding only from real experimental evidence and theory-based provisions: 1) the quark-gluon plasma is already an experimental fact, 2) the dependence of the binding energy per nucleon from the number of nucleons in the nucleus is both experimentally and theoretically accurate, so we can assert that at the present moment the technical conditions for an uncontrolled conversion of all the chemical elements in the elements of Fe-Ni-Co group are already established, with the probability of catastrophic consequences for the Earth still extremely low, but 3) the possibilities of colliders are growing at a high speed and the dangerous threshold can be overcome in a very short time. A special group, established by CERN to evaluate the safety of experiments, presented a report which states that the Large Hadron Collider is not dangerous. The other dangerous process, which may occur from the uncontrolled formation of quark-gluon plasma of large volume and density in the conditions of the CERN experiment, is not considered at all. During this process, any substance turns into a cloud of elementary particles, which will condense in the process of cooling into the most energetically favorable state – the elements of the iron subgroup, which have the greatest values of the binding energy of the nucleons in the nucleus. The released energy will support this process till the complete conversion of all the chemical elements of the substance into the elements of the iron subgroup. It is believed that the first experimental results on the quark-gluon plasma were obtained in 1990 at CERN Super proton synchrontrone (SPS) (the concept of a fireball has deeper historical roots [1] and appeared for the first time in the physics of cosmic rays). Then, in 2000, also at CERN, the discovery of this "new state" of matter was announced. In the colliders, the energy of particles and the density of their torrent are continuously increasing, which naturally leads to a more "hot" chromoplasma, and to the increase of its volume and density. According to the prevailing ideas of today, the unlimited expansion of the fireball is very unlikely, but there are other opinions. For example, Academician E. Feinberg believed that the lifetime of fireballs is greatly underestimated [1]; Heisenberg's calculations were already giving the abnormally high cross-section of their formation [2]; and Fermi has long ago presented the scheme which allows a fireball to expand unlimitedly in the flow of the accelerator [3]. The works of B.L. Ioffe were also published [4], which presented the abnormal parameters of the fireball, significantly different from L.D. Landau's calculations [4]. The probability of formation of an abnormally large fireball could be significant. The reaction of "ferruginization" may obtain a global or nearly global nature. The possible protective measures to prevent the probable future catastrophe are being considered, as well as the hazardous geotectonic conditions of the experiments at CERN.

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RER-P14, (Id: 107)

NEUTRINO EMISSION AND THE SAFETY OF NUCLEAR OBJECTS

George Ryazantsev, Daria Minyaeva

anis-mgu@mail.ru

In 1979, there was a serious accident in the U.S. at the Three Mile Island nuclear power plant which involved two power-generating units. In 1986, the world witnessed a large-scale disaster in the USSR at the Chernobyl nuclear power plant that operated four power reactors. The last major accident occurred in March of 2011 in Japan. That accident involved six reactors. It is known that during the nuclear reactions in the reactors the torrents of anti-neutrino are released. At first, the neutrino emission was postulated as extremely high-penetrating, practically non-reactive to the matter. However, the capture cross sections of neutrinos, although really having very low values, are being measured at the extremely rough criteria. The situation here is somewhat similar to what happened to the neutron. Neutron, too, has high penetrating capacity, and often low capture cross sections, but, nevertheless, its cases of resonant interaction processes, that have sections many orders larger than normal, are well studied. From the very beginning of the discoveries of the neutrino, the "pervasive bias" has been adopted in the description of its properties, and little is known about its possible resonant interactions with matter and the research on these interactions. Resonant interactions are widespread in the microcosm and the physics of elementary particles, and it is not prudent to deny their presence for neutrinos, even with a very small probability. It must be said that for the relic neutrinos, the high level of interaction with matter is already widely discussed, but with the caveat that it is not typical for nuclear neutrinos. It is obvious for the greater part of the neutrino energy spectrum, but not for resonance. This is the first point. But there is another point: the interaction of neutrinos with matter is among the weak interactions, but, as pointed out by Academician B.M.Pontecorvo in 1970 [1,2], and discussed even earlier –¬¬ in 1964 – in the works of E.Bialynicka – Birula [3], the interaction between the particles them selves can proceed according to the mechanism of the strong interaction. This radically changes the situation; the presence of two or more neutrino fields close to each other can lead to a strong interaction between them, precisely: 1) to a sharp acceleration of the inverse beta process, which will lead to a large release of additional energy, and 2) to an increase in the fraction of excited nuclei in fissile material, which will lead to a decrease in its critical mass, and to an uncontrolled change of regimein the reactor to a supercritical state. Therefore, the work of two or more reactors located near each other is extremely worrying. The tendency to a greater increase in the number of cooperating power units (up to 7-8) is clearly showing. The conception of independence of the adjacent units, which is the prevailing conception at present, may appear misleading. At present, the most dangerous situations exist in Japan, Canada and India (NPPs with 7-8 power units); Ukraine has a nuclear power plant with 6 units (Zaporozhye); in Russia there are stations with 4-5 units. In addition to the mutual influence of nuclear power units, the question of the effect of natural neutrino torrents on their work also requires a systematic study. The methods of detecting the interactions of nuclear power units according to the neutrino mechanism are being discussed.

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RER-P15, (Id: 109)

RADIOACTIVITY OF TUNA SAMPLES CONSUMED IN SAUDI ARABIA

Nasser Alkhomashi[a], **Mohammed Al Khorayef**[b]

[a] *King Abdulaziz City for Science and Technology (KACST), Saudi Arabia*
[b] *Department of Radiological Sciences, College of Applied Medical Sciences, King Saud University, Saudi Arabia*
khomashi@kacst.edu.sa

Studies of radioactivity in sea foods are important in estimating the radiological hazards and dose exposure to the public. The importance has increased following Japan’s devastating 2011 earthquake and the following nuclear accident of Fukushima power plant. This is because there is a fear about risks of leaked radiation from the Fukushima Daiichi nuclear power plant to the Pacific Ocean which might have potential impacts on the marine food web. Fish and other sea foods normally concentrate radioactive elements particularly, ^{137}Cs and ^{134}Cs in their flesh which are eventually passed to humans. Saudi Arabia is importing different types of sea foods from all over the world including countries from the Pacific Ocean and Japan. Hence, there is a need to analyse the radioactivity levels in samples of sea food consumed in Saudi Arabia for safety consumption. In this study canned tuna samples which were produced in Japan and other places in the world were collected in different supermarkets of Riyadh. The samples were produced in July 2011 to 2012 a period which is post Fukushima nuclear accident of April 2011. The samples were analysed for ^{137}Cs, ^{134}Cs and ^{40}K using gamma spectrometry to provide information that can verify the extent and the nature of the level of radionuclides in fish associated with nuclear accident of Fukushima in Japan.

RER-P16, (Id: 111)

RADIOACTIVITY IN WATER FROM URANIUM MINING REGIONS

Fernando P. Carvalho, João M. Oliveira, Margarida Malta

Instituto Superior Técnico/Laboratório de Protecção e Segurança Radiológica
carvalho@itn.pt

Uranium mining and milling is known to produce enhancement of environmental radioactivity. In particular through surface runoff, waste water discharges, acid mine drainage, and seepage, radioactivity levels may increase in the surrounding areas and contaminate groundwater and surface waters. Results from radioactivity surveys in the center north of Portugal to assess the impact of past uranium mining activities showed that uranium series radionuclides in water may vary in a wide range. For example, in drainage from milling tailings at Urgeiriça, dissolved uranium (^{238}U), radium (^{226}Ra) and polonium (^{210}Po) were 35700 ± 1100, 1084 ± 30, and 700 ± 40 mBq/L, respectively. In the river Dão in the region, concentrations of the same radionuclides were 8.0 ± 0.3, 5.9 ± 0.8 and 9.7 ± 0.4 mBq/L, respectively, at background level and thus much lower. Water from open pits of flooded old uranium mines were often also high, such as in Mortórios mine, with 19890 ± 520, 34.8 ± 3.5 and 5.8 ± 0.2 mBq/L for the same radionuclides. In water from contaminated irrigation wells near the Cunha Baixa mine, concentrations were 4152 ± 122, 732 ± 53, and 5.1 ± 0.2 mBq/L. These water bodies and irrigation wells were found contaminated beyond reasonable level for water use, and water treatment and remedial measures were applied, including supply of alternate water. However, in such a uranium bearing granite regions of Portugal, concentration of radionuclides in water bodies outside the influence of old uranium mines were determined sometimes at high levels as well. For example, the water from a bore hole in a farm near Espinho village displayed 999 ± 29, 819 ± 42, and 2782 ± 150 mBq/L, respectively for ^{238}U, ^{226}Ra, and ^{210}Po. Water from another bore hole in Reboleiro area displayed concentrations of 4205 ± 184, 29.9 ± 1.3, and 33.0 ± 1.6 mBq/L, respectively for the same radionuclides. These naturally radioactive waters, sometimes with alpha emitting radionuclide concentrations higher that in uranium drainage from old mines, likely result from water contact with uranium mineralizations, sometimes under oxic other times under anoxic conditions. This calls the attention to the need for systematic radioactivity screening of water supplies in granite and uranium bearing areas. Proper water management and radiation protection in such regions should encompass waste waters and mine waters, but also natural waters.

RER-P17, (Id: 117)

MOBILIZATION OF RADIONUCLIDES AND HEAVY METALS FROM MILL TAILINGS IN A NORTHERN BOREAL ENVIRONMENT

Hanna Tuovinen[a], Esa Pohjolainen[b], Dina Solatie[c], David Read[d], Jukka Lehto[a]

[a]*University of Helsinki, Laboratory of Radiochemistry*
[b]*Geological Survey of Finland*
[c]*Finnish Radiation and Nuclear Safety Authority*
[d]*Loughborough University*
hanna.p.tuovinen@helsinki.fi

There is increasing awareness of the radiological impact of non-nuclear industries that extract and/or process ores containing naturally occurring radioactive material (NORM). These industrial activities may result in significant environmental problems if the waste generated during processing is not adequately managed. In 2010, a new project was launched in Finland, the object of which is to study the mobility of radionuclides and heavy metals from diverse mill tailings in a northern boreal environment. The project is funded by the Academy of Finland and involves the Universities of Helsinki and Loughborough, the Geological Survey of Finland and the Finnish Radiation and Nuclear Safety Authority. Three sites are being investigated: Talvivaara nickel mine, a former phosphate mine in Sokli, Lapland and a former pilot scale uranium mine in Paukkajanvaara.

The Talvivaara deposits in Sotkamo comprise one of the largest known sulphide nickel resources in Europe. It is an operational, open cast mine where Talvivaara Mining Company applies bioheap leaching to extract the metals from the ore. The leaching process has been shown to be heat generating and therefore suitable for the sub-arctic climatic conditions of Eastern Finland. In heap leaching, uranium dissolves in the pregnant leach solution (PLS) along with main base metals. Currently, the uranium is diverted into a gypsum pond. The radioactive progeny from the ^{238}U series are also mobilized and fractionate depending on chemical properties and the ambient conditions.

The Sokli complex is the westernmost deposit in the Devonian Kola alkaline rock province (ca. ^{365}Ma) and was discovered by Rautaruukki Oy in 1967. At the end of the 1970s, pilot scale mining and mineral processing took place at the site. The latter did not include chemical treatment of the apatite ore; processing was limited to removal of gangue minerals by physical methods. The mill tailings were deposited adjacent to the enrichment facility. The deposit is presently being developed by Yara International for beneficiation of the regolithic phosphate ore which overlies the magmatic carbonatite. In addition to the phophorus ores themselves, the carbonatite massif contains other minerals, such as niobium, iron and vermiculite. Apatite, which is known to exhibit elevated concentrations of uranium and thorium, is especially rich in the niobium ore.

The Paukkajanvaara mining site started operation in 1959. The mine was basically a test site for assessing the feasibility of larger scale uranium mining. The ore was milled and enriched at the mining site. Mining proved to be uneconomic, and the operations ceased in 1961. In the late 1970's the entrance of the mining shaft was covered with a concrete slab and the rest of the area including tailings, waste-water ponds etc., were abandoned. They were left untouched for nearly 30 years until Finnish Radiation and Nuclear Safety Authority initiated a review. Their results indicated that ambient radiation levels at the site had increased by 0.5 μSv/h as a direct result of the earlier mining operations. Rehabilitation was completed by 1994 after which the area was released for outdoor use without restrictions. The aim of the project is to generate new data from these three mines leading to a better understanding of the mobilization of radionuclides especially ^{226}Ra, ^{210}Pb and ^{210}Po and heavy metals in a northern boreal environment. The results will also play an important role in estimating radiation doses to the local population resulting from past and anticipated disposal of mill tailings. A short summary of the results gained to date from each site is given in the poster presentation.

RER-P18, (Id: 137)

TIME EVOLUTION OF SPECIATION OF RADIONUCLIDES ADSORBED ON SPECIMENS OF HOST ROCK ENCASING A REACTOR

Yulia Konevnik

IPHE RAS
leonenko@gmail.com

Three major variants for decontamination of nuclear sites are considered in Russia: (i) dismantling; (ii) conversion; and (iii) burial in-place. The concept of decontamination of a shutdown industrial uranium graphite reactor (IUGR) by burial in-place was accepted by Rosatom in 2009. The safety of a buried IUGR is based on a system of protective barriers consisting of both engineered barriers and natural ones, the latter being the rocks that confine the reactor. The natural barrier capacity to function as a safety barrier depends on the geological and geochemical structure of the rock mass and its sorption properties with respect to different radionuclides.

In this work, radionuclide sorption characteristics are evaluated for rock samples taken from the location zone of a shutdown industrial uranium graphite reactor, using groundwater of a composition that is analogous to that of the groundwater near the reactor location zone, under both aerobic and anaerobic conditions.

Over the course of two years samples were investigated to determine the sorption kinetics for U(VI), Np(V), Pu(IV), Am(III), and some fission products: Co(II), Cs(I), and Sr(II). This study showed that after water-rock interactions for 1-2 months, the derived distribution coefficients (Kd) continued to increase in long-term experiments up to two years. The experiments showed that the rock masses around the IUGR have high sorption characteristics for the studied radionuclides.

To investigate the reversibility of radionuclide adsorption and the strength of the radionuclide bonds with the rock, the adsorbed radionuclide speciation and variability has been studied by the Tessier technique. The proportion of strongly fixed radionuclide species exceeds 50 % of the total. The results showed that over time the speciation of radionuclides changes in two major ways: (i) the quantity of radionuclides that are strongly bound to the residual fraction and insoluble under acidic treatment increases with time, coupled with a decreasing proportion of radionuclides bound to exchange and carbonate fractions; and (ii) the quantity of adsorbed radionuclides bound to the Fe/Mn oxide fraction increased over time, at the expense of all other fractions.

This study demonstrated that the rock has reducing properties, reducing Np(V) to Np(IV) and U(VI) to U(IV), which decreases the mobility of these radionuclides in the deep geological environment. From the data obtained it is concluded that reduction by the Fe(II)-bearing minerals contained in the rocks confining the hosting massive of IUGR has occurred. Thus, the rock mass will function as an anti-migration protective barrier with respect to the radionuclides contained in a decontaminated IUGR, including the irradiated graphite disposed in the rock mass.

RER-P19, (Id: 140)

MOBILITY OF RADIOACTIVE CESIUM IN SOILS ORIGINATED FROM THE FUKUSHIMA DAIICHI NUCLEAR DISASTER; APPLICATION OF EXTRACTION EXPERIMENTS

Yoshikazu Kikawada[a], Masaaki Hirose[b], Atsushi Tsukamoto[c], Ko Nakamachi[c], Takao Oi[d], Teruyuki Honda[c], Hiroaki Takahashi[e], Katsumi Hirose[d]

[a]Department of Materials and Life Sciences, Faculty of Science and Technology, Sophia University
[b]Graduate School of Science and Technology, Sophia University
[c]Graduate School of Engineering, Tokyo City University
[d]Faculty of Science and Technology, Sophia University
[e]Graduate School of Engineering, Tohoku University
Kikawada y-kikawa@sophia.ac.jp

The mobility of radioactive cesium (Cs) in contaminated soils affected by the Fukushima Dai-ichi nuclear disaster in 2011 was studied by single-step and sequential extraction experiments. The Fukushima Dai-ichi Nuclear Power Plant (FDNPP) accident in March 2011 resulted in serious radioactivity contamination in areas adjacent to the FDNPP. Meanwhile, radioactive cesium originated from the accident was detected over a wide range of the northeastern half of Honshu, the main island of Japan. The chemical forms of the released radioactive materials are still not clear. However, it is highly probable that the behavior and mobility of Cs newly deposited on soils due to the accident are different from those of stable Cs that has existed in soils before the accident, because of the difference in chemical forms between them. In this study, we have conducted extraction experiments using several extractants on radioactivity contaminated soils collected in Japan after the accident, then discussed extraction behaviors of radioactive and stable Cs connected to their chemical forms.

The preliminary extraction experiments on non-contaminated soils revealed that stable Cs in soil was little extracted (less than 1 %) with Milli-Q water and 0.11M acetic acid (HOAc, pH 2.8), and that the extractants containing ammonium salts could partially extract Cs from the soils. The extracted portions of Cs with extractants containing ammonium salts are obviously higher than those with extractants containing cations other than ammonium like sodium, magnesium and calcium. This means that aqueous solutions containing ammonium salts are effective to extract Cs from soils.

Based on the findings from the preliminary experiments, we performed the three-step sequential extraction using Milli-Q water, 1 M NH_4OAc solution (pH 7) and 0.11 M HOAc in this order as extractants on some contaminated soils. The results of the sequential extraction experiments indicate that only a few percent of radioactive Cs was extracted with the 1 M NH_4OAc solution, and additionally radioactive Cs was partially extracted at the HOAc step after the NH_4OAc step, whereas extracted portions of stable Cs in each step were less than those of radioactive Cs. The result reveals that radioactive Cs newly deposited on soils due to the FDNPP accident has apparently a higher mobility than stable Cs commonly existing in the soils, although most of the radioactive Cs is kept fixed in soils, surviving extraction processes.

We also performed single-step extraction experiments using several extractants on contaminated soils. The results of extractions with strongly basic solution suggest that humic acid plays an important role in the extraction of Cs from soils at least in the high pH range where it can dissolve, since the amount ratio of humic acid to fulvic acid and the content of total organic carbon (TOC) in the leachates seem to be correlated with the extracted portion of Cs from the soils. Thus the characteristics of the soils such as amounts of organic matters and their properties probably control the mobility of Cs in soils.

RER-P20, (Id: 148)

VERTICAL MIGRATION OF $^{137}C_S$ IN THE UNDISTURBED SOIL PROFILES IN THE BASIN OF PČINJA RIVER, SOUTHEASTERN SERBIA

Jelena Petrović[a], Snežana Dragović[b], Ranko Dragović[c], Milan Đorđević[c], Mrđan Đokić[c], Mirjana Ćujić[a]

[a]*Institute for the Application of Nuclear Energy, University of Belgrade, Serbia*
[b]*Institute of Nuclear Sciences Vinča,University of Belgrade Belgrade, Serbia*
[c]*University of Niš, Faculty of Science and Mathematics, Department of Geography, Niš, Serbia*
jelenap@inep.co.rs

The ^{137}Cs activity concentrations in six undisturbed soil profiles collected during 2013 in the basin of Pčinja River, southeastern Serbia, were determined gamma-ray spectrometrically. Soil samples were collected at 5 cm intervals up to 50 cm depth at each location. The value of ^{137}Cs activity concentration when each soil layers of all soil profiles considered equal, ranged from 0.29 to 70.9 Bq kg^{-1}, with a mean value of 10.7 Bq kg^{-1}. Vertical migration of ^{137}Cs activity concentration was shown by unique profile which represents calculated average value based on the measured values of ^{137}Cs activity concentration for all six soil profiles by layers, in order to obtain general behavior of ^{137}Cs in soil in the basin of Pčinja River. It was noted that ^{137}Cs activity concentration decreased with soil depth up to 40 cm and then slightly increased down the profile, which could be consequence of different mechanical, mineralogical and chemical composition of soil layers in the analyzed soil profiles. The highest amount of total ^{137}Cs in the soil (25 %) was found in the first soil layer (0-5 cm), while the lowest one (2.46 %) was found in the eighth soil layer (35-40 cm). Based on the results for the unique profile 74.3 % of the total ^{137}Cs in the soil was found in the first four soil layers (from 0 to 20 cm) and only 25.7 % was found in the last six soil layers (from 20 to 50 cm), which indicates the slow migration of ^{137}Cs in the deeper soil layers.

RER-P21, (Id: 184)

PU(V) AND PU(IV) OXIDATION STATE DISTRIBUTION IN NATURAL CLAY

Galina Lujaniene[a], Karel Štamberg[b], Remigijus Juškėnas[a], Ieva Kulakauskaitė[a], Dušan Vopálka[b]

[a]SRI Center for Physical Sciences and Technology, Savanorių ave 231, Vilnius, LT-02300, Lithuania
[b]CTU in Prague, Department of Nuclear Chemistry, Prague 1, Brehova 7, Czech Republic
lujaniene@ar.fi.lt SRI

Environmental behavior of Pu isotopes can be strongly affected by oxidation–reduction reactions which can result in changes of their speciation, solubility and transport. Pu(V) and Pu(IV) sorption to three well characterized samples from the industrial exploitation site Šaltiškiai in North Lithuania was used to study their sorption kinetics and oxidation state distribution in natural clay systems. The composition of clay mineral coatings and their leaching during the sequential extraction procedures were investigated by means of the Mössbauer spectroscopy and X-ray diffraction. Pu (IV) and Pu(V) were added to achieve their initial concentration of 3×10^{-10} mol×L^{-1}. Solids were separated by centrifugation at 6000xg after a desired time.

Pu activity concentrations were measured by alpha spectrometry. The oxidation state distribution analysis was performed using thenoyltrifluoroacetone (TTA), bis(2-ethylhexyl) hydrogen phosphate (HEDHP) and 1,3-diphenyl-1,3-propanedione (DBM) solvent extraction as well as Pu(III, IV), Pu(V), Pu(VI), Pu(IV) and Pu(IV polymeric) species were separated.

In the natural clay systems the Pu oxidation state distribution analysis in the liquid-phase indicated a comparatively high content (up to 75 %) of Pu(III/IV) at pH~5, while polymeric species of Pu(IV) were found to be the dominant species at higher pH. Pu oxidation states in the solid-phase were determined after the desorption step using 3 mol×L^{-1} HCl, and Pu(III,IV), Pu(V) and Pu(VI) as well as Pu(IV) at pH~0 were analyzed in parallel. The content of Pu(III) was calculated from mass balance analysis. The obtained results showed that Pu(V) was mainly reduced to Pu(IV), and a small portion of Pu(III) found in the system was explained as a result of reduction by iron-bearing minerals such as montmorillonite and siderite present in the Triassic clay samples.

Experimental data obtained from the laboratory and field observation were used in modeling. The kinetic curves were evaluated by fitting the experimental data with six different types of kinetic models derived for the following six control processes: mass transfer (DM), film diffusion (FD), diffusion in the inert layer (ID), diffusion in the reacted layer (RLD), chemical reaction (CR) and gel diffusion (GD).

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RER-P22, (Id: 197)

PECULIARITIES OF PLUTONIUM ISOTOPIC RATIO DETERMINATION BY ELEMENTAL MASS SPECTROMETRY

Andrius Puzas[a], Paulius Genys[b], Vidmantas Remeikis[a], Rūta Druteikienė[a]

[a]*Center for Physical Sciences and Technology, LITHUANIA*
[b]*Vilnius university, LITHUANIA*

Inductively coupled plasma high resolution mass spectrometry (ICP-MS) is widely used technique for ^{240}Pu/^{239}Pu isotopic analysis tool which leads to use plutonium isotopic composition to assess the artificial radionuclide source in the environment fast and accurately. ICP-MS measurements usually are performed in low resolution mode (m/dm = 300) to enhance and maximize plutonium signal sensivity. In this measurement mode various interferences emerge from sample solutions and are likely to overlap plutonium isotopic signal. To study occurring interferences soil samples were used. They were prepared by using ion exchange and extraction chromatography separation techniques. It was determined that $^{238}U^{1}H^{+}$ interfering ion must be taken into the account if $^{238}U^{+}$ signal in the sample exceeds 1E5 cps. However, to take into the account $^{238}U^{1}H^{+1}H^{+}$ interference is not necessary. Besides, it is strongly not recommended to use hydrochloric acid as a final stabilizing matrix as serious $^{204}Pb^{35}Cl^{+}$ interferences occur on 239 a.m.u mass. For final stabilizing matrix five solutions were tested and it was found that the best one to use is ultrapure nitric acid as it creates the lowest background signal on ^{239} and ^{240} a.m.u masses.

RER-P23, (Id: 206)

^{210}Po AND ^{210}Pb IN FUR OF DOMESTIC ANIMALS

Karolina Szymanska

Faculty of Chemistry, University of Gdansk
karolina_szymanska14@wp.pl

The aim of the study was to determine ^{210}Po and ^{210}Pb in fur samples collected from 15 breeds of dogs Canis familiaris living in the northern Poland.

The average values of analyzed radionuclides in analyzed dog fur ranged from 0.46±0.02 $mBq \cdot g^{-1}$ to 15.05±1.13 $mBq \cdot g^{-1}$ for ^{210}Po and from 0.31±0.03 $mBq \cdot g^{-1}$ to 9.82±0.53 $mBq \cdot g^{-1}$ for ^{210}Pb. The highest activities of ^{210}Po and ^{210}Pb were measured for small long-haired dog Maltese while the lowest in small long-haired Yorkshire terrier and Poodle toy. The values of the ^{210}Po/^{210}Pb activity ratio were calculated from 0.82±0.09 for Yorkshire terrier to 5.16±0.45 for Bolognese.

Generally, both ^{210}Po and ^{210}Pb radioisotopes accumulation did not depend on dog sex. Higher values of ^{210}Po and ^{210}Pb were found in long and rough-haired dogs. Further, our experiments showed the hair from dogs living in villages contained more ^{210}Pb than dogs living in the cities and dogs eating dry food accumulate more ^{210}Po in their hair in comparison to fresh or mixed food eating dogs.

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^{241}Pu IN SEABIRDS

Dagmara Struminska-Parulska, Karolina Szymanska

Faculty of Chemistry, University of Gdansk
dagmara.struminska-parulska@ug.edu.pl

The paper presents unique data of plutonium ^{241}Pu study in seabirds from northern Eurasia, permanently or temporally living at the southern Baltic Sea coast. Together 10 marine birds species were examined: 3 species of permanently residing at the southern Baltic, 4 species of wintering birds and 3 species of migrating birds; about 150 samples were analyzed. The obtained results indicated plutonium is non-uniformly distributed in organs and tissues of analyzed seabirds. Generally the highest plutonium concentrations were found in the digestion organs and feathers, next in skeleton, and the lowest in muscles. Among analyzed birds the highest ^{241}Pu concentration was found in viscera, its activities in the digestive organs ranged from 9.7 ± 2.5 μBq$\times$g^{-1} ww (13.0 % of total ^{241}Pu) in great cormorant (P. carbo) to 228 ± 39 μBq$\times$g^{-1} ww (79.6 % of total ^{241}Pu) in velvet scoter (M. fusca). High ^{241}Pu concentrations were also found in liver where ranged from 21 ± 4 μBq$\times$g^{-1} ww in velvet scoter (M. fusca) (2.2 % of total ^{241}Pu) to 159 ± 31 μBq$\times$g^{-1} ww in tufted duck (A. fuligula) and feathers where ranged from 15 ± 4 μBq$\times$g^{-1} ww in great cormorant (P. carbo) (11.6 % of total ^{241}Pu) to 132 ± 59 μBq$\times$g^{-1} ww (34.2 % of total ^{241}Pu) in common eider (S. mollissima). The main source of plutonium in analyzed marine birds was global atmospheric fallout as well as the Chernobyl accident, which was confirmed by plutonium activity ratios of ^{241}Pu/$^{239+240}$Pu as well as ^{238}Pu/$^{239+240}$Pu.

On the basis of the average ^{241}Pu concentrations in the southern Baltic Sea biocenosis components the plutonium content in marine organisms increases as: seabirds < fish < phytobenthos < phytoplankton < zooplankton < zoobenthos. The authors would like to thank the Ministry of Sciences and Higher Education for the financial support of this work under grant DS/530-8120-D384-14.

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^{241}Pu IN THE SOUTHERN BALTIC SEA ECOSYSTEM

Dagmara Struminska-Parulska, Karolina Szymanska

Faculty of Chemistry, University of Gdansk
dagmara.struminska-parulska@ug.edu.pl

Most contamination studies have focused on alpha emitting plutonium isotopes so far. ^{241}Pu is less important in terms of its radiotoxicity than the α-emitting plutonium radionuclides ^{238,239,240}Pu but is quite significant because of its huge contribution to the whole plutonium fallout. Our previous experiments on air samples indicated extreme increase of ^{241}Pu amount in atmospheric dust in April 1986. The available information about the bioaccumulation and distribution of ^{241}Pu in the Baltic Sea ecosystem and Poland territory is still very limited. The main purpose of the present work was to complete the present knowledge and estimate the further levels of the Baltic Sea environment contamination.

The highest total ^{241}Pu concentration in seawater was found in the Słupsk Bank (3.35±0.17 mBq×dm^{-3}) and this area had the highest concentration of ^{241}Pu connected to suspended matter as well (1.94±0.12 mBq×dm^{-3}). High concentrations of ^{241}Pu in the central part of the southern Baltic Sea can be a result of Baltic water circulation.

The ^{241}Pu activity in phytoplankton sample from the Pomeranian Bay was 1.06±0.09 mBq×g^{-1} dw. Within zooplankton samples the highest ^{241}Pu activity was found in samples from the central part of the southern Baltic (2.66±0.16 mBq×g^{-1} dw) and from the Gdańsk Deep (2.64±0.70 mBq·g^{-1} dw). In zooplankton samples, similar situation to seawater samples was noticed – the highest concentrations of ^{241}Pu were found in the central part of the southern Baltic Sea, and similarly to seawater it could be a result of Baltic water circulation. Generally the data show significant differences in ^{241}Pu concentrations among all the species examined. The highest values of ^{241}Pu activities for whole organism were found in fish from Perciformes: benthic round goby (0.863±0.066 mBq×g^{-1} ww) and pelagic perch (0.666±0.001 mBq×g^{-1} ww). The lowest ^{241}Pu activity was found in flounder (0.104±0.009 mBq×g^{-1} ww). The plutonium was also non-uniformly distributed between the organs and tissues of the analyzed fish, especially pelagic herring and cod as well as benthic flounder.

In sediments, the highest amount of plutonium was found in the middle parts of all analyzed sediments and came from the global atmospheric fallout from nuclear tests in 1958-61. The distribution of ^{241}Pu in analyzed sediments samples was not uniform and depended on the sediment geomorphology and depth as well as on its location.

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POLONIUM ^{210}Po IN EDIBLE MUSHROOMS COLLECTED IN NORTHERN POLAND

Karolina Szymanska

Faculty of Chemistry, University of Gdansk
karolina_szymanska14@wp.pl

The main aim project was ^{210}Po determination in caps and stems of mushrooms from Leccinum pseudoscabrum, Leccinum aurantiacum, Leccinum vulpinum, Leccinum duriusculum and Leccinum quercinum collected in Pomorskie, northern Poland. Mushrooms are organisms which contain a lot of water (75-90 %). Mushrooms absorb heavy metals such as mercury, chrome, cadmium and radionuclides: e.g. polonium, uranium, plutonium from the environment (soil, air). Our studies have shown that the radionuclides are included not only in green , but also in mushrooms. Radioactive elements are taken either from the soil, through the mycelium or directly from the entire surface gathered in the fruiting bodies. As a result of the Chernobyl accident radioactive contamination of the environment has grown considerably. Many European countries were contaminated with significant amounts of radioactive elements.

In our research natural polonium ^{210}Po were determined. ^{210}Po is characterized by high radiotoxicity and its main sources in the environment are water, food, urban pollution and the Chernobyl accident. The average ^{210}Po concentration in caps and stem mushroom ranged from 0.85±0.09 mBq·g-1 in Leccinum quercinum stem to 10.77±0.47 mBq·g-1 in Leccinum pseudoscarbum cap. Analysis of ^{210}Po concentrations in mushrooms showed its higher values in caps than stem. This means the main source of ^{210}Po is wet and dry atmospheric fallout. The studies showed interspecies differences among all analyzed speciec and Leccinum pseudoscarbum (10.15 mBq·g-1) as well as Leccinum aurantiacum (11.83 mBq·g-1) accumulated more polonium than Leccinum vulpinum (2.22 mBq·g-1), Leccinum duriusculum (3.65 mBq·g-1) and Leccinum quercinum (3.57 mBq·g-1).

RER-P27, (Id: 212)

SORPTION OF CHEMICAL ELEMENTS BY PLANKTON IN THE PRESENCE OF HUMIC ACID

Evgeny Polyakov[a], Margarita Chebotina[b], Valentina Guseva[b], Ilya Volkov[a], Nikolai Khlebnikov[a]

[a] *Institute of Solid State Chemistry, UB RAS*
[b] *Institute of Plant and Animal Ecology, Ural Branch RAS*
polyakov@ihim.uran.ru

Humic acids (HA) are one of few omnipresent natural substances, which govern the migration trends of chemical elements in the biosphere. Being a complex mixture of high molecular organic compounds, they take part in accumulation, aqueous transfer and sorption of chemical elements in natural environment. The impact of HA on the sorption of stable trace elements and radionuclides in the geochemical media still remains a subject of intensive investigations. The role of HA complexes formation in the bioavailability (sorption) of microelements by plankton, lake plankton in particular, is significantly less studied. To determine the formal characteristics of trace elements sorption by living (active) and dead (inactive) species of lake plankton and to quantify the effect of HA concentration on these characteristics, we have performed an experimental investigation of the sorption systems “lake water - plankton – trace elements” under laboratory conditions. The plankton samples were collected in the Beloyarskoe Reservoir (Urals, RF). Plankton was chosen as a model object because of its leading role in the distributive biosedimentation of chemical elements in continental reservoirs. Due to its high productivity and accumulation ability, plankton is supposed to be one of the best bioindicators of contamination of water ecosystems with radionuclides and other pollutants, as well as a natural sorbent of trace elements [1].

The list of the microelements used in the sorption experiments included more than 50 chemical elements, the level of which in the lake water was above the detection limits of ICP-MS ELAN 9000. The experimental results of the analysis of sorption behavior of trace elements with respect to plankton are discussed in the presentation. It was found that for the most trace elements studied sorption by plankton (both active and inactive species) obeys the Langmuir law. The presence of soluble HA in water medium results in the reduction of the distribution coefficients of selected microelements towards active plankton. It is deduced that lake plankton interacts with trace elements in lake water and may be considered as a promising bio-sorbent of trace elements and radionuclides.

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RER-P28, (Id: 226)

EXPLORATION OF RADON-RICH WATERS IN CRYSTALLINE TERRAINS BY GAMMA METHOD IN SPITE OF RADIOACTIVE DISEQUILIBRIUM

Viktor Goliáš[a], Lenka Hrušková[a], Tomáš Lipanský[a], Tadeusz Przylibski[b], Radek Procházka[c]

[a]*Charles University in Prague*
[b]*Wrocław University of Technology*
[c]*Lesní 1079, Dobřichovice*
wiki@natur.cuni.cz

Radioactive mineral waters (rich in dissolved ^{222}Rn) are highly valued for their medical use. Therefore they have been intensively explored in last years (2005–2014) in Orlica-Sněžník dome and Krkonoše-Jizera crystalline areas. Springs of radioactive medicinal water are bound up with the Cambrian/Ordovician orthogneisses (the Krkonoše, Kowary and Jizera orthogneiss).

For these purposes an exploration method has been developed as a combination of GIS (ArcMap 9.1–10.1) for the area preparation followed by field radiohydrogeochemical mapping. As basic GIS layers a geological map 1:50000, topography, airborne gamma spectrometry, linear structures from Remote Sensing were used.

The field radiohydrogeochemical mapping was realized in scale 1:10000 in perspective areas selected by GIS preparation. All water manifestations (wetlands, springs, man-made objects) were measured by gamma as an indicative method. In case of positive results (increased gamma in water) the water was sampled and a passportized field record was written. The exploratory groups were equipped with sensitive field scintillometers RP-11 with RFS-05 gamma probes. The ^{222}Rn activity in water samples was determined by the emanometric method (RP-25) at the field base. Control analysis in the laboratory by LSC (QUANTULUS) was made. Standardization of all methods is commonplace.

More than 50 water sources with activity above 1500 Bq/L (i.e. "radioactive mineral waters") were found in the whole territory. The highest radon activity reaches 6215 Bq/L in case of the Michael spring near Nové Město p. Smrkem. Waters are cold (5–9.5 °C) and low-mineralized (TDS < 100 mg/L), ^{222}Rn is the only important component.

Gamma activity of fresh flow water is close to zero; it is free of the short-lived ^{222}Rn gamma active progeny (^{214}Pb and ^{214}Bi). Field measuring of fresh water gamma activity growth indicates its effective age about 7 minutes only. But the gamma activity is really detectable in frequent cases where there is a slowdown in the flow and mud or sediment of organic material is created. In fact, we have a lot of evidence from the field Gamma dose rate in water reaches 4624 nGy/h. Relationship of gamma (gamma dose rate in water) and radon-in-water activity is complicated; both quantities correlate freely. It depends on the specific situation of every single spring. Generally we can say that the gamma dose rate is a function of radon-in-water activity, water velocity and flowing water volume: $D_w = f(A_v, v, V)$. Gamma method, in spite of radioactive disequilibrium, is useful for exploration of radon-rich waters in crystalline terrains on the basis of our empirical findings in the field, much better than the "blind" method.

RER-P29, (Id: 249)

EXAMINATION OF ^{238}Pu, ^{239,240}Pu AND ^{137}Cs RADIONUCLIDE DIFFUSION IN SOILS AND LAKE BOTTOM SEDIMENTS

Sarunas Buivydas, Evaldas Maceika, Nikolaj Tarasiuk, Benedikta Luksiene, Vitold Filistovic, Eva Koviazina, Marina Konstantinova, Andrius Puzas

State Research Institute Center for Physical Sciences and Technology
bena@ar.fi.lt

Application of an appropriate model and transfer parameters for radionuclide migration in soils and fresh water ecosystems (e.g. lakes) to predict the long-term radionuclide behaviour is of great concern. Transfer of radionuclides in lake ecosystem is mostly governed by the processes of diffusion, perturbation of soil or lake bottom sediments and transport of long- lived radionuclides with the water flows. In order to evaluate values of diffusion coefficients 3 core samples were taken in the vicinity of Vilnius city (Lithuania): in upland and flooded soils (to the depth of 30 cm) as well as in lake bottom sediments (to the depth of 40 cm). ^{238}Pu, ^{239,240}Pu and ^{137}Cs activity concentrations in profile layers were measured. Two radionuclide activity concentration peaks were characteristic in flooded and upland soil cores. In sediments, single radiocesium and plutonium activity concentration peaks were observed at the same depth, which depends on the sedimentation rate in the lake (~4.7 mm×y^{-1}). The activity concentration ^{238}Pu/^{239,240}Pu and isotopic ^{240}Pu/^{239}Pu ratios have shown the global fallout from nuclear weapons testing to be the main Pu contamination source in the studied environmental systems. ^{137}Cs/^{239,240}Pu activity concentration ratio values were sufficient for the evaluation of the contribution of Chernobyl-derived radiocesium.

Fitting the deepest slopes of the vertical profiles in the lake bottom sediments of the respective radionuclide activity concentration peaks with Gauss functions, it was found that effective diffusion coefficients (for the period from 1963) of plutonium and radiocesium were ~0.21 and ~0.16 cm^2×y^{-1}, respectively. According to deeper slopes of radiocesium activity peaks the determined diffusion coefficients in cores of the flooded and upland soil samples were also about the same (~ 0.06 and ~0.07 cm^2×y^{-1}, respectively). Deepening rates of the activity concentration peaks related to the supposed mobile fraction of both radionuclides were larger in the flooded soil core from the old channel (~0.27 cm×y^{-1}). In the upland soil core they were equal to ~0.16 and to ~ 0.12 cm×y^{-1} for plutonium and radiocesium, respectively.

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RER-P30, (Id: 251)

MONITORING OF RADIOACTIVE CONTAMINATION OF POLISH SURFACE WATERS IN 2012-2013*

Agnieszka Fulara, Małgorzata Kardaś, Barbara Rubel, Maria Suplińska, Adam Adamczyk

CENTRAL LABORATORY FOR RADIOLOGICAL PROTECTION
fulara@clor.waw.pl

Radioactive isotopes of anthropogenic origin have appeared in the environment as a result of human activities. The main sources of these radionuclides were 1) atmospheric testing of nuclear weapons done in the years 1945-1980 with particular intensity in 1951-1958 and later in 1961-1962 and 2) the Chernobyl nuclear reactor accident in April 1986. The greatest contribution to the radioactivity level in the environment caused by artificial radionuclides was done by radioisotopes of cesium (^{137}Cs) and strontium (^{90}Sr).

Monitoring of radioactive contamination in the terrestrial and marine environment in Poland was performed by Central Laboratory for Radiological Protection (CLOR) from early seventies. An extended monitoring program of radioactive contamination of Polish surface waters was carried out by CLOR since 1992, as a work done on request of the National Fund for Environmental Protection. In the frame of this monitoring the samples of water were collected twice of year (spring and autumn) from the sampling points located along two main Polish rivers: Vistula River and Odra River and in selected polish lakes situated in different part of the country.

In 2012-2013 the water samples were taken from 7 sampling points on river Vistula and her tributaries, 5 sampling points on river Odra and her tributaries and 6 lakes situated in lake districts Drawskie and Lubuskie, region of Warmia and Mazury, Suwalki region and Lublin Province. Determinations of ^{137}Cs and 90Sr in twenty liters water samples were performed by radiochemical method and activity concentration of these radionuclides were measured using low level beta counter.

In 2012-2013 the average activity concentrations of ^{137}Cs in the drainage basin of the Vistula ranged from 2.99 mBq/l to 6.58 mBq/l, of Odra River from 2.44 mBq/l to 6.11 mBq/l and in lake waters varied from 1.92 mBq/l to 7,96 mBq/l. The average activity concentrations of ^{90}Sr in river waters ranged from 1.89 mBq/l to 8.00 mBq/l, and from 1.98 mBq/l to 22.84 mBq/l respectively and in water of lake from 1.69 mBq/l to 6.19 mBq/l

Both, the annual average concentrations of analysed radionuclides and the data obtained for single determinations for water do not differ from data obtained in previous years. Monitoring of radioactive substances in Polish surface waters leads to the conclusion that ^{137}Cs and ^{90}Sr contamination of rivers and lakes on the Polish area is still low. Our determinations confirm that new releases of radioactive isotopes into the environment, with a significant impact on water contaminations, were not observed in Poland.

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Pb-210 AND Po-210 IN SOME MEDICINAL PLANTS

Elena Puchkova, Oksana Bogdanova

Saint-Petersburg State University
evpuchkova@yandex.ru

In recent decades, a global trend has been observed in an increased consumption of medicinal plants and herbal formulations, which makes monitoring of herbal medicines to be an actual problem as regards their pollution with heavy metals, pesticides and radionuclides [1]. The highly-toxic are long-lived decay products of U-238 Series, ^{210}Pb and ^{210}Po. In plants, which are used for making medicinal formulations,the ^{210}Po content can be as high as several tens of Bk/kg [2].

The aim of the present work was to determine specific radioactivity of ^{210}Pb and ^{210}Po in medicinal plants, which are commercially available via the network of pharmacies, and to estimate the effective radiation dose due to ^{210}Po in humans for a 30-day course of treatment with phyto-teas prepared by infusion from these herbs. Po-210 in samples and in aqueous extracts were determined by alpha-spectrometry. The samples were digested with a mixture of $H_2O_2 + HNO_3$(conc.). The aqueous extracts were obtained according to the recommended procedure. ^{210}Po was quantitatively self-deposited on nickel discs,the remaining solution having been kept for 6 to 8 months for ^{210}Po to accumulate from ^{210}Pb. After that period ^{210}Po was deposited again. As a tracer to check chemical yields,a mixture of ^{208}Po and ^{209}Po was used. All data are recalculated for the time the samples were made.

Six samples were studied. They are:
1. Quercus dalechampii Ten.;
2. Alpinia officinalis L.;
3. Ledum palustre L.;
4. Betula pendula Roth;
5. Plantago major L.;
6. Artemisia absinthium L.

Specific radioactivity of ^{210}Pb was from 1.3 (Alpinia officinalis L.) to 18.1 (Ledum palustre L.) Bq/kg d.w. and that of ^{210}Po was from 94 (Betula pendula Roth) to 2257 (Ledum palustre L.) Bq/kg d.w. The ^{210}Po/^{210}Pb ratio in the samples under study substantially exceeds unity, which means that the origin of ^{210}Po in there is not related only to radioactive decay of ^{210}Pb. A fraction of the “unsupported” ^{210}Po is mere 0.2–5.0 % of the total amount of the radionuclide, whereas the “unsupported” ^{210}Po fraction is close to 100 %. Analogous results are given in [3]. The obtained data can be explained by a predominant absorption of ^{210}Po over ^{210}Pb by plants from the environment. For example, it is known that the mean value of the ^{210}Po/^{210}Pb ratio in air is 0.17, in atmospheric deposits, from 0.1 to 0.54, whereas in soil it is close to 1.0 [4]. The mean annual dose of radiation for the population of the Russian Federation due to ^{210}Pb, ^{210}Po, ^{228}Ra, and ^{226}Ra radionuclides in food and drinking water is estimated to be at a level of 164 µSv/yr [5].The radiation exposure due to ^{210}Po, which enter the human organism with a daily consumption of 100-300 mL of medicinal plant infusions for 30 days, is from 2 to 21 µSv. It amounts from 1 to 13 % of mean annual dose. Based on the above, a conclusion is drawn on that the relative contribution of phyto-teas into the effective annual radiation dose due to Polonium-210 in humans is substantial and should be taken into account.

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^{210}Po IN DIFFERENT TYPES OF TEAS

Elena Puchkova, Oksana Bogdanova

Saint-Petersburg State University
evpuchkova@yandex.ru

As to their biological effect, ^{210}Pb and ^{210}Po - radionuclides are in a group of the most toxic ones. ^{210}Pb and its daughter products are mainly formed in the atmosphere following alpha-decay of ^{222}Rn. Then, together with dry and wet depositions, these products are precipitated on the soil surface and plant leaves, the latter being known as a plant part with an enhanced content of ^{210}Po [1]. As teas are globally the second only to drinking water as regards the volume consumed, the determination of ^{210}Po in teas is an actual problem.

The aim of the present work is to determine specific activity of ^{210}Po in different types of teas (black and green ones) and to estimate the effective annual radiation dose due to alpha-particles of ^{210}Po that enters the human organism when drinking tea. The content of ^{210}Po in samples and aqueous extracts thereof was determined by alpha-spectrometry. The aqueous extracts were obtained by brewing 10 g of tea in 200 mL of boiling water for 10 minutes. The effective annual radiation dose was calculated assuming that the daily consumption was 10 g of dry tea. Experimental results and calculations are presented below.

Sample and country of origin;
Specific radioactivity of ^{210}Po,Bk/ kg; Fraction of extracted ^{210}Po, %;
Effective annual radiation dose due to ^{210}Po, μSv/yr
Black Teas
1.Princess Nuri (India); 7.3±1.4; 17 %; 5
2.Krasnodar (Russia); 12.7±3.5; 1.5 %; 1
3.Lisma (Ceylon); 16.7±4.6; 4 %; 2
4.Talk (India); 24.5±4.8; 4 %; 3
Mean 15.3±5.0; 6.6 %; 3
Green Teas
5.Bird Ceylon Tea; 1.0±0.3; 11 %; 1
6.Jaf Tea (Ceylon); 3.2±0.8; 55 %; 9
7.Bird of Paradise; 3.5±1.0; 18 %; 3
8.Princess Java (China); 24.4±4.2; 13 %;
9 Mean 8.0±3.0; 24.3 %; 6

Variations of ^{210}Po specific radioactivities in the samples under study may be attributed to varying ^{222}Rn concentrations in the surface air and different soil properties of the tea gardens. The mean ^{210}Po concentration in the samples of black tea is approximately two times that of in the samples of green tea, a possible reason for this being specific processing technologies for different types of tea. The raw material used for making green tea is treated with steam at temperatures from 95 to 100 °C [2], the weakly bounded Polonium species (e.g., those of in dust particles) being taken off the tea-leaf surface. When making black teas, there is no stage of steam treatment and ^{210}Po is not removed from the tea leaves. When making green tea in China, instead of steam treatment it is another procedure that is used, that of roasting the raw material at temperatures from 65 – 75 °C [2]. It cannot result in the removal of ^{210}Po from the leaf surface, and in the "Princess Java" green tea produced in China there are more radionuclide than there is in teas from Ceylon.

Green tea aqueous extracts are known to contain more organic substances than those ones from black teas [2]. The higher ^{210}Po content in extracts from green teas might be an indirect indication of a change of the physico-chemical state of the radionuclide during the stage of processing the tea raw material. It is possible that a certain part of the radionuclide transforms from the initial inorganic species into an organic one.

On drinking green teas, the maximum effective annual dose due to ^{210}Po, which is equal to 9 μSv/yr, is comparable to the total annual dose due to ^{210}Pb, ^{210}Po, ^{228}Ra, and ^{226}Ra nuclides acquired from drinking water and is estimated to be 10 μSv/yr [3].

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RER-P33, (Id: 257)

DETERMINATION OF URANIUM REFERENCE LEVELS IN THE URINE OF WARSAW RESIDENTS (POLAND)

Ewa Starościak, Lidia Rosiak

Central Laboratory for Radiological Protection
starosciak@clor.waw.pl

Uranium isotopes U-238 and its decay product U-234 and also U-235 are isotopes primary existing from the beginning of the earth. These isotopes are present in all components of the environment. The main source of uranium isotopes passing into the human body is drinking water and food. Uranium is toxic both chemically - as a heavy metal and radiochemically - as an emitter of alpha and gamma radiation. The most of uranium absorbed by man is excreted through the kidneys, the urine is therefore a good biomarker for it. The aim of the study was to:

1. Determination of the concentration of U-238, U-234 and U-235 in daily urine samples of people not having documented work with uranium isotopes.

2. Calculation of the absorptions and effective doses, based on the daily excretion of uranium isotopes with the urine, to determine reference level for the evaluation of internal contamination. Daily urine samples were collected from residents of Warsaw, adults who had never worked with uranium compounds and children. U-238, U-234 and U-235 in urine samples were determined radiochemically in the presence of the marker U-232. In all examined cases, the radioactive concentration of U-235 were below the limit of detection to be 0.5 mBq/l. U-238 activity concentrations of the tested samples for adults ranged from 3.83±0.93 to 30.54±1.7 mBq/d (average : 16.1±3.4 mBq/d) and the U-234 concentration were in the range of 4.96±0.95 to 28.61±2.6 mBq/d (average : 12.31±1.09 mBq/d). For children an average daily urinary excretion of U-234 was 1.81±0.74 mBq/d and of U-238 was 1.23±0.37 mBq/d.

There was a correlation between daily uranium excretion and person's age for U-234 and U-238 (respectively $R_2 = 0.48$ and $R_2 = 0.44$). This indicates that the amount of daily uranium excreted increases with age, but it is not dependent on sex. On the basis of data on a daily excretion of uranium isotopes in urine daily and annual absorption of these isotopes were calculated. It was assumed that uranium introduced into the blood from the digestive tract is in equilibrium with the uranium present in the human body, and the transmission factor $f_1 = 0.02$ is the same for all components of the diet. The average annual ingestion of U-238 and U-234 for adults was 4.58±0.34 Bq/year and 5.97±0.97 Bq/year respectively. With annual ingestion of uranium isotopes the mean effective dose was calculated. This dose for adults inhabitants of Warsaw was 0.21 µSv/year from U-238, and 0.29 µSv/year from U-234, giving a total dose of uranium equal to 0.50 µSv/year. This dose represents approximately 0.05 % of the annual dose limit for the population.

The calculated average daily and annual ingestion of U-234 and U-^{238} for children were respectively 1.89 mBq/d and 0.69 Bq/year and 1.28 mBq/d and 0.46 Bq/year. Calculated the annual ingestion of U-^{238} for children are about 10 times lower than the average ingestion of this radionuclide for adults 5.0 Bq/year. Average effective doses for children of U-234 and of U-238 were at 0.02 µSv/year, giving a total dose of uranium equal to 0.04 µSv/year. Total effective dose for children is 10 times lower than the annual dose received by adults.

RER-P34, (Id: 258)

POLONIUM - 210 AND LEAD - 210 IN URINE SAMPLES OF WARSAW RESIDENTS

Lidia Rosiak, Ewa Starościak

Central Laboratory for Radiological Protection
rosiak@clor.waw.pl

^{210}Po is natural, short-lived ($T_{1/2}$ = 138.3 days) alpha radiation emitter. It occurs in Earth crust in trace amounts as a product of radioactive Uranium–Radium decay series. The isotope is found in small amounts in human environment: air (<0.5 mBq/m^3), drinking water (about 0.5 mBq/L), food (20-200 mBq/kg), tobacco (13.3 mBq/cigarette in Poland) and cigarette smoke (9.62 mBq/cigarette in Poland). Polonium introduced into the body is strongly radiotoxic, damages circulatory system and lungs. In the case of ^{210}Po igested by humans, the content of this radionuclide in the human body can be determined based on the analysis of excreta such as urine samples. ^{210}Po is a daughter of ^{210}Pb which is beta and gamma emitter of half-decay $T_{1/2}$ = 22.3 years. In small quantities, it is present in the human environment: air (<0.1 mBq/m^3), drinking water (approximately 1.5 mBq/l), food (43-155 mBq/kg). ^{210}Pb in the atmosphere, in addition to natural origin, artificial isotope of nuclear explosions origin is introduced (particularly in the years 1952 to 1962). ^{210}Pb is toxic both as a heavy metal, accumulating in the human body and as a radioactive isotope.

The aim of the study was the determination together ^{210}Po and ^{210}Pb in urine samples of people not occupationally exposed (smokers and non-smokers). Urine samples of adults Warsaw inhabitants were collected. There were analyzed daily samples and two days samples. The average volume of the sample was 1.73 l/24 h (range 0.9-2.3 l/24 h).

The samples, after the addition of the tracer ^{209}Po, were evaporated almost to dryness with the addition of about 50 ml of concentrated HNO$_3$. To the thus prepared samples perchloric acid was added in order to drive off the nitric acid. Samples were evaporated and the residue was dissolved in a 0.5 M solution of hydrochloric acid with a small addition of ascorbic acid (complexing metal ions such as Fe^{3+}). This was followed by deposition of ^{210}Po and ^{210}Pb on a nickel disc dimensions f = 23.8 mm, thickness 0.5 mm, coated on one side with teflon. Deposition was carried out, stirring the solution, for 6 hours at 85 °C, all the while controlling the temperature and liquid level. After the deposition disc was removed, rinsed with water, ethanol and dried. Then the measurement of ^{210}Pb beta radiation was carried (thin film covering the disc to eliminate alpha radiation). Next the measurement of ^{210}Po alpha radiation was perforemed.

Fluctuations in activity concentration of ^{210}Po in the urine are quite substantial, from 1.01 mBq/l in urine sample of 81 year old woman tobacco smoker to 13.38 mBq/l in urine sample of 62 year old man, also a smoker of tobacco. Average ^{209}Po yield pattern was 42 %. Concentrations of radioactive ^{210}Pb in urine are less diverse and range from 0.86 mBq/l in urine sample of 59 year old non-smoker male to 8.97 mBq/l in urine sample of 62 year old female non-smoker. On average, tobacco smokers excreted per day in urine 5.84 ± 6.23 mBq/d (range 1.84 - 21.01 mBq/d) of ^{210}Po isotope and on average 7.37 ± 4.42 mBq/d (range 1.86 - 15.78 mBq/d) of ^{210}Pb isotope. Non-smokers excreted in the urine per day on average 4.23 ± 2.81 mBq/d (range: 2.35 - 10.30 mBq/d) of ^{210}Po and 6.76 ± 2.97 mBq/d (range: 1.86 - 11.14 mBq/d) of ^{210}Pb. Daily excretion of ^{210}Po with urine increases with age insignificantly. The highest values were observed for persons at the age of about 60 years.

RER-P35, (Id: 265)

THE SORPTION OF NICKEL(II) AND EUROPIUM(III) IN THE ABSENCE AND PRESENCE OF COMPETING METAL CATIONS ON VARIOUS OXIDE MINERALS WITH DIFFERENT SURFACE PROPERTIES

Sinikka Virtanen[a], Jenna Knuutinen[a], Nina Huittinen[b], Thomas Rabung[c], Jukka Lehto[a]

[a]*University of Helsinki, Department of Chemistry, Laboratory of Radiochemistry*
[b]*Institute of Resource Ecology, Helmholtz-Zentrum Dresden-Rossendorf e.V*
[c]*Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology*
sinikka.m.virtanen@helsinki.fi

Studies on the competitive sorption of radionuclides and other metal ions are often conducted using elements with similar chemical properties, such as oxidation states. A study by Bradbury and Baeyens [1] suggests that metal ion sorption on clay minerals is non-competitive when the metal ions have significantly different chemical properties. Thus, metals with same oxidation states and a similar tendency towards hydrolysis would compete with one another, while metals with different properties would not. For example, competition for the surface sorption sites would occur for Eu(III) and La(III) but not for Eu(III) and Ni(II). The effect of sorption competition has to be considered correctly in performance assessment calculations for nuclear waste repositories, in order not to overestimate the retention of radionuclides in the presence of multiple solutes.

In the present study, the possible sorption competition of metal cations on oxide minerals with different pH dependent surface charge properties is investigated by batch sorption experiments. At first the influence of pH on the sorption behaviour of europium(III), lanthanum(III) and nickel(II) on different minerals is investigated in a series of experiments without a competing cation. In a second step, sorption competition studies are conducted using Ni(II) and Eu(III) that have different oxidation states and hydrolysis behaviour and with Eu(III) and La(III) that have similar chemical properties to resolve whether or not the findings of Bradbury and Baeyens can be applied for the investigated mineral systems. The oxide minerals TiO_2, ZrO_2 and α-Al_2O_3 were chosen based on their different surface charge properties. Experiments are done with and without the competing element in buffered solutions in a glove box under N_2 atmosphere. The competing element is added before, at the same time or after the primary metal addition to distinguish the role of different kinetics of sorption and desorption. The metal concentration of at least one element has to be high enough to be outside of the ideal sorption range where site saturation effects are expected to occur. Initial results indicate that Eu(III) and Ni(II) are not competing for the same sorption sites as the hypothesis of Bradbury and Baeyens [1] suggests. The batch experiments are still on-going and a summary of the main results will be given in the presentation.

[1] Bradbury M. H. and Baeyens B., (2005) Experimental measurements and modelling of sorption competition on montmorillonite, Geochimica et Cosmochimica Acta, 69, 4187-4197.

RER-P36, (Id: 282)

COMPARATIVE STUDY OF RADIOACTIVITY IN NORM SAMPLES USING ICP-MS AND INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

Jong Myoung Lim, Hoon Lee, Young-yong Ji, Mun Ja Kang, Geun Sik Choi, Kun Ho Chung, Hyun Cheol Kim

Korea Atomic Energy Research Institute
jmlim@kaeri.re.kr

As an attempt to reduce the social costs and apprehension arising from radioactivity in the environment, an accurate and rapid assessment of radioactivity is highly desirable. Naturally occurring radioactive materials (NORM) are widely spread throughout the environment. Concern regarding the radioactivity from these materials has therefore been growing over the last decade. To determine the proper handling options, a rapid and accurate analytical method that can be used to evaluate the radioactivity of radionuclides (e.g., ^{238}U, ^{235}U, ^{232}Th, ^{226}Ra, and ^{40}K) should be developed and validated.

Typically, α-spectrometry has a major disadvantage of a long counting time, while it has a prominent measurement capability at a very low activity level of ^{238}U, ^{235}U, ^{232}Th, and ^{226}Ra. Contrary to the α-spectrometry method, a measurement technique using ICP-MS allows radioactivity in many samples to be measured in a short time period with a high degree of accuracy and precision. For both techniques, however, the pretreatment process consequently plays an important role in the measurement uncertainty. Thus, a method development and validation should be performed. A method was developed for a rapid analysis of natural radioactive nuclides using ICP-MS. A sample digestion process was established using $LiBO_2$ fusion and Fe co-precipitation. A magnetic sector field ICP-MS (SPECTRO MS) was used for a rapid determination of the radionuclide concentration. For an evaluation of the accuracy and precision of the method, certified reference materials (CRMs) were analyzed using an established process. The analytical results of CRM samples were in agreement with the certified concentration values.

In this study, the radioactivity concentration in raw materials (e.g., bauxite, bentonite, ceramic, clay, monazite, and zirconium sand) and by-products (e.g., coal fly and bottom ash) was determined using ICP-MS and $LiBO_2$ fusion method. To validate the analytical results using the method evaluated in this study, duplicate samples were also analyzed using an instrumental neutron activation analysis.

RER-P37, (Id: 291)

BIOLOGICAL BARRIER FOR NITRATE IONS IN ENVIRONMENTS

Alexey Safonov[a], Varvara Tregubova[a], Tamara Nazina[b], Victor Ilin[a], Tamara Babich[b], Elena Zakharova[a]

[a] *Frumkin"s Institute of Physical Chemistry Russian Academy of Science*
[b] *Vinogradskiy Institute of Microbiology Russian Academy of Science*
alexeysafonof@gmail.com

Disposing of the nuclear industry wastes in Russia and the U.S.A. in the 20th century have led to significant amount of storages not equipped with appropriate effective/protective barrier systems. This pose risks of environmental pollution through dissipating harmful macrocomponents and radioactive nuclides. The basic RW macrocomponent are nitrate ions present at concentration levels from 10 to 350 g/dm^3. These are rather toxic for ecosystem for the and are characterized by high migration level. The factor that can significantly impact to the migration profiles of nitrate and metals in the environment is the influence of biochemical processes. The purpose of this work is to create a barrier for the immobilization of nitrate ions in subterranian freshwater through the intensification of biochemical processes by organic matter around the artificial pond – surface repository B-2 with LRW at the Siberian Chemical Combine. It will be the part of the existing barrier system of the conserved repository B-2 at Siberian Chemical Combine. Nowadays there is new geochemical barrier based on silicate polymers in groundwater around the conserved repository. It can block main radionuclides with very high efficiency, but can’t slow-down the nitrate ion migration risk. The concentration of nitrates in groundwater around the conserved repository can crease up to 5000 mg per liter. The essence of the biobarrier method is to stimulate the vital processes of autochthonous (indigenous) microorganisms leading to the destruction of nitrate ions to ecologically safe molecular nitrogen by injecting to contaminated zone as organic substrates into groundwater around the repository.

In laboratory conditions, indigenous bacteria of groundwater samples were proved to be able to decrease nitrate concentration from 3-5 g/l to 10-15 mg/l when were amended with acetate, sucrose, lactate, or glucose in concentration 1-5 g/l as electron donor and carbon source. These results are the scientific basis for the development of biobarrier technology. This biotechnology could improve the existing barrier system of repository B-2. The project was supported by grants: Russian Foundation for Basic Research (№ 13-04-92105 and 14-03-00067)

RER-P38, (Id: 292)

TOXIC EFFECTS OF RADIOACTIVE WASTE COMPONENTS ON MICROBIAL CELLS IMMOBILIZED ON BIOSENSOR

Alexey Safonov, Anastasia Alexandrovskaya, Varvara Tregubova, Alexey Kluev, Vladimir Andreev

Frumkin"s Institute of Physical Chemistry Russian Academy of Science
alexeysafonof@gmail.com

During the period of nuclear power facilities in the world, Russian Federation and the United States have accumulated a significant amount of radioactive waste (RW) in liquid form, which contacted with the biosphere in accidental emissions and while being stored in open repositories. Radioactive waste in the environment cause number of toxic effects by ionizing radiation and chemical components, especially nitrate salts in concentrations up to 300 g per liter, oils, EDTA and other chelating agents, and heavy metals. Toxic effects caused by exposure of radioactive waste components are key issues in radioecology and environmental biotechnology, for example, for monitoring nuclear objects after conservation. To assess the toxic effects on ecosystems test model (algae, plants, protozoa, arthropods, fish) are usually used, but such methods are often expensive and long-termed process.

Aim of this paper, is to assess the toxicity of radioactive waste on the ecosystem by electrochemical method based on the respiratory activity of aerobic bacterial cells immobilized on the modified Clark electrode. This method allows to obtain data of the waste components concentration effect on the rate of cellular respiration. Recognizing element (bioreceptor) on the basis of immobilized cells was fixed on the measuring surface of an oxygen electrode Clark type using a nylon mesh Immobilization of cells.

For that we use a cell suspension, which contains 10 μg cells . The time of single measurement is 6–8 min. For work we use aerobic organotrophs bacteria from groundwater samples exposed radioactive waste from PO "Mayak" and Syberian Chemical Combine. Nitrate ions, metals, organic compounds concentration effects on the process of cellular respiration are established.

RER-P39, (Id: 294)

DISTRIBUTION OF ^{137}Cs, $^{238,239+240}$Pu AND ^{241}Am IN SOILS AND LAKES FROM THE CENTRAL SPITSBERGEN

Edyta Łokas[a], **Zbigniew Zwoliński**[b], **Grzegorz Rachlewicz**[b]

[a]*H.Niewodniczanski Institute of Nuclear Physics Polish Academy of Sciences*
[b]*Institute of Geoecology and Geoinformation, Adam Mickiewicz University in Poznan*
edyta.lokas@ifj.edu.pl

Soils play an important role in accumulation of airborne radionuclides. Plutonium isotopes released by nuclear weapons testing are still present in the environment, especially in soils. There are several sources of radioactive contamination in the European sector of the Arctic. The most substantial include global weapons fallout, fallout from nuclear weapons testing near Novaya Zemlya and from Chernobyl accident, and discharges from the nuclear reprocessing plants Sellafield (UK) and La Hague (France). The aim of this study was to investigate activity concentrations, activity ratios and inventories of ^{137}Cs, ^{238}Pu, $^{239+240}$Pu and ^{241}Am in 8 soil profiles and 3 bottom sediment profiles from tundra lakes of Petuniabucta coast (Central Spitsbergen). The loose and poorly developed soils were collected from raised marine terraces covered with sandy-gravel sediments (PET1, PET2, PET3) and from coarse-grained screes (PET4, PET6, PET8). The Ebbadalen tundra lakes (PEL1, 2, 3) occupy shallow depressions underlain by mineral soil or thin peat in permafrost terrain.

Results obtained in this study show differences in activities of artificial radionuclides among the investigated profiles. The highest activities of ^{137}Cs, ^{238}Pu, $^{239+240}$Pu and ^{241}Am observed in profile PET4, reached 123±11 Bq/kg, 0.13±0.04 Bq/kg, 3.82±0.31 Bq/kg and 1.2±0.1 Bq/kg, respectively. Artificial radionuclides in most of the tundra soils were concentrated in the upper 4 cm but in one profile (PET5) maximum activity concentrations each radionuclide was observed at 10 cm depth. The deeper occurence of radionuclides in profile PET5 can be explained by occasional accumulation of aluvial deposits in that site. Location of activity maxima points to accumulation of 10 cm thick deposits during last 50 years. The activity ratios provide important information on the origin of radioactivity in soils, as they can be used to distinguish between global (stratospheric) and regional (tropospheric) sources of these radionuclides. Isotopic analysis of plutonium reveals provenance of this radionuclide, for example whether the plutonium burdens are associated with bomb fallout or are derived from other sources. The ^{238}Pu/$^{239+240}$Pu activity ratios varied from 0.02 ± 0.01 to 0.07 ± 0.02, suggesting global fallout as the dominant source of Pu (0.03-0.05). The $^{239+240}$Pu/^{137}Cs activity ratios varied from 0.02 ± 0.01 to 0.09 ± 0.02 and exceeded published global fallout ratio for Svalbard of 0.05. The ^{241}Am/$^{239+240}$Pu activity ratios ranged between 0.32 ± 0.04 and 1.24 ± 0.13 and exceeded the global fallout ratio for Svalbard of 0.37 due to the relatively higher geochemical mobility of Pu vs. Am and/or ingrowth of Am from the decay of ^{241}Pu.

The ^{137}Cs inventories in each profile were lower than the deposition fluxes (2.2 kBq/m^2) reported for Svalbard. The $^{239+240}$Pu inventories varied between 20.1 ± 1.6 to 50.3 ± 5.0 Bq/m^2 and exceeded values of $^{239+240}$Pu 14 - 26 Bq/m^2 from atmospheric weapon testing.

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RER-P40, (Id: 297)

CESIUM-CONTAINING COMPLEX OXIDES OF THE POLLUCITE STRUCTURE. SYNTHESIS, PROPERTIES, PREPARATION OF CERAMICS WITH HIGH RELATIVE DENSITY AND ITS RADIATION TESTS

Aleksey Troshin

Lobachevsky State University of Nizhni Novgorod
lehanich89@mail.ru

Complex oxides with the structure of the mineral pollucite ($CsAlSi_2O_6$) represent a large group of compounds and they are basic for the development of materials for different purposes, including immobilization of cesium from waste of radiochemical industries and preparation of medical sources radiation. The number of such oxides has increased significantly basing on isomorphism of atoms in the crystal lattice and calculations modeling compounds of phosphorus-containing phases [1]. Isomorphic substitution of aluminum by boron leads to the increase of cesium mass fraction and growth of the specific activity of the compound in the case of a radioactive isotope. Inclusion of boron in the phosphorus-containing pollucite-like phases provides new possibilities for the development of materials for nuclear medicine (boron neutron capture therapy, BNCT) and ceramics - neutron absorbers. Oxides with pollucite structure containing boron and aluminum $Cs[MgR_{0.5}P_{1.5}O_6]$, where R = B and Al, were synthesized using a sol-gel process, and they were characterized by X-Ray diffraction. Structural studies for obtained compounds were performed (Rietveld refinement). The thermal expansion was studied by using of the methods of high- and low-temperature X-Ray analysis at temperatures range from -100 to 800 °C ($\alpha = (7.3 - 8.6)\times10^{-6}$ deg^{-1}), thermal (tested up to 1200 °C) and hydrolytic stability (T = 90 °C, 1.46×10^{-5} g/(cm$^2\times$d)) were studied also. The obtained compounds were used for synthesis of the ceramics by spark plasma sintering. The relative densities of ceramics were up to 98 % [2]. We found that the complex oxides – analogues of pollucite - have high chemical and radiation stability. The obtained ceramic materials were irradiated with $^{132}Xe^{26+}$ ions (E = 167 MeV) in the fluence interval from $6\bullet10^{10}$ to $1\bullet10^{13}$ cm^{-2}. The amorphization took place at a fluence of 1.2×10^{12} cm^{-2}. The conditions of the metamict form transition into the crystalline form on heating were found. The crystal-chemical modeling of isostructural compounds was carried out with a deficit of cesium in the cavities of the structure of the general formula Cs_1-x[Mg_1+x-y$R_{0.5}$-2x +0.5y$Li_{0.5}$y$P_{1.5}$+xO_6], where R = B, Al; $0 \le x \le 0.2$; $0 \le y \le 0.8$.

References:
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RER-P41, (Id: 302)

DEVELOPMENT OF AUTOMATED SYSTEM FOR CONTINUOUS REMOTE CONTROL OF RADIOACTIVITY EMITTED BY NUCLEAR POWER PLANTS

Vladimir Kolotov, Dmitry Grozdov, Yury Lavrukhin, Nikolay Dogadkin

Vernadsky Institute of Geochemistry and Analytical Chemistry
kolotov@geokhi.ru

Automated system for radiation control of air space near the nuclear power plant based on using of non-stop remote gamma-spectroscopic control of nuclear power plant radioactive emission (mainly from ventilation pipe) is developed. The task of the system consists in estimation the potential risk of terrain contamination outside the nuclear power area. The system should provide authorities of different level with information concerning radionuclide composition and dose rate, both in the case of normal emission and the emergency one up to level 7 (according to the INES international scale of nuclear events). It is extremely important to detect early stage of any event.

The system hardware consists of spectrometric stations (manufactured in Russia) connected with computer's net. The station includes the collimated scintillation NaJ (Cs) detector of 63×63 mm size, connected with intellectual MCA. It has been found that for reliable detection of radioactive emission of the nuclear power plant eight stations evenly located at the 500-800 meters distance from the ventilation pipe are sufficiently.

The input information and results of data processing are stores in SQL-data base. The data processing software is based on the original algorithms coded by C# language. It includes processing of scintillation gamma-ray spectra, including evaluation of multiplets. A method for computation of full energy peak efficiency for voluminous atmospheric sources (radioactive gas stream escaping from ventilation pipe) has been developed. The computation uses the dependence of full energy peak efficiency value for arbitrary point as function of distance and angle. The atmospheric stream geometry is set by normal distribution, with parameters dependable on meteorological state of atmosphere.

The computations of full energy peak efficiency for voluminous radioactive atmospheric sources a modeling by the Monte-Carlo method has been used [1]

The original method for radionuclides identification is developed. Both mathematical methods and elements of expert system are used. To increase the identification reliability it is suggested to use different radionuclides libraries optimal to various types of emergency events using fuzzy logic. It is assumed that the developing system will be integrated with system of radiation control of nuclear power station. It will allow assisting decision support center to accept adequate solutions in the case of problems. The successful tests of different parts of the system were carried out at the Kalinin and Kursk nuclear power plants, Russia.

[1] D.S. Grozdov, V.P. Kolotov, Y.E. Lavruhin, N.N. Dogadkin. Computation of full energy peak efficiency for voluminous radioactive atmospheric sources using remote scintillation gamma-ray spectrometry. Abstract presented at RadChem14.

RER-P42, (Id: 303)

THERMODYNAMIC QUANTITIES OF COMPLEX FORMATION OF ND(III) AND AM(III) WITH SMALL ORGANIC ACIDS AS A FUNCTION OF IONIC STRENGTH AND TEMPERATURE

Melanie Müller[a], **Franziska Taube**[a], **Margret Acker**[b], **Steffen Taut**[b]

[a]*Institute of Analytical Chemistry, TU Dresden*
[b]*Central Radionuclide Laboratory, TU Dresden*
melanie.mueller@tu-dresden.de

Thermodynamic data for actinide-organic complexes are required for long term safety assessment of nuclear waste disposal. Particular attention should be paid to higher ionic strengths, which are to be expected in salt and clay rock formations. Higher temperatures have also to be considered, since temperatures can go up to 100 °C in the near field of radioactive waste disposal. Up to now most of the available thermodynamic data for actinide complexation with dissolved or suspended natural organic matter are related to low ionic strength and 25 °C.

In this work we present detailed thermodynamic data for the complex formation of trivalent neodym (as an chemical analogue to americium) and americium with ethanedicarboxylate (oxalate) and methanedicarboxylate (malonate) at various ionic strengths (up to 3 mol kg^{-1} NaCl) and temperatures (25 °C to 55 °C). The isothermal titration microcalorimetry (ITC) was used for the direct determination of reaction enthalpy ΔRH of complex formation. With a sample volume of just 200 µL the method is applicable for actinide solutions. Additionally, spectrophotometric titration experiments were performed in order to determine the species distribution and complex stabilities. In preparation of complexation studies we determined ionic strength dependent protonation constants of oxalate by ITC and compared the results with literature values. The formation of the first protonation step is an endothermic process. With increasing ionic strength the ΔRH decreases towards zero. The standard state thermodynamic data log K°, $\Delta RH°$, $\Delta RS°$, $\Delta RG°$, which were determined from the conditional thermodynamic data using the specific ion interaction theory (SIT), are in excellent agreement with literature values.

The formation of 1:1 Nd(III)-oxalate complex is a two-phase exothermic process. A fast and a slow part can be distinguished. This effect is a matter of current investigations. In the case of Am(III) we performed a spectrophotometric titration under comparable experimental conditions. No peculiarities were observed in the spectra and a 1:1 complex species with a stability constant of log K°110 = 6.8 ± 0.1 was determined. This is the first time that the value is determined by a spectroscopic method and the results are in good agreement with the literature value [1]. ITC experiments with the Nd^{3+} -malonate system were carried out at ionic strengths between 0.25 and 3 mol kg^{-1} (NaCl) and at 25, 35, 45 and 55 °C. All ITC traces show an endothermic complex formation. At 25 °C and I = 1 mol/kg the reaction enthalpy ΔH is 11.2 kJ mol^{-1} and the entropy is 95 J mol^{-1} K^{-1}). These results are close the values reported for the analogue Eu(III) complex in NaClO4 [2]. With increasing ionic strength ΔRH is shifting towards zero whereas it is increasing with increasing temperature. At the investigated concentration range the formation of the 1:1 complex species is predominantly. Conditional thermodynamic data were determined from the curves and the ionic strength corrected data log K°, $\Delta RH°$, $\Delta RS°$ and $\Delta \varepsilon$ for the $NdMa^+$ species are reported in this work.

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RER-P43, (Id: 304)

COMPOSITE DUST-SUPPRESSING COATINGS CONTAINING NANOSIZED SORBENTS SELECTIVE TO CESIUM, COBALT, AND NICKEL RADIONUCLIDES

Svetlana Bratskaya[a], Veniamin Zheleznov[a], Risto Koivula[b], Valentin Avramenko[a], Alexander Mironenko[a], Anna Mysyanovich[c], Alla Synytska[d], Frank Simon[d], Risto Harjula[b], Dmitry Marinin[a]

[a]*Institute of Chemistry FEBRAS, Vladivostok, Russia*
[b]*Laboratory of Radiochemistry, University of Helsinki, Finland*
[c]*Max-Planck-Institut für Polymerforschung, Mainz, Germany*
[d]*Leibniz-Institut für Polymerforschung, Dresden, Germany*
sbratska@ich.dvo.ru

Here we report on development, characterization and performance evaluation of new materials based on selective to radionuclides nanosized sorbents stabilized in water dispersible nanoparticles (latexes). These new materials can be applicable as fixatives (dust suppressors), when latexes are film-forming, and as colloid stable sorbents for decontamination of solid bulk materials, when any type of latex, preferably containing carboxylic groups on the surface, is used. Two different series of polymeric nanoparticles were synthesized and tested as a polymer matrix for inorganic sorbents immobilization. The first type of particles was based on polystyrene and composed of polystyrene either pure (homopolymer) or copolymerized with different amounts of acrylic acid in order to obtain carboxyl-functionalized latex particles. The second type was poly(silane acrylate)-based copolymer nanoparticles, consisting from butyl acrylate, methyl methacrylate, polymerizable silane and functional comonomer (either methacrylic acid or aminoethyl methacrylate hydrochloride). All particles were synthesized in direct (oil-in-water) miniemulsion system by free-radical (co)polymerization.

As selective inorganic materials colloidal SnO_2 and MnO_2 with mean particle size 10 nm and 200 nm, respectively, have been synthesized. Co(II) ferrocyanides were synthesized directly in the presence of carboxylic latex particles. Composites containing SnO_2 nanoparticles selective to radionuclides of nickel and cobalt have been prepared using carboxylic and aminolatexes as a martrix, the maximum loading degree was about 60 mg of SnO_2 per 1 g of latex. Sorption properties of composite latex/inorganic sorbent materials have been investigated toward ^{63}Ni, ^{57}Co (SnO_2), ^{137}Cs (Co (II) ferrocyanides), ^{90}Sr (manganese oxides) in the presence of competing ions. Distribution coefficients up to 105 ml/g were reached for cesium radionuclides and for nickel and cobalt radionuclides on SnO_2 in $NaNO_3$ solutions The highest distribution coefficients of ^{90}Sr (~3500 ml/g) in the presence of competing Ca^{2+} ions (0.1 g/L) were reached for manganese oxides.

Dust suppressing formulations based on film-forming poly(silane acrylate) latexes containing Co(II)ferrocyanide and poly(silane aminoethyl) latexes containing SnO2 have been prepared and drop casted on model contaminated sand. The leaching of ^{137}Cs and ^{57}Co radionuclides from coated sand surface was efficiently suppressed (leaching degree below 1 %), when the content of Co(II) ferrocyanide and SnO_2 in composite coatings was as low as 1.3×10^{-6} mol/cm^3 and 8.3×10^{-4} mol/cm^3, respectively. Acknowledgements: Financial support for ERANET-Russia project (STProject-144) of the 7th EU Research Framework Programme is gratefully acknowledged.

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FIRST SHRINKAGE PARAMETERS OF SLOVAK BENTONITES CONSIDERED FOR ENGINEERED BARRIERS IN THE GEOLOGICAL REPOSITORY FOR RADIOACTIVE WASTE AND SPENT NUCLEAR FUEL

Renata Adamcova, Vladimir Suraba, Adrian Krajnak, Michal Galambos

Comenius University in Bratislava, Faculty of Natural Sciences
adamcova@fns.uniba.sk

In a previous research for the deep geological repository of radioactive waste and spent nuclear fuel, the swelling potential of bentonites from Slovak deposits was evaluated by indicative parameters (Atterberg liquid limit) and by swelling pressure tests (Adamcova et al., 2009). The noticed absence of data on shrinkage behaviour initiated a pilot research of bentonite shrinkage parameters in Slovakia (within the project VEGA 1/0828/13 granted by the Slovak Ministry of Education). Comparison of Slovak, Austrian, German and British Standards for shrinkage test methods showed that Slovak Technical Standards (STN) pertain to undisturbed soil samples, where shrinkage depends not only on the current moisture, but also on the grain size distribution and porosity. Shrinkage limit ws (%) and relative linear shrinkage Ls (%) determined according to the foreign technical standards are independent from those properties, because sample preparation brings all soils to equal starting conditions: sieved to grain size below 0.5 mm, water added to reach moisture w near the liquid limit wL, suspension smeared without bubbles into standard moulds. Applied Austrian ONORM B 4411: 2009 offers three test procedures for ws. First, ws was determined by manifold measuring of the sample weight and volume during drying. Calculation followed from the moisture vs. relative volume plot with a linear trend line. Results were compared to data from the other two methods. Highest Ls (up to 32.5 % of the initial length) was observed in bentonite J250 from the Jelsovy Potok deposit, the best Slovak bentonite because of its swelling potential and excellent sorption properties for radionuclides (Galambos et al., 2009; Galambos et al, 2010a; Galambos et al, 2010b; Galambos et al., 2011). Reaching of the shrinkage limit (ws = 11 %) was indicated also by a color change from light brownish grey (2,5Y 6/2) to light grey (2,5Y 7/1 - Munsell Soil-Color Charts, 2009). Because ws is lower than the equilibrium moisture of the bentonite J250 under room conditions, which is 14 %, bentonite blocks might shrink and gaps between them open due to high temperature around the containers with radioactive waste and spent nuclear fuel in the geological repository, until water from the host rock mass intrudes and bentonite swells. Results indicated the necessity of further shrinkage tests, this time on bentonite powder compacted to high-density segments. Methods described in STN 72 1019 were recommended as relevant for the assessment of their total shrinkage.

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RER-P45, (Id: 312)

NEW INSIGHTS INTO URANYL INTERACTION WITH PROTEINS

Quentin Raffy[a], **Isabelle Billard**[b], **Rémi Barillon**[a]

[a]*IPHC - Strasbourg University*
[b]*IPHC - CNRS*
quentin.raffy@iphc.cnrs.fr

Given uranium toxicity, comprehension of uranyl interaction with biological material of human relevance is of utmost importance, from the whole body scale to the molecular level. At the molecular level, uranium interaction with proteins has attracted a lot of attention, in particular the blood serum proteins Human Serum Albumin (HSA) and Transferrin, which are likely to transport uranyl in the body and therefore to play a key role in its toxicity [1-5]. It is well known that uranyl undergoes complex speciation at physiological pH, and can form complexes with serum small molecules such as carbonates, making the study of such systems rather intricate.

The interaction of uranyl with a protein was studied, while taking into account all known uranyl species that could exist at physiological pH. Bovine Serum Albumin (BSA) is well known to bind several metals, and shares similarities with Human Serum Albumin, which makes it a good candidate for a uranyl-binding protein model. The interaction was followed by means of UV-Visible spectroscopy, circular dichroism and fluorescence measurements (static and time-resolved). Strong fluorescence quenching of the protein was observed upon uranyl addition. Addition of BSA to a uranyl solution also resulted in uranyl fluorescence quenching. The data obtained were treated using speciation software CHEAQS and a fitting program developed in the laboratory.

On this experimental basis, the model proposed, involving two successive complexations of several uranyl moieties is in very good agreement with the experimental data. Our results allowed determination of the number of uranyl moieties complexed by the protein, as well as the corresponding equilibrium constants. Further experiments are in progress to determine the functional groups of the proteins involved in the complexation.

The experimental protocol and data analysis could be applied to virtually any protein containing enough fluorescent residues to measure the quenching induced by uranyl addition. Further studies with HSA are in progress, and first results will be also presented and compared to the literature [2,6].

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RER-P46, (Id: 316)

POLONIUM (^{210}Po), LEAD (^{210}Pb) AND URANIUM (^{234}U, ^{235}U, ^{238}U) CONTAMINATION OF ENVIRONMENT SURROUNDING PHOSPHOGYPSUM WASTE HEAP IN WISLINKA (NORTHERN POLAND).

Grzegorz Olszewski, Alicja Boryło, Bogdan Skwarzec

University of Gdansk, Faculty of Chemistry, Institute of Environmental Protection and Human Health, Laboratory of Analytical and Environmental Radiochemistry
olszewskigrzesiek@gmail.com

The aim of this study was to examine the concentrations of ^{210}Po, ^{210}Pb, ^{234}U, ^{235}U and ^{238}U in surface soils samples collected in the area of phosphogypsum waste heap in Wiślinka (northern Poland) and assessing its impact on the surrounding environment. Concentrations in analyzed soils samples were estimated between 3.0±0.2 mBq×g^{-1} dry wt. and 324.5±15.41 mBq×g^{-1} dry wt. for ^{210}Po and between 3.6±0.2 mBq×g^{-1} dry wt. and 229.9±5.4 mBq×g^{-1} dry wt. for ^{210}Pb. ^{210}Po/^{210}Pb activity ratios were in the range of 0.70±0.05 to 2.15±0.13. The abbreviation may be connected with the agricultural use of fertilizers. The results for uranium suggest that ^{234}U, ^{235}U and ^{238}U radioisotopes that are present in the vicinity of phosphogypsum waste heap are of natural origin (^{234}U/^{238}U activity ratio between 0.81±0.08 and 1.22±0.11, and ^{235}U/^{238}U between 0.029±0.008 and 0.062±0.013 are typical for soils). The activities of ^{238}U,^{234}U and ^{235}U ranged from 2.20±0.17 mBq×g^{-1} dry wt. to 108.68±3.03 mBq×g^{-1} dry wt., from 2.31±0.17 mBq×g^{-1} dry wt. to 108.68±3.03 mBq×g^{-1} dry wt. and from 0.08±0.03 mBq×g^{-1} dry wt. to 3.88±0.57 mBq×g^{-1} dry wt., respectively. The highest activities of ^{210}Po and ^{210}Pb were measured in samples collected on both slope and bottom of the phosphogypsum heap. Much lower results were obtained for samples collected from distant areas, what is probably connected with both erosion and leakages from phosphogypsum waste heap into surrounding environment. Lower results for 234U and ^{238}U in the vicinity of phosphogypsum stack in comparison to ^{210}Po and ^{210}Pb activities in this area may be explained by the fact that during the process of phosphoric acid production polonium migrates to phosphogypsum fraction and uranium to phosphoric acid. It is connected to higher solubility of uranium in phosphates. Surprisingly, the highest concentrations of uranium radioisotopes were measured in samples collected from more distant sample collection sites. This fact must be correlated with the use of phosphoric fertilizers in agriculture. For a clearer picture of the radioactive contamination of the area of phosphogypsum waste heap in Wiślinka, we decided to create interpolation maps for every radioisotope using natural neighbor interpolation and ordinary kriging geostatistical method in Spatial Analysis and Decission Assistance (SADA) software. This allowed us to isolate zones that are categorized by different activities of ^{210}Po, ^{210}Pb, ^{234}U, ^{235}U and ^{238}U: the foot of the waste heap, the slopes of the waste heap, agricultural fields and the opposite riverbank of Martwa Wisła river. Additionally, we plotted graphs that described analyzed radioisotopes distribution on the distance from the phosphogypsum landfill. This helped us to isolate the zone described by the highest activities of uranium, polonium and lead radioisotopes.

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RER-P47, (Id: 317)

CATALYTIC WET OXIDATION OF METAL ION COMPLEXING AGENTS BY H_2O_2 USING HOMOGENEOUS AND HETEROGENEOUS Fe (III) SPECIES

Vera Labko[a], Artsiom Radkevich[a], Ekaterina Parkhomchuk[b], Ksenia Sashkina[c], Yuri Davydov[a]

[a]*Joint Institute for Power and Nuclear Research - SOSNY, National Academy of Sciences of Belarus*
[b]*Boreskov Institute of Catalysis SB RAS*
[c]*Novosibirsk State University, Russia*
veryn12@gmail.com

A large amount of liquid radioactive wastes are formed during nuclear power plants operating. Radionuclides contained in the wastes are predominantly in the form of stable complexes with organic ligands, such as EDTA, citric and oxalic acids, which complicates the heavy metal separation. Concentrating and processing of liquid radioactive wastes can be greatly simplified after the removal of these organic compounds. Catalytic wet oxidation of complexing agents by H^2O^2 using Fe (III) species is a promising way for radioactive waste purification.

The presenting work considers a method of catalytic wet hydrogen peroxide oxidation (CWHPO) of EDTA using homogeneous and heterogeneous Fe(III) species. The solutions of mono- and polynuclear hydroxo complexes of Fe (III) have been obtained and studied as homogeneous catalytic systems. Several types of Fe (III) containing zeolites ZSM-5 with different particle morphology and texture, including nanozeolites and hierarchical zeolite, have been synthesized and tested as heterogeneous catalysts. The activity in CWHPO of different Fe (III) species was measured by barometric cell method and total organic content determination.

In homogeneous 1 mM Fe (III) catalytic system the highest hydrogen peroxide decomposition rate was observed at $pH = 2.5$ when mononuclear Fe(III) hydroxo complexes were predominant. The reaction rate was found to be decreased at $pH = 1.5$ and 3.0 when hydrated and polynuclear hydroxo complexes were formed, respectively. At $pH > 3$ Fe (III) hydroxide precipitated and the reaction rate was negligibly low. Unlike homogeneous system zeolitic one allows proceeding the reaction at a significantly wider pH range. Heterogeneity of the Fe (III) catalytic sites in the zeolite appeared to result in effective use of the hydrogen peroxide and a deep oxidation of a substrate. A comparative study of stability and activity of Fe (III) species supported onto the zeolite and amorphous SiO_2 has been made in oxidation of low and high molecular weight organic subtances by H_2O_2. Catalytic site protection by zeolitic matrix plays a key role in the reactions and could be potentially explored for development of technology for purification of waste water from nuclear power plants.

RER-P48, (Id: 318)

ACTIVITY OF ^{210}Po IN THE BLOOD AND URINE OF THE RESIDENTS OF THE TRICITY AGGLOMERATION

Grzegorz Romanczyk, Alicja Borylo, Bogdan Skwarzec

University of Gdansk
g.romanczyk@gmail.com

The natural radionuclide polonium is daughter of ^{238}U decay series. ^{210}Po is radionuclide with half-lives of 138.38 days. Polonium is one of the most radiotoxic natural radioactive isotopes to man due to its high specific activity and its emission of high-LET alpha radiation. Less than 0.05 g of the radionuclide is considered a lethal dose (LD50/30). Man is exposed to radioactive ^{210}Po by natural processes, mainly from the oral intake of foodstuff and drinking water. Especially large amounts of polonium are taken in during cigarette smoking as well as food of marine products. The large amounts of polonium are observed in protein-rich food, such as shellfish and crustaceans, and also observed among populations consuming large amount of reindeer and caribou meat, e. g. in Subarctic area.

The aim of this study was to establish the polonium ^{210}Po concentrations in blood samples and urine. Healthy urine and blood are not toxic. However, there contains compounds eliminated by the body as undesirable. The tested group constituted patients from Medical University of Gdansk and volunteers from Tricity aglomeration. Eating fish and cigarette smoking are factors that according to many researchers affects the amount of this radionuclide in the human body. The questions about smoking and frequency of fish eating were included in questionnaire for the patients and volunteers. This is very important because human biomonitoring of ^{210}Po has been conducted for a long time, but it is still not fully known and understood.

The human blood samples about volume 10 ml were collected from 43 patients ischaemic heart disease (IHD) from Medical University of Gdansk. The reason for choosing this particular group was purely accidental. The urine samples were collected from 37 volunteers from Tricity agglomeration (Gdansk, Sopot, Gdynia). Urine samples were collected throughout the day. The daily amount of urine excreted by volunteers ranged from 600 to 3500 ml. The research was approved by the Independent Bioethics Committee for Scientific Research of the Medical University of Gdansk.

The results of this work indicate that the activity of ^{210}Po in human blood and urine was in the wide range between 140±14 mBq and 888±36 mBq in total blood without two patients (3072±270 mBq and 2901±245 mBq in total blood) and from 1.48±0.09 mBq to 19.41±0.81 mBq in urine samples respectively. The higher activity of this radionuclide was observed for smoker and ex-smoker groups. The patients and volunteers were subdivided in groups: males and females, cigarette smokers, non-smokers and ex-smokers were taken into account. The results indicated that the ^{210}Po activity was widely distributed in the each group of analyzed patients and volunteers. The difference between ^{210}Po activities in human blood and urine of ex-smokers/smokers and eating habits is statistically significant. The obtained results of ^{210}Po activity in the human blood and urine are probably related to the consumption of fish and smoking. Human sex and age had no effect on excretion of polonium from the urine during the day.

RER-P49, (Id: 326)

COMPARATIVE STUDY OF THE THERMAL, HYDROLYTIC, RADIATION STABILITY AND MECHANICAL PROPERTIES OF Cs, Ba, Sr, AND Ln-CONTAINING CERAMIC MATERIALS FOR RADIOCHEMICAL PROBLEMS AND APPLICATIONS.

Dmitriy Mikhailov[a], **Albina Orlova**[a], **Valeriy Volgutov**[a], **Vladimir Chuvil'diev**[a], **Alexey Nokhrin**[a], **Maksim Boldin**[a], **Nikita Sakharov**[a], **Oleg Belkin**[a], **Vladimir Skuratov**[b], **Nikita Kirilkin**[b]

[a]*Nizhny Novgorod State University*
[b]*JINR, Dubna*

Knowledge of the behavior of materials in radiation fields need if ones are elaborated for radwaste immobilization. Also it is important to prepare a ceramic with high density for aims: medical, research and material science problems, consolidation and transformation of radwaste. Among these materials deserve special attention mineral-like. Natural "experience" shows the ability to save (stability) of mineral-like materials under the influence of heat, pressure, hydrolytic solubility, radiation fields in a long time.

Used for a long time methods for the synthesis of ceramics (cold pressing with following hightemp firing; multistage hot pressing) have several disadvantages: prolonged exposure to high temperature, low relative density of the resulting product, multi-stage processes, high energy and time costs. This work focuses on the development and multitasks application of new methods for the synthesis of high-density ceramics (Spark Plasma Sintering), reducing temperature, duration of the process and the number of steps on the example of monophase polycrystalline compounds.

The objects of research were following compounds: $Ca_{0.25}Sr_{0.25}[Zr_2(PO_4)_3]$ (NZP-type); $CsBa(Sr)[Fe_2(PO_4)_3]$, $Cs_2[Mg_2(WO_4)_3]$ (langbeinite type); $NdPO_4$ (monazite type); $Y_{(1-x)}Gd_xPO_4$ (x = 0, 0.05, 0.25; xenotime type); $Cs_{0.875}Ba_{0.125}Li_{0.125}Zn_{0.875}Al_{0.5}P_{1.5}O_6$ (pollucite type). This chemical compositions were choose as stable mineral-like matrixes, containing Cs, Ba, Sr, Ln jointly or separately.

At the first stage we obtained the samples of composition as powders by using the sol-gel process. Step by step the gel formed and then powders were heated, dispersed and examined by X-Ray analysis. Then ceramics on the base of compounds named were sintered by Spark Plasma Sintering (SPS) method.

Obtained powders and ceramic pellets were tested for thermal stability up to 1350 °C, hydrolytic stability in distillated water (20 and 90-100 °C (Soxhlet extractor, 7-28 days). Prepared cylindrical tablets (d = 10, 20 mm) were irradiated with accelerated Xe-ions (E = 167 MeV) stream at $6\times10^{10} - 1x10^{13}$ fluences (1/sm2). The experiments were carried out at room temperature on the IC-100 FLNR JINR (Joined Institute of Nuclear Research) cyclotron.

All compositions were stable after heating up to 1100 °C. High relative density was reached for all compounds by using SPS method for 0-5 min: 99,6-99,9 % (NZP); 96,2-99,9 % (langbeinite); 98,3 % (monazite); 98,8-99,9 % (xenotime); 99,9 % (pollucite). Ceramic materials with NZP and pollucite-like structure were stable after radiation till 1×10^{13} fluences ($1/sm^2$) [1, 2].

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RER-P50, (Id: 356)

IMMOBILIZATION OF RADIONUCLIDES INTO THERMAL INSULATION WASTE

Vitaly Epimakhov, Mikhail Oleinik, Sergey Mysik

evn@niti.ru Nikolaevich

Large amounts of low-density thermal insulation mineral wool waste contaminated by radionuclides arise from NPP operation. Melting of this waste reduces its volume by more than 10 times. Mineral fibers begin to lose their elastic properties at 440 °C and to soften at 700 °C. The minimum process temperature for molten fiber formation is ~ 1500 °C. Experiments were performed on mineral wool mats with specific activity of Cs-137 $(4.0\text{-}8.8)\times10^8$ Bq/kg. The experiments employed an industrial induction furnace as a waste melter. The melter was a graphite crucible with an opening provided at the bottom, through which the formed melt flowed down by drops into a receiving container. During the experiment, the melt discharge rate was from 1.8 to 2.2 kg/h, the melt temperature was 1350-1370 °C, and the rate of power consumption was 8.3 kW×h/kg. The solid-aerosol carry-over was not larger than 0.5 % and volatile loss of Cs-137 was only 2.8 % from the melting process. To reduce the mineral wool melting temperature from 1350-1370 °C to 1170-1190 °C, a low-melting fluxing agent, namely FeO (at least 10 wt. %), was used. The true density of the “frozen” mineral wool melt without addition of fluxing material was 2.7 g/cm^3 and with addition of 10 % CaF2 the density increased to 2.8-2.9 g/cm^3. Additional experiments were performed with crushed mineral wool incorporated into Portland cement modified by Cambrian clay as a sorption agent. The crushed wool was admixed to cement slurry with water-to-cement ratio of 0.7 and claycement ratio of 0.1. The density of produced cement compounds was about 1.8 g/cm^3. Measurement of Cs-137 leaching from the thermal insulation waste forms has shown that addition of a fluxing agent to melt increases (almost by an order of magnitude) the radiocesium leach rate from the conditioned waste. But in any case this leach rate is of 10^{-7} g/cm^2×day order after 150 days of the experiment. For comparison, Russia’s regulatory maximum value for Cs-137 leach rate from vitrified high-level waste is 1×10-7 g/cm^2×day. For low- and intermediate-level wastes stored in standard concrete facilities, the acceptable rate of radiocesium leaching after 150 storage days is not higher than 1×10^{-3} g/cm^2×day. Cemented thermal insulation waste forms with addition of clay comply with this requirement (the leach rate is $\sim1.0\times10^{-4}$ g/cm^2×day after 150 days).

RER-P51, (Id: 367)

MITIGATING THE ENVIRONMENTAL IMPACT OF HIGH SALT LIQUID RADWASTE CONCENTRATES INCORPORATED INTO CEMENT PACKAGES

Vitaly Epimakhov, Sergey Mysik, Mikhail Oleinik, Olga Amosova

evn@niti.ru

The use of sulfuric acid instead of nitric acid for regeneration of cation-exchange resins arising from NPP operations produces sulfates which can form crystalline hydrates. Based on this capability, cement instead of bitumen can be used as a matrix for binding liquid radwaste (LRW), and high salt concentrates can be incorporated into Portland cement. Experiments simulating inundation of waste storage containers were performed. The experiments used a model salt solution representing an average composition of LRW from the VVER plants and containing 45 % Na_2SO_4 of the total mineral content. Test solutions with a salt concentration from 200 g/l to 800 g/l and temperature of 80 °C were immobilized into cement matrix with water-to-cement ratio of 0.60 and addition of Cambrian clay as a sorbing agent. The percentage of added clay was about 10 % of the total cement weight. The produced cement packages included from 6.7 to 25.1 wt. % of salts. Radionuclides were released from the cement surfaces into water with a rate of 10^{-1} $g/cm^2 \times day$ for the first 24 hours of the experiment and after 90 days the rate of radiocesium leaching by diffusion was below 0.5×10^{-3} $g/cm^2 \times day$ meeting Russia's regulatory requirements (1×10^{-3} $g/cm^2 \times day$) for standard concrete storage facilities. An increase in the test solution salt concentration from 200 g/l to 800 g/l resulted in an increase of the diffusion coefficient (De) from 0.5×10^{-5} to 2.8×10^{-5} cm^2/day. However, this value is much below the regulatory requirements ($\leq 8.6 \times 10^{-4}$ cm^2/day) on concrete disposal containers for radioactive waste. Since calcium sulfates are higher soluble than calcium aluminosilicate cement matrix, the maximum release of Cs-137 (2.2-3.0 % of the original activity), the most mobile radionuclide, from 200 L cement packages is mainly determined by surface leaching and occurs during the first three months of storage. This period is considered as the time of inundation scenario. The maximum diffusion leaching of Cs-137 taking its half-life into account will be observed during the first storage 20 years and the estimated release will be 10 times lower (below 0.2 % of the original value) than that by surface leaching even for cemented concentrates with a salt concentration of 800 g/l. After 300 storage years the predicted radioactivity release will be maximum 0.004 % of the original activity. Therefore, waste concentrates produced from LRW with a significant percentage of sulfate salts can be immobilized into Portland cement forms modified with sorbent clay which securely fix radionuclides even in case of high salt concentrates (up to 800 g/l).

RER-P52, (Id: 389)

THE MATRIX INFLUENCE ON THE DETERMINATION OF LOW URANIUM CONCENTRATIONS

Alena Zavadilova, Barbora Drtinova, Dusan Vopalka

Czech Technical University in Prague, Faculty of Nuclear Sciences and Physical Engineering
alena.zavadilova@fjfi.cvut.cz

We refer about a development of the measurement technique enabling the determination of low uranium concentrations. The method was inspired by a commercially available KPA method (kinetic phosphorescence analysis). It is fast, sensitive, and non-destructive, allowing the uranium concentrations determination on a mass basis of μg U/l.

Contrary to the conventional KPA method it is in our approach not necessary to use an external standard as a reference sample. Moreover the solid state laser is used instead of nitrogen or dye laser and thus no dye solution preparation is required and no laser tube degradation appears. As an excitation source we use the solid state tunable laser, commonly utilized for TRLFS (time resolved laser induced fluorescence spectroscopy) measurement, operating at 416 nm for which the uranium complex fluorescence signal has the highest intensity. Excitation energy was 4.5 mJ. The fluorescence spectra were recorded using the grating monochromator followed by an ICCD camera. To eliminate the influence of possible excitation energy fluctuation on the measured fluorescence intensities, each recorded spectra were normalized with respect to this energy. For every sample ten measurements with 200 acquisitions were realized (the overall acquisition time was ~3 min). Besides the intensity measurement the method enables the study of the emission spectral characteristic and the detail measurement of complexes wavelength shift. Because the fluorescence is strongly temperature-dependent, the temperature of the sample was controlled and stabilized.

In our laboratory, the concentration of uranium is determined mainly in samples resulting from the leachates of rock and sediment materials and of surface water. Therefore we have focused on verifying the applicability of our method for samples with such matrix that could significantly influences the determination of uranium concentration. For that reason we studied the influence of the particular matrix, complexing agent, and the sample pH on the recorded fluorescence spectrum shape and integral intensity. The uranium concentration in samples ranged from 1 to 1000 μg/l. To acidify the samples the HNO_3 was used. To limit the quenching effect and to prolong the UO_2^{2+} life-time, a complexing agent URAPLEX or optionally more available H_3PO_4 was added. We can conclude that for most of the investigated matrixes the described method offered sufficient precision of the uranium concentration determination. On the other side, it was found that the presence of nitrates and chlorides could be problematical. Especially in case of nitrates even the method of standard addition did not offered satisfying results. This behavior is under further investigation.

RER-P53, (Id: 395)

EFFECT OF HIGH IONIC STRENGTHS ON U(VI) RETENTION IN MONTMORILLONITE

Katharina Fritsch, Katja Schmeide

Helmholtz-Zentrum Dresden-Rossendorf
k.fritsch@hzdr.de

Argillaceous rock and clay minerals have properties that make them very suitable for nuclear waste storage. They are practically impermeable and have high sorption capacities. North German clay deposits feature pore waters of particularly high ionic strengths, ranging from 1.8 mol/l to 3.3 mol/l. in the depths relevant for nuclear waste repositories.[1] To enable an informed decision about the long term safety of nuclear waste disposal, the effect of high ionic strengths on radionuclide retention needs to be taken into account.

This work focuses on the uranium retention on montmorillonite (as model clay) in sodium and calcium chloride brines. These conditions are based on the Konrad mine that serves as reference site. There, montmorillonite is a major component. The ground water at a depth of about 480 m has sodium and calcium chloride as main components with an ionic strength of around 2.9 mol/l, and a pH between 5.75 and 6.85.[1]

The effect of ionic strength on uranium sorption on montmorillonite is very small. A true ionic strength effect, which is a decrease of sorption with ionic strength, can solely be observed below pH 6 and only up to an ionic strength of 2 mol/l sodium chloride. In calcium chloride, there are effects that show a positive correlation between sorption and ionic strength in the alkaline pH range but these can be explained with secondary phase formation rather than true ionic strength effects.

In the presence of carbon dioxide, U(VI) sorption decreases in the alkaline pH range regardless of electrolyte due to the formation of uranyl carbonate species. In the absence of carbon dioxide, U(VI) sorption at alkaline pH remains almost as high as the value at the sorption maximum. In general, the sorption maxima in both sodium and calcium chloride lie in the pH range of natural groundwaters in North German clay formations. Relative uranium uptake at the sorption maxima exceeds 99 % for both electrolytes. Desorption experiments show that uranium sorption on montmorillonite in sodium chloride is largely reversible except for very high ionic strengths. In calcium chloride, on the other hand, reversibility depends less on ionic strength and more on pH.[2]

Further results that will be presented concern uranium sorption in a mixed electrolyte that is modelled on the naturally occurring ground waters of the Konrad site.

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RER-P54, (Id: 399)

^{129}I IN THE ANTARCTIC SEAWATER MEASURED BY CARRIER FREE IODINE SEPARATION AND AMS

Xing Shan[a], Hou Xiaolin[a], Aldahan Ala[b]

[a]*Institute of Earth Environment, CAS, Uppsala University*
[b] *United Arab Emirates University*
xingshan@ieecas.cn

Due to low concentration of iodine in seawater, iodine carrier is normally added as carrier for separation of ^{129}I from matrix using solvent extraction, this is not suitable for the determination of low level ^{129}I in the seawater received less anthropogenic ^{129}I such as those collected in south hemisphere including the Antarctic and deep seas, because of contribution of ^{129}I in the iodine carrier to the sample during sample preparation. A simple co-precipitation method for separation of carrier free iodine from seawater for measurement of ^{129}I/^{127}I using accelerator mass spectrometry (AMS) has been reported by our group. In this work, some improvement of this method was completed to able to obtain better measurement uncertainty in AMS measurement. The results reveal that addition of small amount of carrier (0.1-0.2 mg) can significantly improve the measurement accuracy and precision. A certified seawater reference material, IAEA-418 (Mediterranean Sea water) has been successfully analyzed by utilizing the presented method and the concentration of ^{129}I was measured to be 2.36×10^{8} atoms L^{-1} in this sample, which agreed well with the certified value (2.28×108 atoms L^{-1}), as well as the results measured by traditional solvent extraction by addition of 2 mg iodine carrier, indicating reliability of the developed method. Six seawater samples collected from the Antarctic in ^{201}1 were analyzed utilizing the developed method. The results indicate that ^{129}I/^{127}I atomic ratios in the investigated area range from 0.7×10^{-12}~9.9×10^{-12} with a mean of 6.1×10^{-12}, which is close or slightly higher than the reported pre-anthropogenic ratio of 1.5×10^{-12}. The main source of ^{129}I in the investigated area might be attributed to the global fallout of both atmospheric nuclear weapons testing and long distance dispersion of fuel reprocessing releases. This is the first report of ^{129}I in the seawater from the Antarctic, the results shed a light of feasible application of ^{129}I as an oceanographic tracer application of ^{129}I the Antarctic.

RER-P55, (Id: 403)

INTERLABORATORY COMPARISON ON THE DETERMINATION OF RADIONUCLIDES IN WATER, FOOD AND SOIL CONDUCTED BY THE NATIONAL ATOMIC ENERGY AGENCY (NAEA), POLAND

Halina Polkowska-Motrenko, Leon Fuks, Agata Oszczak, Jakub Dudek, Pawel Kalbarczyk, Michal Zuba, Marta Pyszynska

Institute of Nuclear Chemistry and Technology
h.polkowska@ichtj.waw.pl

Proficiency tests (PT) on the determination of radionuclides in food and environmental samples have been organized by the National Atomic Energy Agency (NAEA), Poland, since 2004. The activity of the following radionuclides: ^{241}Am, ^{137}Cs, ^{3}H, ^{239}Pu, ^{226}Ra and ^{90}Sr were determined in water, food and soil. The PTs have been conducted by the Institute of Nuclear Chemistry and Technology (INCT), Warsaw, Poland and procedure adopted by the INCT is presented in the paper. The test materials: water, milk powder, wheat flour and soil, were prepared by spiking blank materials with standard solution of the radionuclide of interest. The activity concentrations were calculated and associated uncertainties were evaluated before sending the test materials to the laboratories. The results provided by the participants were statistically evaluated by means of z and zeta scores as well as using the International Atomic Energy Agency (IAEA) criteria for trueness and precision. Observed trends and some benefits for the participants have been presented.

RER-P56, (Id: 407)

RADIOACTIVITY AND HEAVY METAL CONCENTRATIONS AND ASSESSMENT OF HAZARD INDICES IN SEDIMENTS FROM ZHUSHAN BAY AT TAIHU LAKE, CHINA

Mingli Zhang[a], **Mingli Zhang**[a], **Xiaolin Hou**[b], **Jixin Qiao**[b], **Hao Yang**[a]

[a]*School of Geography Science, Nanjing Normal University, China*
[b]*Center for Nuclear Technology, Technical university of Denmark, Risø Campus, DK 4000 Roskilde, Denmark*
geozhml@163.com

Surface sediment cores from the Zhushan bay of Taihu lake in China were collected. In this study, the concentration of eleven heavy mentals(Al, Co, Cr, Cu, Mn, Ni, Ti, V, Zn, Pb, Cs) and the radioactivity of two radionuclides (^{210}Pb and ^{137}Cs) were investigated. The mean concentration of Cr, Cu, Ti, Pb indicated is slightly higher than the background values, and the rest doesn't exceed the background value. Compared with the levels in the Environment Quanlity Standard for soils of China (EQSS), the mean values of main heavy metals, such as Pb, Zn and Cr, is located level 1 of soil quanlity, which showed the concentration of these elements is ordinary in the sediment. while the concentration for Cu is located level 2 which indicated there is minor enrichment for Cu. The situation was confirmed by the enrichment factor (EF) of heavy metals showing the samilar result. In terms of radioactivity concentration for ^{210}Pb and ^{137}Cs, the mean 139.9 Bq/kg for ^{210}Pb and 21.3 Bq/kg for ^{137}Cs were more lower than the limited value 260 Bq/kg and 120 Bq/kg according to the Standard soil of quality assessment for Exibition site (SSQAE) of China. The study result implied that the lacustrine sediment can be retired to the farmland or used to be construction materials in the ecological enginnering of dredging process.

RER-P57, (Id: 409)

ASSESSMENT OF RADIATION AND CHEMICAL RISK IN SOILS BY RADIOMETRIC AND RADIOANALYTICAL METHODS

Ruveyda Kubra Ileri[a], **Sema Erenturk**[a], **Rahime Oral**[b], **Sevilay Haciyakupoglu**[a], **Ayse Nur Esen**[c], **Sabriye Yusan**[b], **Filiz Gur**[b], **Murat Belivermiş**[d], **Onder Kilic**[d], **Fatma Kocbas**[e], **Mustafa Akiner**[f]

[a]*Istanbul Technical UniversiIstanbul Technical University, Energy Institutety, Energy Instıtute*
[b]*Ege Üniversity, Faculty of Sciences, Department of Biology*
[c]*Istanbul Bilgi University, Faculty of Engineering*
[d]*Istanbul University, Faculty of Sciences, Department of Biology*
e[g]*Celal Bayar University, Faculty of Arts and Sciences, Department of Biology*
[f]*Rize University, Faculty of Arts and Sciences, Department of Biology,*
ileriru@itu.edu.tr

Chernobyl and other nuclear accidents have demonstrated that high levels of radiation can result in impacts on plants and animals, however little is known about the long-term effects of chronic exposure on biodiversity or other population and ecosystem level effects. The overall aim of this study is to assess the impacts of chronic exposure to radioactivity and chemical pollutants. The study area on the Eastern Black Sea Region, Turkey has metal mining (Fe, Au, Ag, Mn, Mo, Cu, Pb and Zn) and industrial facilities, having elevated levels of both heavy metals, and affected the fallout of radionuclides after Chernobyl. Results for radiation and chemical pollution were obtained from the analysis of soil samples taken from 6 sites. All soil samples were measured for gamma, beta and alpha activities. Also, elemental concentrations of soil samples were determined by instrumental neutron activation analysis and X-ray fluorescence analysis. In summary, to assess radiation and chemical pollution risk, the possible impact of long-term behaviour of the radionuclides and elements in soil should be taken into consideration. This type of study does however need to provide regional background levels for these important radioactive and chemical pollutants. Additional studies will be performed to estimate the exposure for the diversity and plants from radioactive and chemical pollutants.

RER-P58, (Id: 425)

ISOTOPIC ANALYSIS AS AN INDICATOR OF THE GROUNDWATER STABILITY

Paweł Grabowski[a], Magdalena Długosz-Lisiecka[a], Henryk Bem[a], Rolf Romer[b]

[a]Technical University of Lodz, Faculty of Chemistry
[b]Deutsches GeoForschungsZentrum
pgrabowski@pw.plock.pl

Natural radionuclides can be very good indicators of all hydrological and biogeochemical phenomena occurring in the water environment. Typical uses of environmental isotopes include the identification of source of water and solutes, determination of water flow paths, assessment of nutrients within the ecosystem, water budget. A few elements exhibit variations in their isotopic composition, resulting from radioactive decay its precursors present in the geological formations. These isotopic ratio variations can be used as natural fingerprint of rock – water interaction and applied in weathering and hydrology studies. In this work activity ratio of uranium and radium isotopes (^{234}U/^{238}U, ^{228}Ra/^{226}Ra), as well as of the stable strontium isotopic ratio (^{87}Sr/^{86}Sr) were determined in selected thermal groundwater, ground and surface water samples from central Poland. Uranium isotopes after co-precipitation with hydrated manganese dioxide were separated from other natural radionuclides by extraction chromatography resin (Dowex 1x8). The activity concentrations were determined by using α spectrometry with PIPS detector (Canberra). ^{228}Ra was determined by gamma spectrometry after co-precipitation with MnO$_2$, whereas ^{226}Ra was determined by liquid scintillation counting. Strontium isotopic ratio after separation from other element by extraction chromatography resin (Dowex 50Wx8) was determined by thermal ionization mass spectrometry (TIMS). The average isotopic ratio for different type of water sample from Poddebice and Uniejow was shown in the Table 1.

Table 1 Activity and isotopic ratio in different type water.
location water type ^{234}U/^{238}U ^{228}Ra/^{226}Ra ^{87}Sr/^{86}Sr
Poddebice thermal groundwater 0,923±0,020 1,64±0,35 0,708492±0,000014
deep well water 1,115±0,063 1,23±0,71 0,709454±0,000130
river water 1,027±0,116 2,67±1,14 0,709718±0,000466
Uniejow thermal groundwater 0,744±0,094 0,641±0,043 0,708441±0,000002 river water 1,232±0,161 1,95±0,49 0,709256±0,000059
The observed differences in these ratios confirms that the uranium, radium and strontium isotopic ratio can be useful indicator for determination of stability of the underground water reservoirs.

RER-P59, (Id: 6)

ADSORPTION OF TRIVALENT LANTHANIDES AND ACTINIDES BY MARINE SEDIMENTS

Ioanna Liatsou, Maria Efstathiouloannis Pashalidis

Chemistry Department, University of Cyprus
liatsou.ioanna@ucy.ac.cy

Knowledge of the chemical behaviour of (radio)toxic elements in natural/environmental systems is of fundamental importance for the performance of environmental impact assessments and the application of protection measures after possible contamination. The interaction of actinides with marine sediments is of particular interest because marine sediments constitute the final receptors for the majority of actinides (Th, Am, Pu). In order to study the chemistry of trivalent actinides (e.g. Am(III), Cm(III)) often trivalent lanthanides are used as analogues, because lanthanides in aqueous solutions are generally stable in the trivalent oxidation state, present similar chemical behaviour as trivalent actinides, are non-radioactive and posses useful spectroscopic/fluorescent properties. In this study we have investigated the interaction of Nd(III) and Eu(III) with two different types of marine sediments as a function of various parameters (e.g. pH, [M(III)]o, I, tcontact) to evaluate their effect and get more information on the adsorption of Nd(III) and Eu(III) by marine sediments. Sorption of Eu(III) by marine sediments from aqueous solutions of varying pH 4 – 6.5, fixed ionic strength of 0.1 M ($NaClO_4$) and at room temperature has been studied by fluorescence spectroscopy (LFS). In this context, the effect of the particle coating with natural organic matter (NOM, e.g humic acid) on the adsorption properties of the sediment samples has also been studied. According to the experimental results the adsorption of Nd(III) and Eu(III) ions by marine sediments is (a) a relatively fast process (b) the adsorption data are well described by the Langmuir isotherm and (c) the adsorption properties (e.g. adsorption capacity, pH and ionic strength effects) of the different sediment types differ significantly from one another, depending on the (surface) composition.

RER-P60, (Id: 445)

SHORT-TERM VARIATIONS OF THE ^{7}Be WET DEPOSITION IN THE EASTERN PART OF THE CZECH REPUBLIC

Petra Kolіčová, Petr Alexa, Radim Uhlář

Technical University of Ostrava
petra.kolicova@vsb.cz

^{7}Be is a natural radioisotope (half-life 53.3 d) produced in cosmic-ray spallation processes on atmospheric nitrogen and oxygen. We sampled individual rain events (September 2013 – March 2014) in a collector (1 m above the roof of the Technical University of Ostrava) and simultaneously collected relevant meteorological data from the station on the same roof. Rain samples were filtered and the ^{7}Be content in collected water was determined by gamma spectrometry. We studied the correlation between the ^{7}Be wet deposition and precipitation amount, precipitation intensity, elapsed time between individual rain events, cloud types and the air-born-dust PM10 and PM2.5 concentrations before and after the individual rain events [1] and tested the models proposed in the literature [2,3].

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RER-P6, (Id: 212)

SORPTION OF CHEMICAL ELEMENTS BY PLANKTON IN THE PRESENCE OF HUMIC ACID

Evgeny Polyakov[a], Margarita Chebotina[b], Valentina Guseva[b], Ilya Volkov[a], Nikolai Khlebnikov[a]

[a]*Institute of Solid State Chemistry, UB RAS*
[b]*Institute of Plant and Animal Ecology, Ural Branch RAS*
polyakov@ihim.uran.ru

Humic acids (HA) are one of few omnipresent natural substances, which govern the migration trends of chemical elements in the biosphere. Being a complex mixture of high molecular organic compounds, they take part in accumulation, aqueous transfer and sorption of chemical elements in natural environment. The impact of HA on the sorption of stable trace elements and radionuclides in the geochemical media still remains a subject of intensive investigations. The role of HA complexes formation in the bioavailability (sorption) of microelements by plankton, lake plankton in particular, is significantly less studied. To determine the formal characteristics of trace elements sorption by living (active) and dead (inactive) species of lake plankton and to quantify the effect of HA concentration on these characteristics, we have performed an experimental investigation of the sorption systems “lake water - plankton – trace elements” under laboratory conditions. The plankton samples were collected in the Beloyarskoe Reservoir (Urals, RF). Plankton was chosen as a model object because of its leading role in the distributive biosedimentation of chemical elements in continental reservoirs. Due to its high productivity and accumulation ability, plankton is supposed to be one of the best bioindicators of contamination of water ecosystems with radionuclides and other pollutants, as well as a natural sorbent of trace elements [1].

The list of the microelements used in the sorption experiments included more than 50 chemical elements, the level of which in the lake water was above the detection limits of ICP-MS ELAN 9000. The experimental results of the analysis of sorption behavior of trace elements with respect to plankton are discussed in the presentation. It was found that for the most trace elements studied sorption by plankton (both active and inactive species) obeys the Langmuir law. The presence of soluble HA in water medium results in the reduction of the distribution coefficients of selected microelements towards active plankton. It is deduced that lake plankton interacts with trace elements in lake water and may be considered as a promising bio-sorbent of trace elements and radionuclides.

This work is supported by RFBR-Ural (grant #13-03-96061) and UB RAS (grant #12-T-3-1019).

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Nuclear Analytical Methods (NAM)

Verbal presentations

NAM-I01, (Id: 374)

BIOCHEMICAL NEUTRON ACTIVATION ANALYSIS (BNAA) IN PRE- AND POST-GENOMIC ERA OF PROTEOMICS AND METABOLOMICS

Amares Chatt, Channa K Jayawickreme

Dalhousie University
a.chatt@dal.ca

Neutron activation analysis (NAA) is a well-established analytical technique for the simultaneous measurement of multielement concentrations. The most common forms of NAA are instrumental (INAA), radiochemical (RNAA) and preconcentration (PNAA). We have previously reported the development of speciation NAA (SNAA). We are also interested in the development of biochemical NAA (BNAA) methods for the separation, purification, characterization, and measurement of metalloproteins and organic compounds containing trace elements which are of biological/biochemical importance. We take advantage of the unique features of both techniques. For example, we need an analytical technique capable of analyzing a few milligrams of solid as well as liquid samples non-destructively and independent of chemical species, and of determining trace levels of several elements simultaneously within a short time in a matrix largely composed of carbon, hydrogen, nitrogen, oxygen and sulfur. Of course, the technique should provide excellent precision, accuracy, sensitivity, and detection limits. NAA meets all of these requirements. The biochemical techniques of interest are dialysis, ammonium sulphate precipitation, gel filtration, ion exchange and hydroxyapatite chromatography, high-performance liquid chromatography, chromatofocusing, isoelectrofocusing, isotachophoresis, sedimentation equilibrium and enzymatic assay. We called this combination of two techniques BNAA which is ideally suited for studying metalloproteins, protein-bound trace elements, and organometallic compounds. We observed that most of the trace elements in bovine kidneys, for example, were largely concentrated in the cytosol fraction. More than 70 % of As, Br, Cl, Co, K, Na and Rb, about 65 % of Cd, and 30-35 % of other elements except Se (14.4 %), Cr (15.6 %) and Mo (24.6 %) were detected in this fraction. Elements such as Ca, Cr, and Se were more abundant in the nuclei fraction with concentrations of 34 %, 75 % and 73 %, respectively. The dialysis experiments showed that more than 90 % of Ca, Cd, Cu, Fe, Mg, Mn, Mo, Se, V and Zn, and possibly As, and I, and about 20 % of Br were bound to macromolecules, mainly proteins. Most of these proteins were stable in the pH range of 3.5 to 10.5. We separated and purified several metalloprotein species. Examples of these species with particular emphasis on Se will be presented.

NAM-V02, (Id: 406)

NUCLEAR AND RELATED ANALYTICAL TECHNIQUES USED TO STUDY ATMOSPHERIC DEPOSITION OF TRACE ELEMENTS AND RADIONUCLIDES IN RURAL AND URBAN AREAS EXPERIENCING ENVIRONMENTAL STRESS

Marina Frontasyeva

Joint Institute for Nuclear Research
marina@nf.jinr.ru

Experience in applying mosses as biomonitors of trace elements and radionuclides in some selected rural and urban areas affected by intense anthropogenic activity is reviewed. Among them the western part of the Kola Peninsula (NW Russia), the most heavily industrialized area in the entire Arctic; the South Urals (Karabash) counted among the most polluted areas in the world where human impact on the environment is largely irreversible. The dominant groups of pollutants are heavy metals and long-lived radionuclides from full-scale activities and accidents at the radiochemical "Mayak" Production Association (PA). Moss was successfully used to study distribution of ^{137}Cs and ^{210}Pb in Belarus and Slovakia 20 years after the Chernobyl accident. A combination of analytical data (NAA and AAS in our case) with principle component analysis and GIS technologies allowed pollution source characterization and apportioning in the sampled areas around (1) copper mines in Karabash (RF), Bor (Serbia), South of Poland; (2) Zn-Pb smelters in Baia Mare (Romanai), Krdjali (Bulgaria) and Veles (Macedonia); (3) Fe-V plant in Tula (RF); (4) Fe-Cr industry in Tikhvin (RF) and Mo-i-Rana (Norway); (5) oil refinery industry in Yaroslavl (RF), and (6) thermal power plant in one of Moscow districts. Besides passive (terrestrial) moss biomonitoring, active moss biomonitoring (moss bags technique) showed itself efficient in accessing air pollution in large cities (street canyons of Belgrade and Moscow). The results obtained at local scale in the areas experiencing environmental stress can be used for establishing the emission levels of pollutants and to serve a source of information for health-related institutions.

NAM-V03, (Id: 370)

MEASUREMENT OF SELENIUM LEVELS IN CULTIVATED JAPANESE AND KOREAN OYSTERS AND JAPANESE ROCK OYSTERS USING THE 17.4-s NEUTRON ACTIVATION PRODUCT ^{77m}Se

Michiko Fukushima[a], **Amares Chatt**[b]

[a] *Ishinomaki Senshu University*
[b] *Trace Analysis Research Centre, Department of Chemistry, Dalhousie Universit*
fukusima@isenshu-u.ac.jp

Oysters in Japan are mainly cultivated in Miyagi, Hiroshima, and Hokkaido Prefectures. Sometimes baby cultivated oysters are exchanged between Japan and Korea; so both cultivated oysters are said to be genetically similar. Since Japanese consume a fair amount of raw oysters, it is of interest to compare the elemental levels of oysters from different areas. Soft tissues of cultivated Japanese oysters (Miyagi Prefecture, 2004 Nov, at 1, 6 and 11 m depths), Korean oysters (Koje-do and Kosong in Busan, 2002 Oct, 2004 Jan, and 2005 Dec), and Japanese rock oysters (Honshu Island) were analyzed for selenium levels. The soft tissues, namely hepatopancreas, gill, muscle, and mantle were separated, freeze-dried, pulverized, and analyzed by an instrumental neutron activation analysis (INAA) method in conjunction with Compton suppression spectrometry (INAA-CSS). The method consisted of irradiation of samples for 12 s in a neutron flux of $5x10^{11}$ $cm^{-2}s^{-1}$ using the rapid cyclic pneumatic sample transfer system at the Dalhousie University SLOWPOKE-2 reactor (DUSR) facility, decay for 15-20 s, and counting for 60 s. The 161.9-keV gamma-ray of the 17.4-s nuclide ^{77m}Se was used for assaying selenium. The method was validated using NIST, NRC and NIES certified reference materials. An absolute detection limit of 0.15 µg selenium using NIST SRM 1566b Oyster Tissue was achieved. Selenium levels between Japanese and Korean oysters did not show much difference. The selenium concentrations in Japanese rock oysters showed the following trend: gill > hepatopancreas > mantle > muscle.

NAM-V04, (Id: 188)

COMPARISON OF INAA AND LC-ICP-MS FOR THE DETERMINATION OF AS SPECIES IN MARINE TISSUES

Rolf Zeisler[a], Lee L. Yu[a], Rabia Oflaz[a], Vivian M. O. Carioni[b], Cassiana S. Nomura[c]

[a]*National Institute of Standards and Technology*
[b]*Universidade Federal do ABC, Centro de Ciencias Naturais e Humanas*
[c]*Universidade de Sao Paulo, Instituto de Quimica*
rolf.zeisler@nist.gov

The aim of this work was to acquire traceable quantitative results for total As in whole samples as well as in extracts containing As species. Instrumental neutron activation analysis (INAA) is well suited for such measurements and is used in this work to validate the As mass fraction determined by liquid chromatography combined with inductively coupled plasma mass spectrometry (LC-ICP-MS) in tuna fish and kelp candidate RMs and other marine samples, including certified RMs. INAA was used to determine total As and trace elements in original solids, extracted solids, and in extracts as well as LC fractions; LC-ICP-MS was limited to the determination of As species in extracts. Extraction yields were determined by INAA for a number of common solvents and extraction techniques; the best results were acquired after methanol/acetone/water extraction with sonication. This procedure was used for quantitative As species evaluation with LC-ICP-MS incorporating internal standards and single point standard addition, while the sum of all As fractions was monitored by INAA. In the case of tuna tissue, AB was the predominant species determined by LC-ICP-MS and its As mass fraction was 4.41 ± 0.09 mg/kg. The total extracted As by INAA was 4.88 ± 0.27 mg/kg. In case of the BCR 627 certified RM the sum of AB + DMA was 4.15 ± 0.10 mg/kg, measured as AB = 3.99 ± 0.08 mg/kg and DMA = 0.148 ± 0.010 mg/kg in good agreement with the certified values, and the total As extracted was 4.28 ± 0.18 mg/kg by INAA summing up with As in the residue to 4.75 ± 0.17 mg/kg in excel-lent agreement with 4.81 ± 0.11 mg/kg determined by INAA in the original material. These differences between the techniques may be explained by relatively too high dissolution required by LC-ICP-MS not detecting very low mass fractions of other species in the extracts, and/or retention of As on the column. To completely evaluate the LC-ICP-MS process INAA detection limits were lowered utilizing the Compton suppression technique in the gamma spectrometry to reach below 0.2 ng sensitivity, which is sufficient to determine As in LC effluent fractions. LC effluent fractions were collected according to the time intervals recorded by the ICP-MS, reduced in volume, and transferred and dried on Whatman 542 filter substrate. These were subsequently submitted to INAA. The initial results showed As in the background (blank) fractions of the chromatogram, however most of it due to solvent blank. Arsenic in these fractions is not captured by ICP-MS and thus would explain the difference. Further, the quantitative determination of As by INAA in the chromatogram peaks provided a direct measurement of each separated species and allowed for calibrated determination of each species. Species, including those not available as standards, e.g., the arsenosugars found in kelp, can be accurately determined by INAA and used as calibrants. INAA and LC-ICP-MS thus were successfully used as complementary techniques for characterization and traceability studies related to the development of RMs for As species.

NAM-V05, (Id: 28)

BIOSORPTION OF CHROMIUM AND NICKEL FROM WASTEWATER BY MICROALGAE NOSTOC LINCKIA

Inga Zinicovscaia[a], Ana Valuta[b], Liudmila Rudi[b], Marina Frontasyeva[a], Otilia Ana Culicov[a], Svetlana Gundorina[a], Tatiana Mitina[c], Liliana Cepoi[b]

[a]*Joint Institute for Nuclear Research, Joliot-Curie Str., 6, 1419890 Dubna,*
[b]*Institute of Microbiology and Biotechnology of the Academy of Sciences of Moldova, 1, Academiei Str., 2028 Chisinau, R. Moldova*
[c]*The Institute of Chemistry of the Academy of Sciences of Moldova, 3, Academiei Str., 2028 Chisinau, R. Moldova*
zinikovskaia@mail.ru

The present study relates to the use of microalga Nostoc linkia for the removal of chromium and nickel from wastewater of galvanic industry. During one hour experiment 70 % of chromium and 50 % of nickel were removed from the wastewaters. To determine concentrations of Cr and Ni in wastewater samples atomic absorption spectrometry was used. The samples of dry nostoc biomass after exposure to wastewater were subject to nondestructive instrumental neutron activation analysis. A total of 28 other elements were determined in the microbial cells. The results from NAA of Nostoc linkia showed that along with Cr and Ni, sorption of Fe, Ni and Zn was also very high from wastewater containing Cr and Ba, Fe, Zn from wastewater containing Ni. Fourier Transform Infrared (FTIR) technique was used to understand changes in the chemical structure of Nostoc linckia biomass after interaction with wastewater.

NAM-V06, (Id: 166)

UNRAVELING THE REACTION RATE CONVENTIONS FOR USE IN THE K_0 STANDARDIZATION OF NAA

Frans De Corte

Ghent University, Belgium and Research Foundation, Flanders
fransmans@skynet.be

The majority of developers and users of the NAA k_0 standardization do not realize that this method was launched [1] in terms of the accurate and generally applicable Stoughton-Halperin convention [2] for the description of the (n,γ) reaction rate. Later on, in the article reporting on the first k_0-measurements [3], the more practical Høgdahl convention [4] was introduced instead (as had been done in earlier work on k-factors [5]), which was modified to account for a non-ideal (assumed $1/E1+\alpha$) epithermal neutron flux distribution thereby introducing Ryves' concept of the effective resonance energy [6]. This resulted in a user-friendly protocol, which however ruled out some five (n,γ) reactions with a significant deviation from the ideal 1/v cross section dependence in the thermal neutron energy region. Although in the course of the years it was argued [7] that only a few excluded cases did not justify the changeover from a simple convention like Høgdahl's to a more sophisticated one, finally the rigorously accurate Westcott convention [8] – with introduction of the α epithermal shape factor - was put forward to incorporate the non-1/v cases in the k_0 standardization methodology [9]. Obviously, this turned out to be too complex and impractical for a good deal of the k_0-NAA community, notably in the context of the Kayzero software [10] where use is made of an intermediate comparator factor defined in terms of the Høgdahl convention. Therefore, recently the "extended Høgdahl convention" [11] was launched, which takes into account the non-1/v cross section behavior by rather randomly inserting Westcott's g(Tn) factor in the Høgdahl expression, where Tn is the maxwellian neutron temperature. Although the proof of validity of this extension was based on empirical and hardly on scientific arguments, it can nevertheless be regarded as a valid approach – as shown in the present paper where it is derived from the Stoughton-Halperin convention by introducing a few justifiable approximations. Hence, it can be smoothly implemented in the Kayzero software and in other concentration calculation programs while yielding for the 1/v and non-1/v (n,γ) reactions concentration results which are accurate to acceptable, respectively. This is a promising development in the context of the general applicability of the NAA k_0 standardization.

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NAM-V07, (Id: 114)

RE-DETERMINATION OF THE HALF-LIFE OF ^{229}Th

Zsolt Varga, Adian Nicholl, Mayer Klaus

EC JRC Institute for Transuranium Elements
zsolt.varga@ec.europa.eu

^{229}Th is an alpha-decay nuclide of the neptunium decay series. Though already extinct in nature, ^{229}Th occurs in high amount in spent fuel as the progeny of the long-lived ^{237}Np. ^{229}Th is one of the most widely used tracers in geology, environmental sciences or nuclear chemistry to determine ^{230}Th and ^{232}Th concentrations by mass spectrometry due to the relatively long half-life and to the fact that it does not occur in nature. ^{229}Th as an isotopic tracer plays a special role in nuclear forensics, where its uncertainty associated with its concentration is one of the most dominant components in the uncertainty budget of radiochronometry of illicit nuclear materials1. As the ^{229}Th standards are certified by activity concentration (e.g. Bq g^{-1}), the accurate knowledge of ^{229}Th half-life value is of utmost importance to convert it to amount content (e.g. mol g-1) needed for mass spectrometry. The first precise half-life measurement of ^{229}Th was accomplished by Hagemann et al.2 and gave a value of 7340 ± 160 years. However, a later measurement by Goldstein et al.3 by isotope dilution mass spectrometry reported an approximately 7 % higher half-life of 7880 ± 120 years. Recently, Kikunaga et al.4 measured the ^{229}Th half-life by alpha spectrometry. Their half-life value of 7932 ± 55 years is consistent with the result obtained by Goldstein et al., and the authors suggest that the inaccuracy of the early half-life value is attributed to incomplete separation of ^{233}U from its impurities.

The aim of the present study is to re-measure the ^{229}Th half-life using inductively coupled plasma mass spectrometry (ICP-MS) at lowest possible uncertainty. By the measurement of the ^{229}Th amount content in the certified ^{229}Th radioactivity standard (SRM ^{4328}C), the half-life of ^{229}Th can be calculated. The amount content of ^{229}Th was determined by two independent methods, both traceable to SI. In the first method, the ^{229}Th amount content was measured by isotope dilution ICP-MS technique, using a natural thorium certified reference material as a tracer. In the second method, the ^{229}Th amount content was measured against a completely separated highly-enriched uranium solution. In this case, the applied uranium sample was completely purified from its thorium decay products beforehand at a well-known time. Thus the ^{230}Th daughter product of the ^{234}U, which serves actually as the tracer for the ^{229}Th determination, can be very precisely calculated knowing the ^{234}U content and the elapsed time between the uranium separation and ^{229}Th determination1.

Our measured ^{229}Th half-life of 7921 years with an expanded uncertainty of 56 years ($k = 2$) is in agreement with the latest values. Uncertainty was calculated according to the GUM (Guide for the Expression of Uncertainty in Measurement). The obtained value can help resolve the problem with ^{229}Th half-life discrepancy, and can result in more precise age dating measurements both for geological and nuclear samples.

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NAM-V08, (Id: 254)

ACTIVATION ANALYSIS IN STUDIES OF TEKTITES AND IMPACT GLASSES

Jiří Mizera, Zdeněk Řanda

Nuclear Physics Institute, Academy of Sciences of the Czech Republic
mizera@ujf.cas.cz

Impact glasses and tektites are formed during fall of large meteorites on the Earth surface (impact) by melting and ejection of surface materials, mainly unconsolidated sediments and sedimentary rocks. In the Nuclear Physics Institute ASCR, methods of neutron and photon activation analyses have been utilized for detailed geochemical characterization of a collection of various tektites and impact glasses: Central European tektites - moldavites, Australasian tektites, impact glasses from the Zhamanshin crater in Kazakhstan - irghizites, and the Libyan Desert Glass.

Geochemical analysis of a large representative set of moldavites indicates that a substantial part of their parent materials must have been, besides the surface molasse sediments, also soil layer and plant biomass which are indicated in modavite composition by enrichment in the plant nutrient/essential elements (K, Ca, Mg) and depletion of nonessential elements (Na, Rb, Sr, Ba), similarly to their redistribution during the transfer from soil to plants. The hypothesis has been supported also by analysis of carbon isotope composition of moldavites which is similar to that characteristic of land vegetation.

In irghizites, determined contents of Ni, Cr, Mn, Fe and Co, after subtraction of their background contents from terrestrial source materials, allowed to assign the most probable impactor type as an ordinary L5 or L6 chondrite, and assess a range of the meteoritic fraction in the irghizite parent materials to 4 - 21 wt. %. An explanation has been suggested for lower Ir content in irghizites than matching a chondritic component which is based on significantly lower volatility of Ir compared to other meteoritic constituents as Ni, Cr, Mn, Fe and Co. Unambiguous assigning parent materials and finding a parent crater for the Australasian tektites (AAT) still remains an open issue. After critical evaluation and comparison with literature data, the geochemical data acquired in a representative set of AAT point to a "fingerprint" similarity between AAT and Chinese loess which was discussed in literature as a probable AAT precursor much earlier but later was doubted and abandoned due to generally accepted hypothetical location of the impact to Indochina. The data have been coupled with data available in literature for both AAT and their potential precursors on their isotopic composition (Sr, Nd, Li, B, cosmogenic Be-10). The results, together with considering geographical, ballistic and paleoclimatic aspects, put in serious doubt the location of the AAT parent crater in Indochina and bring extensive evidence for possible location of the crater in the deserts in north-central China which are the source area of the Chinese loess.

Elemental composition of he Libyan Desert Glass (LDG) points to quartz sand as a main component of the parent materials, with admixture of elements implying an aluminosilicate component (clay minerals cementing quartz grains). A depletion of volatile elements (alkalis, Zn, As, Br, Sb, etc.) may reflect their evaporation loss during the impact. Higher Zr contents coupled with elevated contents of heavy rare earth elements may reflect melting of refractory zircon. LDG has recently been associated with the Kebira Crater on the Libya-Egypt border. The impact area was flooded with seawater during Cenomanian/Turonian stage and the assumed origin of LDG parent materials - compact sandstone with accessory minerals - in marine environment has been supported also by previous Li isotope investigation. No contamination of LDG by meteoritic material has been evidenced. The studies have been supported by the projects 205/09/0991 and 13-22351S of the Czech Science Foundation.

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COMMERCIAL OXO-BIODEGRADABLE PLASTICS INVESTIGATED BY NEUTRON ACTIVATION ANALYSIS

Elisabete De Nadai Fernandes, Mateus Boscaro

Nuclear Energy Center for Agriculture, University of São Paulo
lis@cena.usp.br

Plastics are ubiquitous in everyday life with more than 250 million tons being used globally for a multitude of applications, many of them simply not sustainable and acceptable. The millions tons of plastic wastes formed over the past 60 years are affecting animals and human lives and the environment. The environmental impacts of increased accumulation of plastic wastes are becoming unbearable. For example, in the oceans, the biggest dump of plastics, they are breaking down and leaching toxins compromising marine life. In landfills, plastic materials release harmful chemicals into groundwater. The chemicals added to plastics are absorbed by humans provoking, among others, hormone alteration. In this context, the chemical industry should take responsibility for replacing persistent and hazardous chemicals with safe ones to minimize those deleterious effects.

In the recent decades, research has been focused at searching degradable polymers, like natural biopolymers or synthetic polymers with additives which facilitate degradation. The oxo-biodegradable plastics are synthetic polymers which have received light-sensitive chemical additives with the objective to initiate or accelerate the biodegradation process by photodegradation, through oxidation and chain scission. The oxidation and molecular weight reduction make the plastic weak and fragile, and biodegraded. As a consequence of manufacturing processes and use of additives and dyes, plastics often contain small amounts of chemical elements that do not take part of the polymer molecules.

In Brazil, the biodegradable polymers have been thoroughly introduced in the main sectors of agriculture, medicine and packaging. Consequently, with the onset of industrial production and commercial application of degradable plastics in the country, the determination of inorganic constituents in these materials has become of utmost importance. This work attempted to the chemical characterization of oxo-biodegradable plastics found in packaging bags commonly distributed in stores and supermarkets, using neutron activation analysis (NAA), a primary method of measurement.

Plastic bag samples were collected directly in shopping facilities near the city of Piracicaba, São Paulo state. Preparation included washing with deionized water, drying and separation of the portions without graphic prints. Analytical portions of 200 mg were packed into high purity polyethylene capsules and irradiated in the nuclear research reactor at IPEN/CNEN, São Paulo, SP. Certified reference materials of polyethylene matrix from IRMM (ERM-EC 680k and ERM-EC 681k) were irradiated together the samples for quality control purposes. The induced radioactivity was detected by high resolution gamma-ray spectrometry with hyperpure germanium detectors in the Radioisotopes Laboratory (CENA/USP). Mass fractions and respective uncertainties were obtained by the k0-standardization method using the Quantu-INAA software. Samples were also analyzed by Fourier transform infrared spectroscopy (FTIR)for polymer identification and complementary chemical characterization.

The elements As, Br , Ca , Co , Cr , Fe , Hf , K , La , Na, Sb , Sc, Ta and Zn could be determined in the oxo-biodegradable bag samples in a wide range of mass fractions. Ca, K and Zn are present in greater abundance in plastic bags due to additives with mineral fillers, mainly calcium carbonate, a process which aims reducing costs. Nevertheless, the values obtained for these elements were within acceptable levels, except in some samples for zinc, chromium and cobalt in relation to the standards ABNT NBR 15448-2 and EN 13432 for biodegradable polymers.

NAM-V10, (Id: 128)

DETERMINATION OF IMPURITIES IN PHOSPHORIC ACID BY INAA

Hamid Amsil[a], Jan Kameník[b], Jan Kučera[b]

[a]Centre national de l'énergie, des sciences et des techniques nucléaires (CNESTEN), Morocco
[b]Nuclear Physics Institute, Academy of Sciences of the Czech Republic
amsil.h@gmail.com

The increasing demand for phosphate fertilizers accounts for approximately 90 % of global phosphoric acid use. In the manufacture of phosphoric acid, thermal and wet processes are used. The thermal process has been abandoned for the production of phosphate fertilizers, because of the amount of energy which is needed. Decomposition of phosphate minerals with an acid, mostly sulphuric acid, is the only economic way to produce phosphoric acid. Phosphate ores, mostly in the form of apatite, are of two major geological types. The principal deposits are sedimentary rocks found, e.g., in Morocco, China, Algeria, Jordan, USA. Significant igneous deposits are found, e.g., in Russia, South Africa, Brazil. Whatever their origin apatites can be highly substituted and have variable compositions. More than 25 elements are known or proposed to substitute in the apatite structure [1]. The potentially hazardous elements found in phosphate rocks include As, Cd, Cr, Hg, Pb, Se, U, and V. Some cause difficulties in the reaction system, whereas others, soluble in phosphoric acid, may end up in the product acid. Therefore, there is a need for analytical method capable of accurate determination of the above and other elemental impurities in phosphoric acid. Instrumental neutron activation analysis (INAA) is a method of choice due to its multielemental capability and favourably low detection limits for most of the above elements. The problem is, however, that irradiation of liquid acids is prohibited in most nuclear reactors for safety reasons. Therefore, a sample preparation procedure is required that leads to “solidified” phosphoric acid. For this purpose, Silva et al. [2] employed precipitation with calcium hydroxide and evaporation for determination of uranium in phosphoric acid.

In this work three other procedures were tested, namely (i) deposition of 100-µL amounts of phosphoric acid onto disks of chromatographic paper Whatman 1 and sealing in polyethylene (PE) irradiation capsule without drying, (ii) precipitation of $Ca_3(PO_4)_2$ with $CaCO_3$ in a beaker, (iii) precipitation of $(NH_4)_3PO_4$ by reaction with ammonia vapours in a dessicator (isothermal distillation of NH_4OH [3]) directly in the PE irradiation capsules. The first procedure failed, because of breaking the PE capsules and consequent losses of their content on irradiation. In the second procedure, the activities of ^{47}Ca-^{47}Sc and ^{49}Ca increased background in the gamma-ray spectra that impaired detection limits of trace elements, as well as blank values of Sr and several other elements due to impurities added with $CaCO_3$. Thus, the third procedure appeared superior due to its simplicity and contamination-free nature. INAA results obtained with the third procedure are presented for four brands of phosphoric acid differing in purity (pro analysis and technical grades) and concentrations (75 %-85 %).

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NAM-V11, (Id: 386)

DEVELOPMENT OF ^{151}SM ANALYTICAL METHOD FOR THE PURPOSE OF NUCLEAR WASTE CHARACTERIZATION

Florence Goutelard[a], C. Roure[b], Lionel Bec Espitalier[c], Christèle Colin[a], Carole Frechou[d], Hélene Cazorla[b], Aurelie Calvet[b]

[a]*CEA DEN-DANS/DPC/SEARS/LASE*
[b]*AREVA NC Marcoule, DEX/LAB/MR*
[c]*AREVA NC Marcoule*
[d]*CEA DRT/LIST/LNHB/LMA*
florence.goutelard@cea.fr

In France, nuclear wastes are managed by the French National Radioactive Waste Management Agency (ANDRA). Several repository sites have been built in order to accommodate nuclear waste packages. One is dedicated to the Low and Intermediate Level short-lived Waste. Criteria for 143 radionuclides have been defined by ANDRA which guarantee the safety of the facility. From this long list, ^{151}Sm has to be declared as soon as its activity is over 0.1 Bq/g. The declaration threshold for this radionuclide is very low and the maximum acceptance level in waste packages has been fixed to 4.5×10^5 Bq/g. 151Sm is a fission product with a radioactive period of 90 year. As a pure beta emitter, it must be isolated from the matrices and the interfering radionuclides through chemical separations prior to any measurement. Consequently, a selective radiochemical procedure is needed to measure ^{151}Sm in nuclear wastes.

The LASE (Operator Support Analyses Laboratory) and Nuclab-Prod have shared their radio-analytical skills to develop an analytical method to measure ^{151}Sm in radioactive waste. The analytical process includes 5 steps. First, digestion is performed for organic material, aqueous suspension or solid sample in nitric acid media. Neodynium as carrier and stable samarium as yield tracer are added. In order to reduce the salt concentration, a hydroxide precipitate is completed. Lanthanides are isolated from the other elements still present, by extraction chromatography using the Re-Spec column from Eichrom. A high performance liquid chromatography is implemented in order to separate samarium from the other rare earth element such as europium, neptunium, promethium…. Alpha-Hydroxybutyric acid as ligand agent is introduced in the mobile phase. Injected volume, eluent composition, fraction collection procedure have been optimized in order to assure recovery of Sm over 90 %, no cross-contamination and effectiveness of the separation. This step has been completely automatized. The solution containing samarium is conditioned for liquid scintillation counting.

The presentation will first focus on the optimization of the radiochemical procedures and the way the various elements are discarded. The choice will be argued. The second part of the work will be addressed to the application of the method to nuclear waste, results will be discussed.

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NAM-V12, (Id: 214)

PROMPT GAMMA ACTIVATION ANALYSIS AND IN-BEAM ACTIVATION ANALYSIS AT FRM II

Zsolt Révay, Petra Kudejova, Krzysztof Kleszcz

Technische Universitaet Muenchen FRM II
zsolt.revay@frm2.tum.de

The high-flux cold neutron beam at the Prompt Gamma Activation Analysis (PGAA) facility at Garching makes possible plenty of new applications, which were impossible earlier when using this technique. The thermal equivalent neutron flux in the focal point is 6×10^{10} cm^{-2} s^{-1}, which almost reaches the flux of smaller reactors, but in a beam which is totally free of epithermal or fast neutrons. The sample masses can now be below 1mg, or materials with extremely low cross section (such as deuterium [0.5 mb], oxygen [0.2 mb], or even gasous neon [39 mb]) can be measured with good statistics. In this beam, even radioactive samples can be irradiated whose induced activity was found to be too low to compete with the natural activity. Moreover, in-beam neutron activation analysis (NAA) can also be performed. This method can be combined with PGAA, significantly increasing the number of detectable elements. In the talk, the methodological developments and the most important applications will be summarized.

NAM-V13, (Id: 122)

NGD COLD NEUTRON PROMPT GAMMA-RAY ACTIVATION ANALYSIS SPECTROMETER AT NIST

Rick Paul, Dagistan Sahin, Christoph Brocker, Jeremy Cook, Richard Lindstrom

NIST
rick.paul@nist.gov

An instrument for cold neutron prompt gamma-ray activation analysis (PGAA) has been operational on neutron guide NG7 at the NIST Center for Neutron Research (NCNR) since December 1990. The applicability of this instrument suffers from the presence of the adjacent upper half of the NG7 guide, just 3 cm above the sample position, limiting both sample size and available space for setting up experiments. The scattered neutrons from the upper guide create a gamma-ray background when absorbed by surrounding material, specifically air. The upper beam guide has been painted with lithiated paint on the outer surface to reduce scattered neutrons.

In conjunction with the expansion of the NCNR, a new PGAA instrument has been built on the guide NGD. A 2 cm x 2.7 cm beam of cold neutrons is extracted from the guide into air through a magnesium alloy window upon opening a lead-lined 6Li glass shutter, and is collimated by a ^{6}Li glass aperture mounted just before the sample box. Samples are irradiated in an evacuable aluminum box (273 cm (h) x 171 cm (w) x 247 cm (l))) with removable magnesium alloy windows. A piece of enriched 6LiF mounted downstream serves as a beamstop.

Prompt gamma rays emitted by the sample pass through an adjustable collimating lead aperture and are measured by a high resolution germanium detector with a bismuth germanate Compton shield. The sample cave is shielded by lead and covered with cadmium except in front of the aperture, which is shielded by a piece of lithoflex. The detector cave rests on a moving plate, mounted on precision rails, with an adjustable detector-to-sample distance. Detector signals are processed using a digital signal analyzer.

A gold foil irradiation measured a thermal equivalent neutron flux of 6.8E9 $cm^{-2}s^{-1}$ at the sample position, nearly a factor of 8 higher than the flux for the NG7 instrument. With the detector positioned 70 cm from the sample (twice the sample-to-detector distance at NG7), measurement of prompt gamma-rays from Ti, Fe, Al, Cu, and urea indicated element sensitivities (cps/mg) nearly twice that measured at NG7.

The initial gamma-ray background was high primarily due to scattering of neutrons by air and the sample box windows. Significant reduction in gamma-ray and neutron background was accomplished by installing temporary lithoflex-lined aluminum neutron flight tubes, additional lithoflex shielding inside the sample box and around the detector, boroflex around detector Dewar, and lead shielding between the flight tubes and the detector. The improvements yielded background count rates for H, Al, Cu, Si, and Ge lower than measured at NG7. The H background equivalent to 3.2 μg of H is half that measured at NG7.

The new instrument yields greater applicability, higher neutron flux, and better signal-to-noise ratio than the NG7 instrument. Future improvements will include optimization of neutron and gamma-ray shielding and installation of permanent evacuable neutron flight tubes. The improvement in sample space will allow the mounting of larger samples, addition of automated scanning stages for compositional mapping, automatic sample changer, atmosphere/temperature controlled sample chambers for studying in situ reactions, and additional detectors for performing coincidence measurements.

NAM-V14, (Id: 129)

NEW CULTURAL HERITAGE PROJECTS AT THE HIGH-FLUX PGAA INSTRUMENT IN GARCHING

Petra Kudejova, Zsolt Revay, Krzysztof Kleszcz, Stefan Soellradl

Technische Universität München
petra.kudejova@frm2.tum.de

In the second half of 2013, three independent projects connected to cultural heritage objects emerged at the PGAA facility at FRM II: analysis of clay crucibles for provenance study, determination of chlorine content in rusted iron artefacts and minor element analysis of bronze coins with increased precision for selected elements like e.g. Pb, Zn, Fe or Sn. For all three projects, the high intensity cold neutron flux is essential: either many samples should be measured during a short period, or the low-energy gamma rays should be attenuated to get higher yield for specific high energy gamma rays. In the case of the Chlorine project, about 60 samples were measured in less than 5 days and interesting conclusions could be drawn already.

In this presentation, not only the projects will be discussed but mostly the potential of the high-flux PGAA for valuable objects, like cultural heritage artefacts or micrometeorites of less than 1 mg weight. Also, scanning of the surface of large objects will be presented as well as scanning objects by a collimated pencil beam of 2 mm × 2 mm giving insight into elemental composition of selected parts of given objects. This information can be combined with Neutron Tomography, which can be also run at the PGAA instrument. Exemplary experiments will be presented to demonstrate the diverse applications of the PGAA facility.

NAM-V15, (Id: 217)

FEATURES OF COLD NEUTRON INDUCED PROMPT GAMMA ACTIVATION ANALYSIS AT HANARO RESEARCH REACTOR

Jong Hwa Moon

Korea Atomic Energy Research Institute
jhmoon1@kaeri.re.kr

A new cold neutron prompt gamma activation analysis (CN-PGAA) system has been developed at the HANARO cold neutron source. The CN-PGAA is installed at the end position of a CG2B neutron guide. It was designed to be composed of an n-type HPGe and a BGO and will be operated in single bare, Compton suppression and pair spectrometer modes, and there is a gap for a beam chopper for a time-of-flight PGAA. The sample box is made from Teflon for He-filled or vacuum environments. The neutron beam profile and neutron flux are simulated using a McSTAS code and measured by time of flight and gold activation methods. Neutron temperature at sample position is about 40K and the true integrated neutron flux to be over 5.0×10^8 n/cm^{2}s. Its performance has been tested by using various certified reference materials

NAM-V16, (Id: 177)

NEUTRON DEPTH PROFILING WITH MULTIPIXEL DETECTORS

Jiří Vacík[a], Ivo Tomandl[a], Yesid Mora[b], Carlos Granja[b], Václav Kraus[b]

[a]Nuclear Physics Institute ASCR
[b]Institute of Experimental and Applied Physics CTU
vacik@ujf.cas.cz

Neutron Depth Profiling (NDP) is a specific non-destructive nuclear analytical technique used for determination of depth distributions of some technologically important light elements (e.g., Li and B) in the near surface of solids. The NDP for thick samples (with a thickness > several micrometers) is utilized as a 1D profiling technique that enables to obtain a 1D depth distribution (assuming the uniform lateral distribution). In this case, the measurement is performed with a standard semiconductor detector (or a combination of several detectors arranged in a telescope, etc.) with high energy resolution that, consequently, also allows to obtain high depth resolution (~ 10 nm nominal resolution can be achieved). NDP for thin samples can (advantageously) adapt sophisticated detector systems that enable to detect both reaction products (emitted into opposite directions) simultaneously. Consequently, the sandwich arrangement of the NDP spectrometer (i.e., detector-sample-detector) can dramatically reduce (or even eliminate) the unwanted background and improve the detection sensitivity. Interestingly, as detector systems, placed on both sides of the inspected samples, multipixle detectors (e.g., Timepix, Medipix) can be utilized. Here, the first results of the 3D NDP with multipixle detectors are presented. As samples, thin polymeric foils with B or Li atoms, distributed in the microstructured arrays, were utilized. The obtained data showed that the 3D NDP version proved to be an interesting tool for analysis of the 3D micro-distributions of the NDP-relevant elements in thin samples. This capability might be attractive for electronic industry (where B or Li play an important role) or neutron micro-radiography.

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NAM-V17, (Id: 355)

PHOTO- AND DIGITAL-DETECTORS FOR QUANTITATIVE DIGITAL DENSITOMETRY FOR DISTRIBUTION ANALYSIS OF ORES BY MEANS OF GAMMA-ACTIVATION

Vladimir Kolotov[a], Dmitry Grozdov[a], Nikolay Dogadkin[a], Andrey Shiryaev[b], Victor Korobkov[c]

[a]*Vernadsky Institute of Geochemistry and Analytical Chemistry*
[b]*Frumkin Institute of Physical Chemistry and Electrochemistry*
[c]*Moscow State University*
kolotov@geokhi.ru

In the recent publications (e.g. ref. [1]) it has been shown that application of computer processing of time series digital autoradiograms allows increase significantly the selectivity of local analysis that allows elements mapping for some noble elements in ores using gamma-activation. It was done by means of pixel-by-pixel processing of time series images to recover apparent half-life for each pixel of the image. During the investigations it was detected that the method of quantitative densitometry plays very important role for success of such analysis. Two principally different detectors for quantitative digital autoradiography have been considered. They are: conventional nuclear radiation photo detectors (nuclear film BioMax MR Film,Kodak) and imaging plates (PerkinElmer Inc.). The digital images from photo detectors were obtained by scanning the primary analog one. For testing of both detectors a flat uniformly distributed ^{137}Cs sources have been used.

Photo-detectors. It has been detected that independent development of film detectors under strict implementation of the recommended procedures does not result in acceptable accuracy (usual reproducibility of densitometry is not better than 10 %). Perhaps even small variations in the conditions of detectors development can strongly influence results of densitometry. If development of all detectors will be done simultaneously in the same cuvette without stirring, the solutions while development the obtaining results are quite good (the standard deviation does not exceed 2 %).

Image-plates. One of important differences of image plates from conventional photo detectors is existence of effect of degradation of the hidden image in time. It has been found that the speed of degradation of the hidden image falls down almost to zero after one day ageing the image plate.

Using the described techniques time series of autoradiograms of the copper-nickel polymetallic ore irradiated by bremsstrahlung has been obtained. After computer’s processing a set of meta images for various ranges of a half-life period has been received. The received meta images reflecting radionuclides distributions over the sample surface are in a good agreement with data of scanning electronic microscopy (SEM).

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NAM-V18, (Id: 15)

DIRECT ANALYSIS OF AMERICIUM IN NON-SEPARATED SPENT NUCLEAR FUEL USING HIGH RESOLUTION ICP-OES AND SECTOR FIELD ICP-MS

Michael Krachler, Rafael Alvarez-Sarandes, Paul Carbol, Rikard Malmbeck, Stefaan Van Winckel

European Commission, Joint Research Centre, Institute for Transuranium Elements
michael.krachler@ec.europa.eu

Complementary analysis employing instrumental techniques based on different physical detection principles is a key issue for quality assurance. Lacking matrix-matched certified reference materials, accurate, straightforward analytical procedures for the determination of americium (Am) in non-separated spent fuel employing high resolution ICP-OES and sector field ICP-MS were developed and cross-validated. Using a commercial high resolution ICP-OES spectrometer, the eleven most sensitive Am emission wavelengths were investigated in detail for potential isotopic and elemental analysis. Calibration of the instrumental response was carried out through dilution of a ^{241}Am stock solution (1 550 mg kg^{-1}) that was prepared in-house via chemical separation of the element from a concentrated Pu solution (115 g L^{-1}). Sector field ICP-MS, - and -spectrometry served to characterise extensively the employed Am and Pu solutions for their actual concentration, potential impurities and isotopic purity. Hyperfine splitting of relatively broad peaks (~10 pm) or multiplets, i.e. multiple peaks, were observed for most tested Am ICP-OES emission signals with ^{241}Am and ^{243}Am revealing identical signal patterns. The isotopic shift between ^{241}Am and ^{243}Am was generally small with a maximum difference of only ~3.7 pm found at = 450.945 nm and = 469.970 nm, respectively. As a consequence, the extraction of Am isotopic information from the emission spectra was limited. The use of a high efficiency sample introduction system helped to lower detection limits (LOD) for Am up to two orders of magnitude compared to published values. While the emission wavelength = 283.226 nm provided the lowest LOD of 0.07 mg kg-1, the ICP-OES signal at = 392.625 nm (LOD 0.71 mg kg^{-1}) was best suited for the analysis of Am in spent fuel predominantly containing U and Pu. Both external calibration and standard addition yielded comparable Am concentration results for various spent fuels employing ICP-OES. Calibration of the sector field ICP-MS response for spent fuel Am analysis was accomplished using both ^{232}Th and ^{238}U signals as well as applying the corresponding mass bias. This calibration methodology - frequently used in absence of an Am stock standard solution - was tested against the home-made ^{241}Am stock standard solution underpinning the validity of the calibration approach. One spent (Th,Pu)O2 fuel and two irradiated metallic fuels, having different chemical and isotopic compositions, were analysed for their Am content. Sector field ICP-MS analysis essentially confirmed the Am concentrations obtained using ICP-OES in the three spent fuel solutions with mean values overlapping within their standard deviations. Considering isotopes of other actinides such as U, Pu and curium (Cm), the Am isotopic abundance (^{241}Am, ^{242}Am, ^{243}Am) was established in the non-separated fuel solutions comparing reasonably well with model calculations based on the ORIGEN-2 code. The excellent comparison between ICP-OES and ICP-MS results underpins the accuracy and reliability of the developed analytical procedures and adds substantially to the quality assurance of Am analysis in spent fuel.

NAM-V19, (Id: 57)

DETERMINATION OF THE $^{143}N_D/^{144}N_D$ ISOTOPE RATIO IN VARIOUS TYPES OF URANIUM SAMPLES – A NEW POSSIBLE SIGNATURE FOR THE ORIGIN ASSESSMENT IN NUCLEAR FORENSICS

Judit Krajkó[a], Zsolt Varga[a], Ezgi Yalcintas[b], Maria wallenius[a], Klaus Mayer[a]

[a]*JRC - Institute for Transuranium Elements*
[b]*Forschungszentrum Karlsruhe, Institute for Nuclear Waste Disposal (INE)*
judit.krajko@ec.europa.eu

The ^{143}Nd/^{144}Nd isotope ratio varies (0.510-0.513) in nature due to the ^{147}Sm /^{143}Nd decay. Its value depends on the type of the minerals present and therefore it is widely used in geology for chronometry and provenance measurements with the ε notation. The measurement of ^{143}Nd/^{144}Nd isotope ratio in uranium samples is analytically challenging as the distribution of Nd concentration through the front end of fuel cycle is drastically decreased during the milling and production process.

This work presents a novel method developed for trace-level analysis of ^{143}Nd/^{144}Nd isotope ratio in various uranium-bearing materials, such as uranium ore concentrates (UOC) and uranium oxides (UO_3, UO_2) by inductively coupled plasma mass spectrometry. The aim of the study was to find a possible correlation between the Nd isotopic variations and the geological origin of the investigated U products.

The developed method involves a pre-concentration of Nd using Fe(III) carrier, followed by extraction chromatography to separate the Ln group and a sequential separation of Nd, Sm, and HREE. The distribution of U, Th, and Ln was measured by gamma spectrometry and inductively coupled plasma mass spectrometry (SF-ICP-MS) during the separation process. The isotope ratio measurements were performed by multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS).

The method was validated using Morille reference material. The limits of detection are in the low pg/g range and the achievable cumulative U decontamination factor is in the magnitude of 10^7 - 10^8. The applicability of the method was demonstrated by the determination of ^{143}Nd/^{144}Nd isotope ratio in UOCs, and in high purity uranium samples originated from different uranium milling and refining facilities. For the validation of isotopic measurements La Jolla, JB2 and BCR-2 geological reference materials were applied. The obtained results show that the Nd isotopic ratio is highly variable depending on the mineral type. For instance, isotope ratio measurement of Mary Kathleen UOC shows that the sample has a low ^{143}Nd/^{144}Nd ratio 0.510682(52), which is in good agreement with the value reported earlier by Maas R. et al. By combining the Nd isotopic information with REE pattern in uranium samples, the uranium deposit type, and therefore the origin of an unknown nuclear material can be assessed with higher reliability.

NAM-V20, (Id: 289)

DETERMINATION OF ^{93}Zr, ^{237}Np AND ^{135}Cs IN RADIOACTIVE WASTE BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

Nora Vajda[a], Szabolcs Osvath[b], Peter Nagy[c], Eva Kovacs-Szeles[c], Kornel Fel[c], Zsuzsa Molnar[a], Edit Bokori[a]

[a]RadAnal Ltd.
[b]National Research Institute for Radiobiology and Radiohygiene
[c]Centre for Energy Research, Hungarian Academy of Sciences
vajdanor@gmail.com

The safety and the behavior of radioactive wastes on a 1000000 year time scale are basically dependent on the radionuclide composition. During such a long time period leakage from the waste packages and the depository into the environment cannot be excluded and radionuclide migrations have to be considered. Therefore it is important to know the exact composition of the various waste forms including the knowledge of the extremely long-lived radionuclides even if they occur at micro or trace quantities. ^{93}Zr, ^{237}Np and ^{135}Cs belong to these exotic nuclides that have half-lives of 1.53×10^6 y, 2.14×10^6 y, 2.3×10^6 y, respectively and that are formed in nuclear fission and activation in nuclear reactors. These nuclides can be detected only after pre-concentration and removal of the sample matrix. They do not emit easy to measure gamma radiation and generally nuclear methods do not offer sufficient sensitivity to measure μBq - mBq activities. These nuclides are preferentially detected by high sensitivity mass spectrometric techniques.

Radiochemical methods have been developed for the separation of Zr, Np and Cs based on extraction chromatography using UTEVA resin* for Zr and Np and AMP resin* for Cs separation. Radioactive tracers were used for chemical recovery determination. Radionuclides were detected by inductively coupled plasma mass spectrometry (ICP-MS). Since isotopic standards are not available for ^{93}Zr and ^{135}Cs determination sensitivity factors were determined by non-isotopic tracers. Three different techniques were used for method validation, i) determination of an isotopic standard solution (^{237}Np), ii) isotope dilution mass spectrometry using enriched ^{96}Zr stable isotope standard solution (^{93}Zr), and iii) measurement by an independent analytical technique, i.e. NAA (^{135}Cs).

Radiochemical procedures, measurement and calibration techniques, as well as results of analysis of ^{93}Zr, ^{237}Np and ^{135}Cs in evaporation concentrates originating from a nuclear power plant will be presented. * registered trade name of the products of Triskem International Co.

NAM-V21, (Id: 96)

ACTIVITY MEASUREMENTS OF BARRELS FILLED WITH RADIOACTIVE WASTE

Matjaž Korun, Branko Vodenik, Benjamin Zorko

Jožef Stefan Institute, Ljubljana, Slovenia
matjaz.korun@ijs.si

In barrels with radioactive waste radioactivity may be inhomogeneously distributed. Since the inhomogeneity may be unknown, when measuring the activity of the barrel it is advantageous to use the radiation emitted from it. Consequently, robust methods, capable of yielding the results that are independent on the distribution of the radioactivity within the barrel, must be used.

Gamma-rays emitted from the barrel attenuate in the material within the barrel before escaping from it. Since attenuation coefficients are decreasing functions of energy for multi-gamma-ray emitters it is possible to deduce the amount of material penetrated by measuring their attenuation as a function of energy. This is done with gamma-ray spectrometry by measuring the apparent activity $A_{(E)} = N_{(E)}/T/\varepsilon_{0(E)}/P_{(E)}$, where $N_{(E)}$ denotes the number of counts in the peak at the energy E, T the counting time, ε0 the efficiency of the spectrometer and P the probability for emitting the gamma-ray in a nuclear decay. If for $\varepsilon_{0(E)}$ the efficiency of a non-attenuating source is used, the energy dependence of the detector's response to gamma-rays is taken into account to a large degree. It follows then that e.g. for a source placed on the surface of the barrel the apparent activity is independent on energy. It should be observed that the apparent activity is undetermined to a scaling factor since ε0 is rather arbitrary. The apparent activity is proportional to the flux of gamma-rays through the detector. It is proportional to the flux density, because it is normalized to the efficiency, which measures the volume or the cross section of the sensitive volume of the detector. Also, it is proportional to the activity since it is normalized to the rate of the decaying nuclei.

It is easy to see that a source, homogeneously distributed within the barrel, causes an apparent activity increasing slowly with energy already at low energies. On the other hand, the apparent activity for a point source located inside the barrel at a distance from its surface tends to zero at low energies since here the attenuation of gamma-rays is large. At high energies, the apparent activity of a source embedded into the material within the barrel increases fast with energy. It follows then that from the energy dependence it is possible to extract three apparent activities: one corresponding to the surface contamination, the second corresponding to the contamination homogeneously distributed within the barrel and the third to a point source within the barrel located at a distance from its surface. Since the apparent activity is decomposed into three fractions, so are the count rates. Using the efficiencies, calculated by e.g. ISOCS software, corresponding to the three sources it is possible to arrive at the three activities. The total activity of the drum is the sum of the three activities and its uncertainty is determined from the uncertainties of three activities taking into account the correlations.

With this method four unknowns are necessary to determine: the three activities and the location of the point source. Therefore only gamma-ray emitters radiating at at least four energies in a large energy interval can be measured. The robustness of the method is demonstrated on test data for the radionuclides belonging to the thorium decay chain. It is shown that at count rate uncertainties of 2 % the uncertainty of the total activity is less than 100 % for the worst case which is represented by two point sources, one weak at the surface of the barrel and a strong one located deep within it.

The method described above will be developed and validated as one of the contributions to the EMRP project MetroNORM. The aim of the project is to develop novel instrumentation and methods for accurate, traceable and standardized measurements of NORM material. This method will make it possible to considerably improve the ability to determine total activity of inhomogeneously distributed NORM waste in drums.

NAM-V22, (Id: 310)

COMPUTATION OF FULL ENERGY PEAK EFFICIENCY FOR VOLUMINOUS RADIOACTIVE ATMOSPHERIC SOURCES USING REMOTE SCINTILLATION GAMMA-RAY SPECTROMETRY

Dmitriy Grozdov, Vladimir Kolotov, Yury Lavruhin, Nikolai Dogadkin

Institute of Geochemistry and Analytical Chemistry of the Russian Academy of Sciences
dsgrozdov@rambler.ru

A method for computation of full energy peak registration efficiency for voluminous atmospheric gamma radiation sources (emission of nuclear power plant) using collimated scintillation detector has been developed. The method is based on preliminary experiments on calibration of detector response as a function of distance and angle relatively detector axis with further mathematical extension of the obtained calibration for significantly larger distances.

In the experimental part a quite intensive source of ^{226}Ra has been used. This radionuclide is suitable for calibration purposes because it escapes gamma-rays lying in a wide energy range. The measurements were carried out at the distance of 3-5 meters from detector and 0-90˚ angular range from detector axis. The obtained discrete results has been mathematically processed that results in obtaining of a set of smooth dependences describing the efficiency values as function of distance and angle. The obtained set of dependences has been extended beyond the experimental region and used for efficiency computation for arbitrary points lying in the aperture scope of the collimator used.

The formulated task is needed for resolving more general problem concerning continuous control of radioactivity which releases in atmosphere by nuclear power plants (NPP). At small distances from NPP radioactive emission is a gas stream which may be mathematically described by normal distribution whose parameters depends on the atmosphere state. Computation of full energy peak efficiency for voluminous figure of gas stream escaping from ventilation pipe of NPP lying in the detector’s aperture is carried out by means of Monte-Carlo modelling. The developed model takes into account the radiation absorption in the air depending on the weather conditions (temperature, atmospheric pressure, humidity). The model of the emitted radioactive stream implies different options of radioactivity distributions inside the stream: uniform, triangular and normal one.

The height of the radioactive stream axis over the ground is one of the key parameters controlling the results accuracy. To determine the stream height the following steps are used. At the first step the height in question equated to height of the ventilation pipe. At the second step the minimization of residuals of isotope identification procedure is used as a criterion for computing the actual height value of the stream.

NAM-V23, (Id: 20)

SEQUENTIAL SEPARATION OF TRACE Pu, U AND OTHER ELEMENTS IN ENVIRONMENTAL SAMPLES

Yutaka Miyamoto, Kenichiro Yasuda, Masaaki Magara

[a]*Japan Atomic Energy Agency (JAEA)*
miyamoto.yutaka@jaea.go.jp

Abundance and isotopic ratios of trace uranium (U), thorium (Th), lead (Pb) and lanthanides in environmental samples play a key role to investigate features of the samples. Plutonium (Pu) is an artificial element which originates from nuclear bomb tests and accidental releases from nuclear power plants. The analytical data may give information on origin of the sample, dating of mineral formation, history on mineralization, and age determination of nuclear materials. Abundance and isotopic ratios of an element of interest are generally measured with high resolution inductively-coupled plasma mass spectrometers (HR ICP-MS). In most environmental samples such as rocks, soils, and airborne dusts, trace Pu, U, Th, Pb, and lanthanides are contained with major elements including Na, K and Fe. These major elements and the polyatomic ions including oxides and hydrides of the co-existing elements affect accuracy of analytical results measured by ICP-MS. The analytes, therefore, should be separated from the interfering elements. Chemical separations are good solution for accurate analyses, but the procedures are generally complicated and time-consuming. The authors developed the technique for sequential separation of Pu, U, Th, Pb, and the lanthanides using a single anion-exchange column and mixed media consisting of hydrochloric acid, nitric acid, acetic acid, and hydrofluoric acid. The target elements were completely separated and fully recovered by using our sequential separation technique.

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NAM-V24, (Id: 95)

DEVELOPMENT OF THREE METHODS FOR DETERMINATION OF URANIUM ISOTOPES IN ENVIRONMENTAL SAMPLES BY LIQUID-LIQUID EXTRACTION WITH TRI-ISOOCTYLAMINE OR SOLID-PHASE EXTRACTION BY ANION-EXCHANGE RESIN

Lyubomir Popov

KOZLODUY NPP, Bulgaria
popov_la@yahoo.com

The methods are based on total decomposition of the solid materials by the use of closed vessels microwave acid digestion systems and preconcentration of uranium from the liquid samples by iron hydroxide co-precipitation (after heating in case of underground or carbonated waters). The separation of uranium from interfering radionuclides (thorium, polonium, etc.) and stable matrix elements (iron, calcium, etc.) is attained by liquid-liquid or solid-phase extraction with 10 %-triisooctylamine in xylene or anion-exchange resin (AG 1x4, 100-200 mesh, BioRad) in hydrochloric and sulfuric acid media. The possible interferences from other natural (polonium, thorium, radium, etc.) and man-made (plutonium, neptunium, etc.) radionuclides were studied and successfully eliminated by different approaches. Purified uranium is electrodeposited on a stainless steel disks and then measured by alpha spectrometry. Typical energy resolution of the measured disks is 20-25 keV. The chemical yields of uranium are in the range 80-99 %. The critical steps in the methods were examined in detail. The methods allow determination of uranium isotopes in macro amounts of iron (relatively large sample volumes). The analytical methods had been successfully applied to the determination of uranium isotopes in surface, mineral and tap waters, as well as in bottom sediments (the rivers – Danube, Ogosta and Tzibriza) and soils from Northwestern Bulgaria. The analytical quality of the results was checked by analyzing reference materials with different matrices.

References:
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[2] Popov L (2012) Appl Radiat Isot 70:2370-2376.

NAM-V25, (Id: 391)

ACCELERATOR MASS SPECTROMETRY OF URANIUM: TITANIUM DIOXIDE MATRIX AND HOMOGENEOUS PRECIPITATION

Irena Špendlíková[a], Gönül Keçeli[b], Jakub Raindl[a], Mojmír Němec[a], Peter Steier[c]

[a]*Department of Nuclear Chemistry, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University, 115 19 Prague, Czech Republic*
[b]*Department of Chemistry, Faculty of Engineering, University of Istanbul, 34320 Istanbul, Turkey*
[c]*VERA Laboratory, Faculty of Physics, Universität Wien, 1090 Vienna, Austria*
spendlikovairena@gmail.com

In the environmental studies the determination of low concentrations has always been a key issue and therefore, the concentration step is usually a crucial part of the sample processing. For the extraction of uranium, sorption materials based on titanium dioxides have been proposed and studied for years with promising results. Implementing titanium dioxide materials as a sorption material and as a target matrix into classic methods of sample preparations for ? ^{236}U/^{238}U measurements using Accelerator Mass Spectrometry (AMS) would mean a significant reduction of separation steps in procedures and big simplification of the whole method. This research focused on the uranium separation by homogenous precipitation using tetra-n-butylorthotitanate as a precursor of titanium dioxide and on the potential of titanium dioxide as the AMS target matrix. In order to optimize this method, the experiments with different uranium concentration and amount of TBOT were performed. Last experiments were dedicated for AMS measurements to observe the behaviour of TiO_2 based matrix in ^{236}U/^{238}U measurements using in-house standard Vienna-KkU with ^{236}U/^{238}U isotopic ratio of (6.1±0.4)x10-11. The isotopic ratio of ^{236}U/^{238}U in the sample containing uranium from in-house standard and titanium dioxide was calculated as $(6.16\pm0.04)\times10^{-11}$ which is in very good agreement with the value of the standard. This means that the titanium dioxide based matrix does not influence the measurement of ^{236}U/^{238}U isotopic ratio and is suitable for AMS targets. In addition, it was proved that tetra-n-butylorthotitanate contains no anthropogenic ^{236}U and therefore, can be used in the preparation methods of AMS targets from environmental samples.

NAM-V26, (Id: 238)

LASER ABLATION OF ACTINIDE OXIDES

Keri Campbell, Ken Czerwinski

University of Nevada Las Vegas
campb262@unlv.nevada.edu

The ability to examine elemental and isotopic ratios of fuels, waste forms, and other solids by direct analysis using laser ablation techniques can greatly reduce analysis costs and time. This is particularly true for actinide elements, as they contain useful information of the fuel cycle and nuclear forensics. Current methods to evaluate the composition of used fuel include a lengthy process of digestion and separations [1]. These are often coupled with multiple analytical techniques and complex sample preparations to determine the elemental and isotopic composition. Furthermore all spatial information is lost during the digestion process, eliminating potentially useful data for detailed analysis. The goal of this work is to develop and optimize laser ablation inductively coupled mass spectrometry (LA-ICP-MS) and Laser Induced Breakdown Spectroscopy (LIBS) techniques for the analysis of and fuel, used fuel and waste forms. The materials synthesized for analysis consist of uranium, zirconium and lanthanides composition modeling the main oxide phase in used nuclear fuel [2]. In order to understand the behavior of the selected metal oxides in the LA-ICP-MS system materials will be prepared with concentrations of 0-100 %. The main focus will be the examination of synthesized actinide oxide samples as well as uranium alloys. The project is composed of two tasks that will be discussed. The first task is to prepare and characterize actinide matrices and standards. The second task will be to develop methods for the analysis of actinide materials using LA-ICP-MS and LIBS evaluating each technique for: limit of detection, accuracy, and precision. Optimization of hardware and conditions to overcome technical issues of the systems will be discussed.

NAM-V27, (Id: 124)

OPTIMISATION OF A LIQUID SCINTILLATION COUNTER FOR LOW-LEVEL MEASUREMENT OF LEAD-210

Peter Medley, Andreas Bollhoefer

Department of the Environment, Australia
peter.medley@environment.gov.au

Lead-210 is a natural radioactive isotope that is commonly used in erosion and sedimentation studies. It may also bioaccumulate through the foodchain, which has implications for human ingestion dose assessment and assessment of radiation doses to biota. While analysis via gamma spectrometry is the method of choice for most sediments and soils, the ability to measure low levels of lead-210 is important for many environmental applications, particularly where analyses are required in media such as surface waters or biota tissues. Liquid scintillation counting (LSC) is a popular method for analysis as it enables direct and quick measurement of the beta particle emission of lead-210. This has an advantage over low-level methods that require long waiting times for analysis via the alpha emitting radioactive decay product, polonium-210.

Unfortunately, it is often impossible to reproduce published radioanalytical methods, including those for analysis of lead-210, without contacting the authors, due to information gaps or a lack of detail essential for method development. In particular, the steps required for method optimisation in a new environment can be difficult to extract from a publication and then reproduce, particularly for small laboratories. In this presentation, the process of optimising the analysis of lead-210 via LSC on a PerkinElmer TriCarb instrument is comprehensively detailed, with an emphasis on making this process accessible and reproducible in other laboratories around the globe.

NAM-V28, (Id: 383)

BIOGEOCHEMICAL ASPECTS OF MINERAL CONTENT IN YERBA MATE FROM PARAGUAY

Juan F. Facetti-Masulli[a], **Alicia Dávalos de Sánchez**[a], **Peter Kump**[b]

[a]*Hydroconsult & Comisión de Energía Atómica*
[b]*Josef Stefan Institute-39 Jamova Ljubjana-Slovenia*
jfrafama@rieder.net.py

Yerba mate, Ilex Paraguayensis, is a plant of paraguayan origin used in infusions by the ancient inhabitants of Paraguay as a “reviver”/energy beverage which consumption is lasting up today; furthermore, it is extended almost worldwide. In regard to its mineral content very few studies are known; moreover, none has been published related to the occurrence of REE (rare earth) and other refractory elements in the leaves. In this work, minor and trace elements composition have been investigated by XRF techniques to determine their correlation as well as provenance. The analysis of complex spectra was performed by the AXIL software and the quantitative analysis by the QAES software. Analyzed trace elements were the refractory Rb , Sr, Y, Zr, Nb, Ba, La, Ce, Nd , Y, 3d as Ti,Cr,Ni,Cu, Zn. Minor elements were Mn, Fe which are often related to the above refractory together with S, K, Ca, Br, I, Cs.

NAM-V29, (Id: 311)

EPITHERMAL NEUTRON ACTIVATION ANALYSIS OF FORAGES FROM PERMANENT GRASSLANDS OF NORTH-EASTERN ROMANIA

Otilia Ana Culicov[a], Doina Tarcau[b], Simona Maria Cucu-Man[c], Inga Zinicovscaia[d], Vasile Vintu[b], Costel Samuil[b], Marina Frontasyeva[e]

[a]*Joint Institute for Nuclear Research & National R&D Institute for Electrical Engineering ICPE-CA*
[b]*University of Agricultural Science and Veterinary Medicine of Iasi*
[c]*Department of Chemistry, Faculty of Chemistry "Al.I.Cuza" University of Iasi*
[d]*Joint Institute for Nuclear Research & Institute of Chemistry of the Academy of Science of Moldova*
[e]*Joint Institute for Nuclear Research*
culicov@nf.jinr.ru

The health and performance of grazing ruminants are dependent on the availability of essential mineral elements from pastures but the pastures often fail to supply all needed mineral elements in the quantity adequate for livestock grazing. Species-rich grasslands with Nardus stricta are one of the important environments for animal production not only in Romania but also in other European regions, too. Various studies regarding the biodiversity and the influence of fertilizers on the biodiversity value of the mountain grasslands in the Romanian Carpathians were performed. Nevertheless, a lack of information regarding the natural input of essential macro and trace elements needed in the special metabolic activities exists.

The aim of this study was to characterize the quality of permanent grasslands in a potential area of ecological agricultural production from Dorna area (North-Eastern Romania) by evaluating the content of essential and potential pollutant elements in order to optimize nutritional requirements of ruminants. This investigation is a part of a larger project on the assessment of the influence of organic fertilization on the total polyphenols and tannins content in forages obtained from four natural permanent pastures with predominant Nardus stricta and Festuca rubra L. vegetation. 83 plant samples were dried at room temperature and ground to obtain a homogeneous matrix.

A total of 29 elements were determined by epithermal instrumental neutron activation analysis at the IBR-2 reactor of FLNP JINR: Na, Mg, Al, Cl, K, Ca, Sc, V, Cr, Mn, Ni, Fe, Co, Zn, Se, As, Br, Sr, Rb, Mo, Sb, Ba, Cs, La, Sm, Hf, Ta, Th, and U. The study of the elemental content was financially supported by a grant from the Plenipotentiary of Romania to JINR 81/18.02.2013-56.

Nuclear Analytical Methods (NAM)

Posters

NAM-P01, (Id: 24)

NEUTRON ACTIVATION ANALYSIS OF CHILDREN'S HAIR FROM ALTAI REPUBLIC

Zoya Goryainova

Joint Institute for Nuclear Research
zoyag@yandex.ru

The study focuses on the chemical composition of human hair as an indicator of the level of income of the chemical elements in the human body and its impact on growth and development of children and teenages in the local geochemical conditions. Neutron activation analysis (NAA) was used to analyze 186 samples of hair of children from four villages of Altai Republic. Data for 54 boys and 132 girls in the age of 7 to 17 were analyzed. Significantly higher content of sodium, aluminum and chlorine was observed in the hair of boys over girls. The following short-lived isotopes were determined: Na, Mg, Al, S, Cl, K, Ca, V, Mn, Cu and I. Concentrations of magnesium and calcium were significantly higher in the hair of girls. Iodine, copper, manganese and sulfur concentrations in the hair of boys and girls are close to each other, the differences between the sexes are not significant. Median concentrations of the studied elements in the hair of boys and girls were, respectively: Na – 75 & 50; Mg – 49 & 62; Al – 21 & 13; S – 41150 & 39850; Cl – 1020 & 390; Ca – 608 & 973; Mn –1,1 & 0,82; Cu – 9; I – 0,2 mg/g. It was shown that the high content of calcium and magnesium is observed in the hair of children living in rural areas with high hardness and salinity of drinking water. Iodine concentrations in the hair of studied cohort of children is low, especially in puberty.

NAM-P02, (Id: 27)

SIMPLIFIED DETERMINATION OF URANIUM IN CONTAMINATED SEA SAND SAMPLES BY ALPHA-SPECTROSCOPY AFTER ACIDIC DESORPTION AND LIQUID-LIQUID EXTRACTION

Maria Efstathiou, Ioannis Pashalidis

Chemistry Department, University of Cyprus
efstathiou.p.maria@ucy.ac.cy

In order to develop of a simplified method for the determination of uranium in contaminated sea sand samples by alpha-spectroscopy, we have investigated the applicability of different pre-analytical procedures (e.g. electrodeposition after acidic dissolution using HNO_3 solutions of varying concentration (0.1, 1 M, 2 M and 8 M) andelectrodeposition after acidic dissolution (0.1, 1 M, 2 M and 8 M HNO_3) and liquid-liquid extraction using 30 % tri-butylphosphate in dodecane. According to the experimental data direct electrodeposition after acidic dissolution of uranium from sea sand particles can be successfully applied only to silica sand. On the other hand, analysis of uranium in sand samples containing increased amounts of limestone and iron minerals requires liquid-liquid extraction step to specifically separate uranium from iron and calcium, because the latter form a film on the electrodeposition disc reducing significantly the counting efficiency. Generally, the maximum efficiency of the studied pre-analytical methods is above 70 % and the detection limits of the alpha-spectroscopy about 7 $mBq{\cdot}l^{-1}$, suggesting that the methods studied could be successfully applied as a screening method for the radiometric analysis of uranium contaminated sea sands.

NAM-P03, (Id: 30)

ANALYSIS OF URANIUM AND PLUTONIUM USING ACTINIDE RESIN

Andy King

AWE plc
andy.king@awe.co.uk

Andrew King, Darrell Knight and Andrew Fairhead AWE plc, Aldermaston, Reading, Berkshire, RG7 4PR, United Kingdom A method has recently been developed at AWE for the successful pre-concentration, recovery, separation and measurement of actinides using Eichrom’s Actinide Resin. The method was specifically developed to enable successful isotopic analysis of uranium and plutonium at trace environmental levels using Thermal Ionisation Mass Spectrometry (TIMS). This talk summarises the developed method, associated mass spectrometry results and the challenges which were overcome in recovering and purifying uranium and plutonium. Actinide Resin is known to be very good at selectively pre-concentrating actinides from slightly acidic and neutral solutions making this method attractive for measuring uranium and plutonium isotopic ratios in environmental samples. © British Crown Owned Copyright 2013 /AWE

NAM-P04, (Id: 42)

DETERMINATION OF U,PU, AM /CM ISOTOPES IN ASH RESULTED FROM THE INCINERATION OF NPP CERNAVODA LOW LEVEL WASTE

Gabriela Teodorov[a], Adina Sandru[a], Laszlo Toro[a], Adrian Stafie[b], Dorin Dumitrescu[b]

[a]MATE-FIN srl
[b]NPP Cernavoda
gabriela.teodorov@matefin.com

For the waste management characterization of radionuclides inventory is required. This work presents the method and the results for determination of U, Pu and Am/Cm isotopes in the ash resulted from the incineration of NPP Cernavoda, (Romania) low level activity waste, in order to have accurate information regarding the alpha emitting radionuclide content and a proper classification (LLW, ILW)of the waste.

The sample is traced with U-232, Pu-242 and Am-243, then is decomposed in an open microwave digestion system by a mixture of a strong acids and peroxide. Hydrofluoric acid is used for destruction of silicates. Hydrofluoric acid is eliminated by addition of nitric acid several times. The residue is dissolved in nitric acid and aluminum nitrate solution. Uranium, Plutonium and Americium/Cm isotopes are separated from each other and from other radionuclides and matrix constituents by extraction chromatography . Two columns with UTEVA and TRUE Eichrome resine were used for separation .The sample solution is passed first through UTEVA resin that retains U isotopes, then loading and rinsing effluents are passed through TRU resin that retains Pu and Am/Cm isotopes. A redox adjustment of Pu was done before passing through UTEVA column using Fe(II) and NH_2OH . HCl , and also into the TRU column using $NaNO_2$. Ascorbic acid was used to reduce Fe(III) to Fe (II) in order to prevent the uptake of Fe (III). Uranium was eluted from UTEVA with diluted hydrocloric acid, americium is eluted from TRU with hydrocloric acid and plutonium is eluted from TRU with amonium bioxalat. The sample preparation for alpha spectrometry was done by cerium carrier co-precipitation. Alpha spectrometry of measurements were performed by Ortec Alpha Spectrometer System. average tracer recovery was about 50,6 % for Uranium, 43,7 % for Plutonium and 54,1 % for Americium

NAM-P05, (Id: 45)

RAPID DETERMINATION OF GROSS ALPHA AND BETA ACTIVITY IN SEAFOOD UTILIZING MICROWAVE DIGESTION AND LIQUID SCINTILLATION

Daniel Sas, Jiří Janda, Alena Tokárová

University of defense
daniel.sas@post.cz

This paper describes a method for rapid determination of gross alpha and beta activity in seafood using microwave digestion system for fast sample decomposition and liquid scintillation as a powerful tool for measuring gross alpha and beta activity. The general group seafood was divided into two groups on the basis of the structure, whether it has shell or not. The selected group of radionuclides was chosen with respect to military significance, radiotoxicity, and possibility of potential misuse. ^{90}Sr and ^{239}Pu were selected as model radionuclides. The decomposition of samples was realized by MWS 4 Speedwave (Berghof, Germany) with the method determined to be simple, safe and very effective as evidenced by high chemical yield. The evaluation of this method was conducted by automatic TDCR Liquid Scintilation Counter Hidex 300 SL (Hidex, Finland).

NAM-P06, (Id: 48)

A SIMPLE DETERMINATION OF 41CA BY ICPMS IN CONCRETE SAMPLES AS A TOOL FOR THE DECOMMISSIONING OF NUCLEAR FACILITIES

Maria Letizia Cozzella[a], Mauro Capone[a], Simon Jerome[b], Maria Garcia Miranda[b], Daniel Zapata Garcia[c], Herbert Wershofen[c], Mai Sobrino-Petrirena[b]

[a]*ENEA*
[b]*National Physical Laboratory.UK*
[c]*PTB-Physikalisch-Technische Bundesanstalt*
letizia.cozzella@enea.it ENEA

In October 2011 the European Joint research Project MetroRWM – Metrology for Radioactive Waste Management of the European Metrology Research and Program (EMRP) began, with a total duration of three years. One of the objectives of this project is to develop new measurement methodologies for the assessment of radioactive waste, focusing its attention on waste packages containing solid low and intermediate level radioactive waste consigned to near-surface or geological repository.

In the decommissioning of shielding concrete from nuclear facilities, the radionuclides of interest include ^{41}Ca, ^{55}Fe, ^{60}Co, ^{63}Ni, ^{133}Ba and transuranics. Calcium-41 is of particular interest, due to its ubiquity in reactor bioshields, its bone-seeking chemistry and its radiotoxicity if ingested. Among these radionuclides gamma emitters can be easily determined using gamma-spectrometry. However for the determination of beta and alpha emitters, such as ^{41}Ca, the radionuclides need to be separated individually from matrix and other radionuclides before being measured. Calcium-41 is a long-lived radionuclide produced by neutron activation in the concrete shield around the reactor, ^{40}Ca (n,γ) ^{41}Ca and displays high mobility in the environment and as well bone-seeking bioavailability. Calcium-41 decays to the ground state of 41 K by pure electron capture, emitting X-rays and Auger electrons of very low energy (0.3-3.6 keV). Measurement by X-ray spectrometry is challenging due to the relatively low detection efficiencies encountered in this technique, the low abundance of X-rays from ^{41}Ca (11.4 % for 3.31 keV X-ray) and the possibility of severe interferences produced by other beta-gamma radionuclides with similar energy. It can be measured by liquid scintillation but the procedure is time-consuming because all other radionuclides have to be removed due to the poor energy resolution of beta spectra and the low energy of its X-rays and Auger electrons.

Mass spectrometry techniques such as accelerator spectrometry (AMS) and resonance ionization mass spectrometry (RIMS) have also been used for the ^{41}Ca determination but both of these techniques are expensive and not easily available for the routine analysis. The aim of this paper is to describe a rapid and reliable method for the determination of ^{41}Ca in concrete samples by ICPMS, overcoming the complex and time consuming chemical separation of ^{41}Ca from the matrix.

Samples are firstly ground and fused with $LiBO_2$ and $Li_2B_4O_7$ (in the presence of ~0.5 % LiBr) and then dissolved in dilute acid. Then silicates are removed by means of PEG-precipitation. The acid solution can be analyzed directly, using the reaction cell mode, in order to avoid the polyatomic and isobaric interferences. Preliminary recovery tests using solutions of known concentrations of K and Ca were performed. The average recovery is 101.3 % with a relative standard deviation of 3.2 % showing the method has good reproducibility

NAM-P07, (Id: 63)

IMPLEMENTATION OF CALCULATION CODES FOR CORRECTIONS OF SYSTEMATIC EFFECTS IN MEASUREMENT LABORATORIES

Sofia Jonsson[a], **Henrik Ramebäck**[b], **Tim Vidmar**[c]

[a]*Swedish Defence Research Agency, FOI, division of CBRN Defence and Security, SE-901 82 Umeå, Sweden*
[b]*Chalmers University of Technology, Department of Chemical and Biological Engineering, Nuclear Chemistry, SE-412 96 Göteborg, Sweden*
[c]*SCK-CEN, Belgian Nuclear Research Centre, Boeretang 200, ^{240}0 Mol, Belgium*
sofia.jonsson@foi.se

A vast number of papers are reporting on the development of calculation codes for corrections of systematic effects in gamma spectrometry. Many comparison studies have also been performed where differences and similarities between many of those calculation codes are presented. However, most studies performed in this area are performed for the experienced user or program developers. Despite the high quality of those papers and the important information about the calculations codes, when selecting, implementing and using these codes at different laboratories regular users are often struggling with other issues. This study aimed at considering a user perspective for correction of common systematic effects within gamma spectrometry that measuring laboratories are facing in their daily work.

A coincidence free calibration was established for a volume source at an endcap position by characterising the detector geometry using the calculation code VGSL (Virtual Gamma Spectrometry Laboratory). Furthermore, four different calculation codes (ANGLE, EFFTRAN, GESPECOR and VGSL) were compared by calculating corrections factors for true coincidence summing (TCS), fill degree in the sources and new source-detector geometries. Two of the calculation codes are simulation codes and two are semi-empirical codes. The detector model was optimized with VGSL and thereafter the same model was used in the other softwares.

There are differences in how the correction factors are calculated in the calculation codes, by Monte Carlo simulation or efficiency transfer. Also the degree of details of the detector and source parameters that can be entered varies between the codes. Within the scope of the investigations in this study this has not shown any effects on the results. Furthermore, despite the fact that the detector model only was optimized with one of the calculation codes no clear differences could be observed as a result from this.

The uncertainty of the TCS corrected activities were found to be in the same magnitude as the certified activities in the reference solution itself. When activities were corrected for different filling degrees in the sample sources the deviations from the certified reference solution were generally lower than 5 %. Larger deviations were observed, around 10 % or less, when activities were corrected for new source-detector geometries. Discrepancies between 5 and 10 % are often considered to be acceptable for some applications, i.e. environmental or survey monitoring. This is an important knowledge for cases when it can be motivated to calculate corrections for other source-detector geometries. However, measurements should preferably be performed in source-detector geometries closely resembling the calibration geometry since those corrected activities are associated with lower uncertainties.

The user should carefully select the proper calculation code that will cover the need of the measurements that will be performed, i.e. if TCS corrections are needed and what detectors and sources will be used. When implementing the calculation code at the measuring laboratory it is of greatest importance to validate the calculations and thereby identify within what boundaries the corrections are valid. It can be concluded that all the investigated calculation codes in this study are robust and will give reliable measurement results.

NAM-P08, (Id: 76)

SEQUENTIAL DETERMINATION OF ^{90}Sr, ^{239}Pu AND ^{241}Am IN URINE

Ján Bilohuščin, Silvia Dulanská, Ľubomír Mátel, Veronika Drábová, Veronika Gardoňová

Department of Nuclear Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Slovakia 842 15
bilohuscin@fns.uniba.sk

Urine analyses can be used to assess the performance of the radiation protection control practices. The separation methods used for estimation of radionuclides in urine are often time consuming and of lower sensitivity. The determination of low levels of actinides and strontium in biological samples require lengthy and tedious chemical processes, which include pre-concentration of samples, radiochemical separation, and source preparation. The determination of radionuclides in samples of urine thus requires fast approach due to radiotoxicological nature of Am, Pu and Sr to human body. In recent years, many studies have applied extraction chromatography to radionuclide isolation from urine samples. In our work, molecular recognition sorbents AnaLig®Sr-01 and AnaLig®Pu-02 from IBC Advanced Technologies, and Eichrom´s DGA® resin were used to effectively and selectively pre-concentrate, separate and determine strontium, plutonium and americium in urine samples. Method employs four-columns separation consisting of four different commercial products. First is Eichrom's Pre-filter Material, that removes organic compounds present in urine, which interfere with separation and decrease specific radionuclide sorbtion efficiency. This step improves reduction of carry over between columns in tandem and simplyfies whole separation method that is absent of difficult sample pretreatment steps for coloured material elimination used in other works. After passing through the Pre-filter Material column, urine samples are sequentialy loaded onto second and third column, containing one of the AnaLig® series sorbent, that contain specific crown-ethers, and on fourth, stacked with DGA® resin (branched) in which the extractant system is N,N,N',N'-tetrakis-2-ethylhexyldiglycolamide. Before analysis, samples of urine are acidified with concentrated nitric acid to acquire final concentration of 2 M. Volumes of urine samples varied from 50 ml to 200 ml. Depending on volume, various amounts of $NaNO_2$ were added to secure oxidation of Pu^{3+} to Pu^{4+} form, obtaining three different oxidation states for each used radionuclide, in our case Sr^{2+}, Am^{3+} and Pu^{4+}. These are selectively captured on specific column, providing easy way for separative determination of harmful radionuclides in one sample at once. Radionuclides in columns were eluted with certain volumes of 0.05 M Na4EDTA for AnaLig®Sr-01, 9M HCl with $TiCl_3$ for AnaLig®Pu-02 and with 0,1M HCl for DGA® resin. Strontium samples were counted repeatedly by Cerenkov counting over a 2 week period to monitor the ingrowth of ^{90}Y on TRI CARB 2900 TR (PerkinElmer), while americium and plutonium samples were measured with ORTEC α-spectrometer 576A. Required time of procedure for 100 ml of urine is approximately 2 hours from collection of urine to beginning of measurement. This sequential method does not use phosphate co-precipitation of strontium or plutonium and ashing steps to remove organic compouds, which rapidly quickens and simplifies analysis process. Method separates Sr, Am and Pu from urine with high chemical recoveries and is suitable for use after accidents or emergency situations.

Key words: urine analysis, AnaLig Sr01, extraction chromatography, strontium, plutonium, americium

NAM-P09, (Id: 84)

AN ELEMENTAL PORTRAIT OF THE PORTUGUESE WHEAT COLLECTION (IN 2013) BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

Catarina Galinha[a], Adriano Pacheco[a], Maria do Carmo Freitas[b], Ana Rita Costa[c], Nuno Pinheiro[c], Benvindo Maçãs[c], Ana Sofia Almeida[c], Hubert Wolterbeek[d]

[a]*CERENA-IST, University of Lisbon*
[b]*URSN/CTN-IST, University of Lisbon*
[c]*INIAV, National Institute of Agricultural and Veterinary Research*
[d]*Department of Radiation Science and Technology, Delft University of Technology*
catarina.galinha@ctn.ist.utl.pt

More than just being one of the "big three" cereal crops (with maize and rice), wheat is the staple food of humankind, with a history that is closely intertwined with humanity's own. Even if up to 100,000 plant species have been used -- on a regular or occasional basis -- since prehistoric times to meet the various needs (food, clothing, shelter, health) of an ever growing human population, wheat and its wild ancestors most likely were at the locus of an amazing evolutionary step that turned hunting and foraging/gathering individuals into settlers and, eventually, farmers. Domestication of diploid wild einkorn and tetraploid wild emmer is arguably thought to have begun some 10,000 years ago, although incipient cultivation of autochthonous landraces may have started well before that, in the early Holocene. The origins of such an agricultural beginning can be traced back to the vast and geographically diverse expanses of the Fertile Crescent in southwest Asia and the Middle East, while agriculture itself is, of course, the prominent feature of the so-called Neolithic Revolution, especially in what concerns cereal domestication (the above-mentioned einkorn and emmer wheats, and also wild barley).

The status of wheat as the universal cereal of ancient agriculture has been kept through this day. Tonnage (though not acreage) of wheat grown worldwide may have been overtaken by both maize's and rice's shortly before the turn of last century, yet wheat remains unrivalled as to its latitudinal range of cultivation, crop area proper, caloric and nutritional relevance, and, last but not least, cultural significance at large. Current production is unevenly split between an overwhelming majority of hexaploid bread wheat (about 95 %), and a remaining share of (mostly) tetraploid durum wheat plus small amounts of hulled-grain wheat species (einkorn, emmer, spelt). Given such a background, no wonder that wheat germplasm was among the first to be stored in archival collections and seed banks, despite early general (technical) difficulties in preserving genetic resources as germplasm holdings. Besides, it is only fitting that wheat was the founding subject of one of the longest-running experiments in the history of science, the Broadbalk experiment at Rothamsted, UK (1843-present) -- 170 years and counting!

Following the first morphological and taxonomic inventory of Portuguese wheats (1933), a collection of wheat cultivars has been maintained, replanted and documented by the National Institute of Agricultural and Veterinary Research, specifically by its former division known as the National Station for Plant Improvement (ENMP, Elvas). The ENMP collection has always been an invaluable asset in studies of agronomic and/or genetic development of wheat lines, as well as providing a reference frame for the nutritional evolution of Portuguese wheat crops. This work addresses the current status of major elemental nutrients and contaminants in a pool of 97 accessions of bread (52) and durum (45) wheat. All grain samples were irradiated at the Portuguese Research Reactor (RPI; CTN-IST, Sacavém) for 5 h, at a thermal-neutron flux density of 2.25E12 neutron per square cm and s, together with comparator disks of Al-0.1 %Au. Gamma spectra were acquired with a liquid nitrogen-cooled, high-purity Ge detector. Elemental concentrations were determined through k_0-standardized, instrumental neutron activation analysis (k_0-INAA), and quality control was carried out by concurrent analysis of NIST-SRM 1567a, NIST-SRM 1568a and INCT-OBTL-5. In the discussion, focus will be given to essential nutrients like Fe, Mg, Se and Zn, and also to historical trace contaminants like As, as compared to current ionomic traits in modern European wheats. Special attention is paid to the (low) levels of Se, for which wheat acts as an important source in human diets, with a view to curbing its deficiency in Portuguese cultivars through agronomic biofortification.

NAM-P10, (Id: 88)

INNOVATIVE TECHNIQUE FOR RAPID MEASUREMENT OF POST-ACCIDENTAL ^{89}Sr IN WATER: USE OF THE CERENKOV EFFECT COMBINED WITH COLOR QUENCHING

Kevin Galliez, Céline Augeray, Magalie Mouton, Lucie Tarlette, Corinne Fayolle, Jeanne Loyen, Marc Gleizes

IRSN
kevin.galliez@irsn.fr IRSN

Many techniques have been developed in the interest of measuring radionuclides activity concentration in environment in case of a nuclear accident. Some so called “crisis” techniques are currently under development at the Institut de Radioprotection et de Sûreté Nucléaire in France in order to rapidly measure radioactive isotopes of interest and provide information to the authorities.

Especially, strontium 89 and 90 can be radioactive isotopes of interest. They are both pure beta emitters. Because of their toxicity and the similarity of their physical and chemical behavior with calcium, these elements may be found through the food chain. Strontium 89 has a half-life of 50.5 days and can reach an activity concentration 10 to 170 times higher than strontium 90 in case of accidental reject. After the Fukushima accident, the necessity of quantifying rapidly strontium 89 and 90 appeared. It is therefore essential to measure their activity concentration in the environment [1].

The technique we are going to present concerns the determination of the activity concentration of strontium 89 and 90 in water, according to the ^{89}Sr/^{90}Sr ratio. It consists of two stages: the chemical separation by ionic chromatography and the measurement of the activity concentration of strontium 89 and 90 with a liquid scintillation counter.

The automated separation is performed from the adaptation of an existing ionic chromatography, whose features are not to measure cations but to separate and isolate strontium. It is important to understand that right after the isolation of strontium, the decay product of 90 strontium (yttrium 90) will grow instantly. The measurement step is also singular because of the use of Cerenkov Effect on a quenched sample. The quenching is realized by applying a thin colored film on the sample vial. As beta particles energy of strontium 90 is low for Cerenkov Effect (540 keV), its counting efficiency is very low. The colored quench is therefore used to make disappear the number of counts on the spectrum caused by strontium 90. This way, yttrium 90 ingrowth and strontium 89 decay are exclusively measured ($E^{90}Sr < E^{89}Sr < E^{90}Y$). Successive countings and modeling of the ingrowth/decay kinetics allow us to evaluate the activity concentration of strontium 89, and 90 depending on the ^{89}Sr/^{90}Sr ratio.

The results we are going to present at Radchem 2014 concern the development of the chemical separation by ionic chromatography and measurement of strontium by Cerenkov Effect. Studied parameters such as the quenching parameter to use, the sample geometry and the influence of ^{89}Sr/^{90}Sr ratio will be discussed. Results on proficiency test samples and standard solutions will also be shown. At last, an estimation of the total analyzing time comprising the separation and measurement steps will be given.

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NAM-P11, (Id: 89)

INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS FOR THE DETERMINATION OF GOLD NANOPARTICLES IN MICE TISSUES

JongHwa Moon, Beom-Su Jang

Korea Atomic Energy Research Institute
jhmoon1@kaeri.re.kr

Gold nanoparticles (GNPs) have been utilized in high technology applications such as organic photovoltaics, sensory probes, therapeutic agents, drug delivery in biological and medical applications, electronic conductors and catalysis. GNPs for use as molecular imaging probes and their biodistribution in safety reason have been studied, widely and intensively. The objective of this study was to evaluate the capability of neutron activation analysis (NAA) method to determine GNPs in mice tissues and biological samples. 10 nm GNPs were instilled into a mouse and eleven tissue and biological samples such as blood, bone, brain, gonad, heart, intestine, kidney, liver, lung, spleen and stomach were prepared for NAA. The prepared sample was irradiated for 10 minutes with thermal neutrons using the Pneumatic Transfer System (PTS) at the HANARO research reactor in the Korea Atomic Energy Research Institute (KAERI). Acquisition of the gamma-ray spectrum was carried out using a high purity Ge detector coupled to DSPECPLUS. Intravenously administered GNPs were detected only in the liver and spleen samples. On the contrary, orally administered GNPs were detected in the stomach and intestine samples. High amount of Na in the samples hampered the detection of GNPs and minimum detection limit for GNPs in these samples was approximately 0.01 mg/kg.

NAM-P12, (Id: 94)

DEVELOPMENT AND APPLICATION OF METHOD FOR DETERMINATION OF ^{89,90}Sr IN ENVIRONMENTAL SAMPLES BY THE USE OF NAOH FOR SEPARATION OF STRONTIUM FROM CALCIUM

Lyubomir Popov

KOZLODUY NPP, Bulgaria
popov_la@yahoo.com

The method allows cheap, safe and reliable determination of ^{89}Sr and ^{90}Sr in major environmental materials in sizeable quantities – water (500 L), soil (1000 g), milk (20 L), grass (1000 g), bone (1000 g), etc., routinely or in emergency situations (nuclear power plant accidents, “dirty” bombs, nuclear weapons detonation, etc.). Radiostrontium is leached by aqua regia from the ashes of the solid samples (burned at 550 °C) or it is preconcentrated from the liquid samples by carbonate precipitation. The separation of strontium from the large quantities of calcium is atained by the use of NaOH – under heating or at room temperatures. Due to difference of solubility of strontium and calcium hydroxides in diluted alkaline solution (0.2-0.3M NaOH) calcium hydroxide can be precipitated while strontium hydroxide remains in the solution. When both ^{89}Sr and ^{90}Sr should be reported radiostrontium is separated from the isotopes of barium/radium/lead by precipitation of the latter as chlorides in hydrochloric acid. Otherwise when only ^{90}Sr is expected to be present in the samples then separation (after ingrowth) of its daughter nuclide ^{90}Y (from 90Sr and isotopes of barium/radium/lead) is carried out in sulfate and ammonium hydroxide media. Measurements are performed by liquid-scintillation spectrometer in Cherenkov mode (without scintillation cocktail) of purified ^{89,90}Sr or purified ^{90}Y. Chemical yields of strontium and yttrium is measured respectively by gamma-spectrometry (of ^{85}Sr-tracer) and by titration (of stable yttrium carrier). The critical steps in the method were examined which resulted in reproducible chemical yields in the range 75 – 95 %. The method has been used routinely at 2 laboratories in Bulgaria for analyses of more than 1000 samples in the last 7 years. The analytical quality was checked by analyzing reference materials with different matrices and regular participations in international intercomparisons.

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NAM-P13, (Id: 102)

SELENIUM IN BREAD AND DURUM WHEATS GROWN UNDER A SOIL-SUPPLEMENTATION REGIME IN ACTUAL FIELD CONDITIONS, DETERMINED BY CYCLIC AND RADIOCHEMICAL NEUTRON ACTIVATION ANALYSIS

Adriano Pacheco[a], Catarina Galinha[a], Maria do Carmo Freitas[b], Marek Fikrle[c], Jan Kučera[c], José Coutinho[d], Benvindo Maçãs[d], Ana Sofia Almeida[d], Hubert Wolterbeek[e]

[a]*CERENA-IST, University of Lisbon*
[b]*URSN/CTN-IST, University of Lisbon*
[c]*Department of Nuclear Spectroscopy, Nuclear Physics Institute of the ASCR*
[d]*INIAV, National Institute of Agricultural and Veterinary Research*
[e]*Department of Radiation Science and Technology, Delft University of Technology*
apacheco@tecnico.ulisboa.pt

Selenium (Se) is an essential trace nutrient whose importance in human health is simply not up to par with its relative abundance in the Earth's upper continental crust: it is one of the least-common elements, with an average concentration that makes it rarer than, for instance, gold. Though ubiquitous, Se also features an uneven distribution in agricultural soils, that act as its port of entry into the nutritional path through uptake and accumulation by edible plants, even if such an element is not required for their own growth. Since the Se transfer up the soil-plant-(animal)-human food chain is generally efficient, that soil-Se imbalance easily translates into substantial variation in food-Se content and, ultimately, into significant divergence in human-Se intake.

The ever-increasing attention paid to the role of selenium and selenoproteins in human health stems primarily from an ever-growing body of evidence about not only their actual (general) importance for defending against oxidative stress/damage and thyroid malfunction -- that is against immune failure at large -- but also about their potential (beneficial) effect in a plethora of life-threatening issues (cardiovascular disease, critical illness and, especially, cancer) or, at least, life-deteriorating (cognitive, metabolic and reproductive) conditions. Some evidence may be inconclusive or even inconsistent, yet the relevance of selenoproteins to health seems unquestionable. Such an importance has since been recognised by both global organizations and national authorities, leading to a range of dietary recommendations for Se intake that currently averages 60 and 53 μg per day for adult men and women, respectively.

An extensive investigation of Se levels in cereals and their cultivation soils has been carried out across the main production areas of mainland Portugal, with a view to an eventual Se supplementation of major cultivars. Breads and cereal derivatives (breakfast blends, pastas, etc) make up a considerable share of Portuguese diets, so an increase in the bioavailability of Se through supplementation of crops may contribute to an upgrade in the Se status of the whole population. Cereals are far from being the main sources of Se on a content basis, but they are likely the major contributors to intake on a daily basis. The present paper focuses on the ability of bread and durum wheat -- Triticum aestivum L. and Triticum durum Desf., respectively -- to accumulate Se after supplementation via a soil-addition procedure. Four of the most representative wheat cultivars in the country -- Jordão and Roxo (bread); Marialva and Celta (durum) -- have been selected for supplementation trials, following the same agronomic practices and field schedules as the regular (non-supplemented) crops of the same varieties (seed planting: November 2010; crop harvesting: July 2011).

Soil additions were performed at sowing time, using sodium selenate and sodium selenite solutions equivalent to field supplementation rates of 4, 20 and 100 g of Se per ha. Total Se in field samples was determined by cyclic instrumental neutron activation analysis, via the short-lived nuclide 77mSe (half-life time: 17.5 s) at the Technological and Nuclear Campus (Portugal), and by radiochemical neutron activation analysis, via the long-lived nuclide ^{75}Se (half-life time: 120.4 d) at the Nuclear Physics Institute (Czech Republic). Quality control of the procedures was regularly asserted through analyses of NIST-SRM 1515, NIST-SRM 1567a and NIST-SRM 8433. Results show that soil supplementation at top rate can increase Se contents in mature grains up to 2, 16, 18 and 20 times for Jordão, Roxo, Marialva and Celta, respectively, when compared to grains from non-supplemented crops. These findings are also discussed with respect to Se-biofortification data from another field experiment, in which wheat crops were grown under an alternative Se-supplementation method (foliar application).

NAM-P14, (Id: 127)

IN-BEAM NEUTRON ACTIVATION ANALYSIS AT FRM II, GARCHING

Krzysztof Kleszcz, Zsolt Revay, Petra Kudejova

Technische Universität München, Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II)
krzysztof.kleszcz@frm2.tum.de

The thermal equivalent neutron flux at the prompt gamma activation analysis (PGAA) facility at the Forschungsneutronenquelle (FRM II) at Garching, Germany is 6×10^{10} cm^{-2} s^{-1} which is the highest beam flux reported. This beam intensity is already strong enough to activate samples for the purpose of neutron activation analysis (NAA), too. This option has been used together with PGAA simply performing decay counting after switching off the beam using the same spectrometer used for the in-beam measurement, and proved to be useful in the case of a handful of elements, like Na, Mn etc. The main advantage of in-beam activation is that the beam contains no epithermal or fast neutrons, thus realizing activation in its purest form. Many elements, like Al, Sb, or Ge could not be analyzed in this way, because they appear in the spectral background. Recently, a low-background counting chamber has been installed a few meters away from the PGAA instrument using a 30- % HPGe detector equipped with a mechanical cooler and covered with 10 cm of lead, boron and lithium-containing sheets against neutrons and tin to attenuate lead x-rays. The background conditions are much better for this spectrometer, at the same time the counting efficiency is also higher. This enables us to analyze a larger number of elements off-line. The first results will be presented at the conference.

NAM-P15, (Id: 139)

DETERMINATION OF ^{3}H, ^{36}Cl, ^{22}Na, ^{85}Sr AND ^{133}Ba BY MEANS OF PRECIPITATION METHOD

Lijuan Qian[a], Kerttuli Helariutta[b], Mikko Voutilainen[b], Lasse Koskinen[c], Jussi Ikonen[b], Marja Siitari-Kauppi[b]

[a]*Lanzhou University*
[b]*University of Helsinki*
[c]*Posiva Oy*
qianlj@lzu.edu.cu

Spent nuclear fuel from the nuclear power plants owned by TVO (Teollisuuden Voima Oy) and Fortum, is planned to be disposed at a repository at a depth of more than 400 meters in the bedrock of Olkiluoto (Eurajoki, Finland). The repository system includes multiple release barriers: the nuclear fuel, copper canister with a cast iron insert, bentonite buffer around the canister and backfilling of the tunnels. Furthermore, the surrounding rock is the last barrier if the man-made barriers fail during the passage of time. Safe disposal of spent nuclear fuel requires information about the radionuclide transport and retention properties within the porous and water-containing rock matrix along the water conducting flow paths.

The second in-situ experiment within ONKALO, the underground rock characterization facility in Olkiluoto, as part of the project “rock matrix REtention PROperties” (REPRO) was performed during 2013 using ^{3}H, ^{36}Cl, ^{22}Na, ^{85}Sr and ^{133}Ba as tracer nuclides. The aim is to study the diffusion and sorption properties of nuclear compounds in the rock matrix under real in-situ conditions.

A straightforward way to investigate properties of rock matrix under in-situ conditions is to carry out a water phase matrix diffusion experiment (WPDE2) in a two-meter artificial flow channel along the perimeter of the drillhole. The volume and aperture of the flow channel are minimized by an impermeable cylindrical flow guide inside the packer system. The inlet and outlet positions of water are located at the opposite ends of the packed-off section. WPDE2 tracer test is performed using a slow flow rate that is generated using a piston pump. The experiment is executed using synthetic groundwater to carry the tracer solution. This work presents the determination of radionuclides activities from the WPDE2 experiment giving the breakthrough curves of the radionuclides as a result. Rapid and precise determination of ^{3}H, ^{36}Cl, ^{22}Na, 85Sr and ^{133}Ba is of vital importance in the project. The activity of ^{22}Na, ^{85}Sr and ^{133}Ba can be measured using gamma detector. Due to their electron emissions ^{22}Na, ^{85}Sr and ^{133}Ba disturb the LSC measurement of ^{36}Cl and ^{3}H. So it is essential to seek a simple, convenient way to separate these radionuclides before spectrometric analyses.

From the initial water sample ^{22}Na, ^{85}Sr and ^{133}Ba are measured by gamma spectrometry first. Then NaCl carrier is added in solution. AgCl precipitation is produced and $Ag(NH_3)_2Cl$ solution is measured with liquid scintillation analyzer to obtain the ^{36}Cl activity. $Sr(NO_3)_2$ and $Ba(NO_3)_2$ carriers are added to the supernate and ^{85}Sr and ^{133}Ba are precipitated as carbonates; $SrCO_3$ and $BaCO_3$. This supernate contains ^{3}H and ^{22}Na and remains of ^{85}Sr and ^{133}Ba. Gamma emitting nuclides are measured first and then ^{3}H with liquid scintillation analyzer. ^{22}Na, ^{85}Sr and ^{133}Ba disturb the counting of LSC measurement. Thus using the quench curves determined for each of gamma emitting nuclides in ^{3}H window of LSC, the amount of counts from the disturbing nuclides in ^{3}H window can be calculated and reduced from the actual ^{3}H counts. Then the “clean” ^{3}H activities are determined by using the ^{3}H quench curve.

The separation procedure is optimized. The recovery of ^{36}Cl is about 100 % as well as the recovery of ^{85}Sr while the recovery of ^{133}Ba is slightly less, being about 85 %. The detection limit for ^{3}H in this solution is 1 Bq/g. The precipitation procedure is easy and fast to separate ^{36}Cl from the solution. ^{85}Sr and ^{133}Ba can be removed from the solution by carbonate precipitation in a way that ^{3}H is measurable.

NAM-P16, (Id: 155)

RAPID ANALYSIS OF URANIUM CONCENTRATIONS IN POWDER ROCK SAMPLES BY A DELAYED NEUTRON COUNTING

Gwang-Min SUN, Sunha KIM, Jonghwa Moon

KAERI
gmsun@kaeri.re.kr

A delayed neutron counting system installed at the HANARO research reactor in the Korea Atomic Energy Research Institute was applied to the analysis of elemental uranium concentrations in the rock samples collected at the Samcheok area, northeastern Yeongnam massif, South Korea. For the accurate determination of uranium, the correction of thorium interference was carried out. The resultant values are consistent with the values determined by the ICP-MS. The DNC method was proven to be a very rapid and excellent method for the quantification of the uranium concentration in the geological samples. Keywords: Delayed neutron counting, uranium concentration, thorium concentration, rock samples

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ANALYSIS OF LITHIUM AND BORON OF PRODUCTION AND REAL SAMPLES USING COLD NEUTRON DEPTH PROFILING METHOD

Byung Gun Park, Gwang-Min SUN

KAERI
gpark@kaeri.re.kr

Neutron Depth Profiling (NDP) is a nondestructive near surface method that can analyze the component nuclide concentration versus depth distribution in a sample by detecting the charged particles emitted after the neutrons are absorbed. NDP technique has became an important method to measure depth profiles of light elements such as lithium and boron in lithium battery and semiconductor materials. The Korea Atomic Energy Research Institute NDP (KAERI-NDP) facility has been installed at the HANARO research reactor. For the first application of the KAERI-NDP system, boron implanted and lithium deposition samples were prepared for depth profiling of ^{6}Li and ^{10}B. Additionally, electrode film samples were prepared by disassembling the lithium ion battery used in the mobile phone. The production and real samples were installed at the target chamber of the KAERI-NDP system and irradiated for different times with cold neutrons at the CG1 guide of the HANARO. The charged particle spectra were measured by using ion implanted Si detector. Measured spectra were analyzed and depth profiles of 6Li and ^{10}B were determined. For the production samples where ^{10}B implanted into the Si wafer, peak depth, peak concentration and aerial density was matched with those of SIMS method within 2, 6, 9 %, respectively. In the case of lithium deposition samples, there was a difference of ^{6}Li concentration profile in the deep region for the thick sample. ^{6}Li concentration of the cathode of lithium battery was 5 times higher than that of the anode sample.

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QUALITY CONTROL FOR ROUTINE K_0-NAA APPLICATIONS AT NUCLEAR PHYSICS INSTITUTE, ŘEŽ

Marie Kubešová, Jan Kučera

Nuclear Physics Institute, ASCR
mariekubes@centrum.cz

Implementation of the k_0-NAA in Řež aimed at the development of routine panoramic trace-element analysis method for samples with various matrices and of different origin. To meet the customers' expectations, procedures and practices have been established to ensure the high quality of the results produced, such as, calibration of the equipment used (scales, pipettes, detectors), in-situ determination of neutron flux parameters in irradiation channels of the multipurpose research LVR-15 reactor, use of replicates (if possible), blank analyses, use of certified reference materials, namely NIST SRMs 1547, 1633B, 2711, and/or others in case of availability, preferably with a good matrix-match to the samples to be analyzed. Using results of the SRMSs, control charts are maintained to monitor the long-term stability and quality of the assays. For most elements, agreement is obtained with the certified values within uncertainty margins. A procedure has also been designed to use noncertified values for quality control in the same way as the certified values. In a few cases, however, results deviating from the certified or noncertified values are consistently being found, although the differences are not of a systematic nature. Such cases are topics of our future studies. To test and improve the quality control measures, our lab also successfully participated in several inter-laboratory comparison rounds organized and sponsored by the IAEA using test samples of plant and soil origin provided by the Wageningen Evaluating Programs for Analytical Laboratories (WEPAL).

NAM-P19, (Id: 187)

CHARACTERIZATION OF MULTICRYSTALLINE SILICON FOR PHOTOVOLTAICS BY METHODS OF NEUTRON ACTIVATION ANALYSIS

Barbara Karches[a], Heiko Gerstenberg[b], Gabriele Hampel[a], Petra Kudejova[b], Bernard Ponsard[c], Stephan Riepe[d], Christian Stieghorst[a], Norbert Wiehl[a], Christian Plonka-Spehr[a]

[a]*Department of Nuclear Chemistry of Johannes Gutenberg-University of Mainz, TRIGA*
[b]*Technical University Munich, FRM II*
[c]*Belgian Nuclear Research Center, BR2*
[d]*Fraunhofer Institute for Solar Energy Systems*
karches@uni-mainz.de

The improvement of solar cells by achieving higher efficiencies and lower production costs is getting more important because of the worldwide increase of photovoltaics as a renewable energy source. In this framework, the aim of DFG-Project HA 5471/4-1 (Department of Nuclear Chemistry, Johannes Gutenberg-University, Mainz, “Fraunhofer Institute for Solar Energy Systems” (ISE), Freiburg) is to optimize the methods of manufacturing and analysis of solar silicon.

One manufacturing method is the directional solidification of raw and partly purified silicon (called “feedstock”). Based on their lower segregation coefficients, the impurities accumulate in the liquid stage during the solidification. The so produced silicon has acceptable concentrations of impurities and is called “solar grade silicon” (SoG-Si). For the analyses by means of Instrumental Neutron Activation (INAA) and Prompt Gamma Activation (PGAA) samples from SoG silicon as well as from highly purified silicon after the final solidification step are irradiated at three different research reactors: TRIGA Mainz, BR 2 Mol and FRM II Munich. Of special interest are the dopants boron and phosphorus and the 3d transition metals, which decrease the efficiency of solar cells by recombination of charge carriers. Profiles of these element concentrations in the produced silicon ingot as well as analyses of the impurity concentration in feedstock material and melting pot samples can help to improve the manufacturing method [1].

First results of measurements have shown a specific element distribution in produced silicon, caused by processes of diffusion and segregation [2]. Most of the elements, especially cobalt and boron, follow the Scheil-Equation [3] for distribution during directional solidification. With INAA the elements cobalt, iron, copper, chromium, antimony and scandium could be detected in silicon with a very low detection limit; with PGAA it was possible to measure boron at the ppb-level.

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ACCELERATOR MASS SPECTROMETRY OF URANIUM: COMPARISON OF U_3O_8 AND UF_4 TARGET MATRICES

Irena Špendlíková[a], Miroslav Ješkovský[b], Mojmír Němec[a], Robert Breier[b], Peter Steier[c], Pavel Povinec[b]

[a]*Department of Nuclear Chemistry, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University, 115 19 Prague, Czech Republic*
[b]*CENTA Laboratory, Faculty of Mathematics, Physics and Informatics, Comenius University, 84248 Bratislava, Slovakia*
[c]*VERA Laboratory, Faculty of Physics, Universität Wien, 1090 Vienna, Austria*
spendlikovairena@gmail.com

For determination of $^{236}U/^{238}U$ ratios in environmental samples by accelerator mass spectrometry, the U_3O_8 targets are usually used for the UO^- beam production. Uranium fluoride targets containing no oxygen and hydrogen may offer higher molecular isobar suppression together with a higher accuracy and sensitivity of uranium isotope analysis1. However, the preparation of anhydrous UF_4 targets is more complicated than the preparation of U_3O_8 targets. When introducing inert atmosphere into the dehydration step of the preparation the only partial reduction of oxygen and hydrogen content in the final product of the preparation method was assured. In this work, several U_3O_8 and UF4 targets were tested in the CENTA laboratory using the MC-SNICS ion source and double focusing injection magnet and the targets were prepared using the Vienna KKU standard with $^{236}U/^{238}U$ isotopic ratio of 10-11. The detailed study of anhydrous UF_4 preparation method will be performed in CTU laboratories. The ion current from only one UF^{2-} sample was in average higher by about 50 % than the UO^- current from the U_3O_8 samples. The targets were completely sputtered away, and the estimated ionization yields of UO^- and UF^{2-} were of the order of 10^{-3}. However, with the improved procedure of the UF4 targets production, we expect that even higher ionization yields could be obtained.

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NAM-P21, (Id: 215)

RAPID SEPARATION AND DETERMINATION OF ^{107}Pd AND ^{79}Se FROM INTERMEDIATE LEVEL RADIOACTIVE WASTE FROM NPP A1

Boris Andris[a], **Pražský Miroslav**[b]

[a] *VUJE a.s.*
[b] *WERT s.r.o.*
boris.andris@gmail.com

Palladium ^{107}Pd and Selenium ^{79}Se are amongst nineteen limited radionuclides monitored in wastes disposed at national repositories in Slovak Republic. Both of these radionuclides are pure beta emitters with energies Ebeta,max 150.7 keV; 33 keV respectively. Such low energies of beta spectra make them very difficult to measure. The best possible method of determination is liquid scintillation counting. Even LSC methods are to be much more sophisticated than simple photomultiplier tube measurements; triple-to-double coincidence ratio liquid scintillation counting is one of the best methods to determine these difficult to measure radionuclides. Radiochemical separations of these radionuclides are not even in these days exactly described. Procedures are either very complex or other parts of procedures are dealing only with selenium and palladium as a toxic element and heavy metal therefore the emphasis is on determining with instrumental methods: ICP MS, ICP AES and ICP OES. These methods cannot be used in case of intermediate level RAW. Intermediate level, historic RAW from NPP A1 are presently disposed. Since at A1 NPP occurred INES 4 accident in year 1977, cladding of many fuel assemblies was violated, even one fuel assembly was melted down, whole spent fuel storage, reactor vessel and other storages for fuel assemblies were severely contaminated with fission, activated and transuranic elements with specific activities up to 1011 Bq/kg. This paper is describing development of selenium 79 separation in steps consisting precipitation of selenium into its metallic form and achievement of desired radionuclide purity with ion chromatography. Determination of palladium is studied in few simple precipitation steps with DMG and co-precipitation of other pollutants. Both limited radionuclides are determined with liquid scintillation counting with TDCR.

NAM-P22, (Id: 222)

INSTRUMENTAL PHOTON ACTIVATION ANALYSIS WITH THE MT-25 MICROTRON

I. Krausová, J. Mizera, Z. Řanda, D. Chvátil, P. Krist

Nuclear Physics Institute ASCR
krausova@ujf.cas.cz

Instrumental photon activation analysis (IPAA) is a useful and complementary method to instrumental neutron activation analysis (INAA). IPAA allows determination of number of elements not determinable by INAA, and determination of many elements with a better sensitivity than INAA. Unlike INAA based mainly on the neutron capture reactions (n,gamma), PAA is based on photonuclear reactions, particularly photodisintegration reactions (gamma, n) and (gamma,p), and photoexcitation reactions (gamma,gamma'). These reactions take place only at photon energies exceeding a threshold. This can be utilized in optimizing beam energy at irradiation of a specific sample, when partial suppression of interfering nuclear reactions can be achieved by keeping the maximum photon energy below or only slightly above their threshold. Particularly in analysis of geological samples (minerals and rocks), this reduces substantially, compared to INAA, matrix effects hindering determination of trace elements. Higher penetration of high energy photons and lower activities produced allow also analysis of larger samples.

An effective source of the high energy photon radiation for use in IPAA is the secondary radiation - bremsstrahlung - produced at deceleration of electrons accelerated in a high frequency cyclic accelerator - microtron. The MT-25 microtron built at the Czech Technical University in Prague in the late 1980s, after its takeover and modernization by the Nuclear Physics Institute ASCR in the years 2003-2005, has been utilized regularly for purposes of IPAA. Until recently, IPAA analyses could be carried out only in an offline regime, i.e., in assay of elements providing by photoactivation radionuclides with half-lives long enough for counting with a sufficient count yield even after decay time elapsed between switching off the microtron and manual delivery of sample to a detector. Currently, installation of an automated pneumatic system for rapid sample transport between the beam position and detector in an online regime is being completed which will, regarding numerous short-lived products of photonuclear reactions, provide substantial extension of the analytical range of IPAA. The contribution presents possibilities and recently realized examples of utilization of IPAA with the MT-25 microtron, namely a recently developed and optimized procedures for fast fluorine and nitrogen assay, and their application in analysis of various materials.

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INNOVATIONS AT THE MT-25 MICROTRON AIMED AT APPLICATIONS IN PHOTON ACTIVATION ANALYSIS

Jiří Mizera, David Chvátil, Pavel Krist, Zbyněk Horák, Miroslav Vognar, Zdeněk Řanda

Nuclear Physics Institute, Academy of Sciences of the Czech Republic
mizera@ujf.cas.cz

Microtron is a high frequency cyclic accelerator of electrons with fixed frequency and constant magnetic field. Electrons are accelerated in a cavity resonator by high frequency energy supplied by high pulse power of a magnetron, orbit within an accelerating chamber in circular trajectories with gradually increasing diameters, gaining gradually higher energy, and can be extracted from individual orbits to achieve required beam energy. The accelerated electron beam can be converted into high energy photon radiation - bremsstrahlung - on a target made usually of tungsten. Microtron can thus be used as an effective source of high energy photon radiation for use in photon activation analysis (PAA). With a suitable secondary converter, microtron can be used also as a neutron source suitable for neutron activation analysis. In 1981, microtron MT-22 built at the Czech Technical University in Prague in collaboration with JINR Dubna started operation. After ten years of operation, MT-22 was replaced by a new, chamberless microtron MT-25. In 2003, MT-25 was made over to the Nuclear Physics Institute, ASCR (NPI) and its modernization started aimed at upgrading microtron parameters such as the mean accelerated electron current, quality of the beam and irradiation fields, and attaining better long-run operation stability and reliability. MT-25 delivers highly monoenergetic electrons within the energy range 6 - 25 MeV with the maximum mean beam current 25 microA. Stable operation of MT-25 at a 20 µA mean electron current (at >20 MeV energy) started in 2006, and its utilization for PAA on a larger scale has been re-established. Several, mainly geochemical and cosmochemical studies have been carried out or are underway. Until recently, PAA analyses could be carried out only in the offline regime, i.e., in assay of elements providing by photoactivation radionuclides with sufficiently long half-lives. Currently, installation of an automated system for rapid sample transport between the beam position and detector in the short time, online irradiation regime is being completed which will provide substantial extension of the analytical range of IPAA. The system has been designed as a pneumatic tube system driven by three vacs and controlled by a commercially available modular programmable controller. The irradiation chamber has been designed as a rotation device with the axis of rotation perpendicular to the axis of the beam. The system enables special operations, such as multiple irradiation-counting cycles, counting sample either in a transport/irradiation vial or its manual removal from the vial before counting, etc. An important part of the system is a four-way switch (router) placed above a detector shielding.

Operation of the microtron MT-25 has so far been controlled manually. For a routine operation, especially for repeated short-time irradiations, it is desirable to run microtron in a continuous stable regime with minimum fluctuations of the electron beam energy and current between irradiations of individual samples. Also for this purposes, a new fuzzy control system for the microtron MT 25 has been designed and optimized. The control system is based on a Mamdani-type fuzzy regulator using an operator description and a mathematical model of the microtron. The system allows controlling the energy and the current of accelerated electrons at required values. The fuzzy controller was tested with the aid of the mathematical model with satisfactory results and its optimization was performed with the help of a genetic algorithm. The optimization was performed in two phases, the first one aimed at maximizing speed of the control process and minimizing the control error, and the second one at minimizing the control overshoot. A real control system has currently being tested with encouraging results.

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A NEW FORMULATION OF EFFECTIVE STATES OF “ATOMS IN COMPOUNDS”. APPLICATION TO STUDY HYPERFINE STRUCTURES AND CHEMICAL SHIFTS OF X-RAY EMISSION LINES.

Yuriy Lomachuk, Anatoly Titov, Leonid Skripnikov, Nikolay Mosyagin

Petersburg Nuclear Physics Institute, Gatchina, Russia; Dept. of Physics, St. Petersburg State University, Petrodvoretz, Russia
jeral2007@gmail.com

Concepts of oxidation number state of an atom in a molecule and related theories are extremely useful in chemistry. At the same time, a good (clear and unambiguous) definition of the state of an atom in a molecule does not exist. Various methods of determining it from calculations lead to different results [1]. Each of known definitions has its drawbacks. The methods based on the use of one-electron density matrices (Mulliken or Löwdin populations analyses, etc.) are basis set dependent. The methods that use the electron densities (Bader or Hirschfield charges, Voronoi cells), suggest introduction of some complementary (artificial) notions or partitioning a molecule (solid) on regions in a manner that is not arising from any of physical principles.

There is a number of experimentally observed properties of compounds, depending on a distribution of the valence electron densities or their changes in the atomic core regions. They include chemical shifts of X-ray emission spectra [2], hyperfine structure constants, isotope (volume) shifts, etc. Earlier our group has developed a two-step method to calculate these properties through first-principle based electronic structure calculations within the generalized relativistic pseudopotential approximation followed by a posteriori restoration of the information on the wave functions in the atomic core regions that is missed in the results of pseudopotential calculations [3]. On the basis of this two-step method one can formulate an approach for determining the state of an atom in a molecule (compound). A radius Rc of the core region is determined by the smallness of interaction of valence electrons located within a sphere (r < Rc) with the external (chemical) environment (r > Rc) compared to their interaction with the nucleus and core electrons of a considered atom.

Using the properties of proportionality of valence spinors in the atomic core region with the radius Rc [4], one introduce some new terms: "charges of partial waves" for valence electrons in the core region, "reduced population numbers" and one-center density matrices "reduced on the radial quantum number nr". It is shown that the above-discussed properties characterized by the state of an atom in a compound rather than by chemical bonds are well described by only these terms. Results of calculations of the properties of atoms and molecules are presented.

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PERFORMANCE EVALUATION (PE) SAMPLES AS PART OF LABORATORY QUALITY CONTROL.

Evgeny Taskaev

Eckert & Ziegler Analytics, Inc.
evgeny.taskaev@ezag.com

Role of PE samples in the Laboratory Quality control is briefly discussed. Eckert & Ziegler Analytics (EZA) capabilities are outlined. New Fission products Mixture (FM) is introduced. This mixture of radionuclides represents real fission products resulted from the irradiation of natural or enriched Uranium with thermal neutrons. Analysis of this mixture is real challenge and it can be very valuable tool for training and proficiency testing. Fission mixture has several advantages over existing EZA activation/fission mixture:

- FM contains same array of radionuclides as post-accident samples,

- Over 20 isotopes with reasonable half-lives can be certified,

- Liquid FM samples can test laboratory ability to handle samples properly prior to analysis. Improper sample container, preservation, storage conditions etc. can significantly alter analytical results.

- Gamma spectrometry of this mixture requires extensive knowledge of the methodology and particularly the correct application of software used for gamma analysis. Analytical laboratory will need to:

- analyze complex isotope mixture, properly identify isotopes using key gamma lines and correctly apply interferences,

- properly apply coincidence summing corrections,

- decay results for the reference date,

- properly recognize and calculate parent/progeny pairs like Zr-95/Nb-95, I-132/Te-132, Mo-99/Tc-99 etc.,

- identify additional radionuclides.

- FM can be used to identify non gamma emitting radionuclides like Sr-89, Sr-90, Pu-^{239} etc. based on fission yields, nuclear reactions and irradiation conditions.

Fission mixture samples can be delivered as liquid samples and other configurations like filters and cartridges.

NAM-P28, (Id: 255)

DEVELOPMENT AND VALIDATION OF ROBUST ANALYTICAL METHOD FOR DETERMINATION OF CR-51 IN BLOOD SAMPLES BY LSC

Myroslav Zoriy, Martina Froning, Peter Hill

Reserch Center Jülich
m.zoriy@fz-juelich.de

Cr-51 is a radioactive isotope of chromium having a half-life of 27.7. The decay scheme indicates that 91 % of the time, Cr-51 decays by electron capture directly to the ground state of the V-51 and emitting no gamma rays at all. Only 9 % of the time the Cr-51 decays directly to the excited state of the daughter (V-51m), which then further decays by isomeric transition to the ground state, emitting a 320 keV gamma ray during the process. At the present, Cr-51 is used in many application fields, in particular, in medicine, where, thanks to its chemical properties, Cr-51 has found to be an excellent tool for the labeling of red blood cells in order to measure of mass or volume, survival time, and sequestration studies, for the diagnosis of gastrointestinal bleeding, and to label platelets to study their survival [1]. Nowadays, for the determination of C-51 activity in blood samples, usually, the conventional -spectrometry is applied [2]. In spite the fact that the method utilise almost no (or minimum) sample preparation steps, the careful attention for the calibration geometry should be paid. For instance, the calibration should be performed with the homogenised calibration standard (that is by blood samples is not always easy). On the other hand, the limit of detection, achieved by -spectrometry (depending on the type of detectors) are normally in the range of 10 Bq/g and relatively long counting times are required. However for some clinical studies, where the incorporated doses are sometimes restricted, a method with better detection capability would be absolutely preferable. Because of the electron capture decays the Cr-51 could be also detected using the Liquid Scintillation Counting [3]. Due to its simplicity, sensitivity and relatively simple sample preparation, this method was proved to be a suitable alternative for -spectrometry in order to determine the Cr-51 in blood samples. To prove this in the present study we developed a robust analytical method for measurement of Cr-51 in blood samples in routine mode by means of LSC. The method was validated with the synthetically prepared blood samples from different subjects. Prior to the measurements the samples were microwave digested in order to eliminate the matrix influence. The figures of merits, such as sensitivity, limits of detection and quantifications, precision and accuracy were studied and confirmed the capability of the method to determine the Cr-51 in blood samples in the range of 0,5 Bq per g of sample. All the results will be presented and discussed in details in the frame of current poster presentation.

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NAM-P29, (Id: 288)

APPLICATION OF THE TWO-STEP APPROACH TO INVESTIGAION OF CHEMICAL SHIFTS AND OTHER ELECTRONIC PROPERTIES DETERMINED BY CORE REGION OF HEAVY ATOMS

Leonid Skripnikov, Anatoly Titov, Yuriy Lomachuk

St. Petersburg State University, Petrodvoretz, Russia; Petersburg Nuclear Physics Institute, Gatchina, Russia
leonidos239@gmail.com

Modeling of electronic structure and properties of actinide compounds is of considerable importance for modern radiochemistry. However, reliable and accurate estimates are a great challenge for quantum chemistry of actinides due to strong relativistic and correlation effects in such compounds. A development of theoretical approaches to this problem will stimulate application of a number of experimental techniques of analytic chemistry such as the method of chemical shifts in X-ray emission spectroscopy (XES).

We report application of the theoretical method of generalized relativistic effective core potential [1] followed by the method of one-center nonvariational restoration [2] of valence electron wave function in the vicinity of heavy atoms to calculation of different properties of compounds containing heavy elements including actinides. Basing on the developed atom-in-compound (AiC) concept we demonstrate a possibility to use XES to control a number of properties that are determined by the core region of valence wavefunction. We show its applicability to provide a unified tool for indirect and independent accuracy check of the evaluated AiC characteristics. This is of great importance to the cases where an experimental check is difficult or even impossible [3].

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INVESTIGATION OF HYDROPHILIC MATERIALS AS HYPOXIC PHANTOMS

M. Alkhorayef

Centre for Nuclear and Radiation Physics, Department of Physics, University of Surrey, Guildford, Surrey, GU2 7XH, UK
m.alkhorayef@surrey.ac.uk

Cross-linked hydrophilic co-polymers are candidates for use as phantom materials because they can be modified to have similar elemental compositions to that of body soft tissues. Co-polymers contain both hydrophobic and hydrophilic monomers; the molar ratio of which allows the water-uptake ability to be controlled. By controlling the hydration level, it may be possible to imitate various types and different disease stages of tissues, as well as the extent of tissue hypoxia. A series of experiments was carried out for different types of cross-linked hydrophilic co-polymers; hydroxyethyl methacrylate/Vinyl pyrrolidone (HEMA-VP) and methyl methacrylate/Vinyl pyrrolidone (MMA-VP) were hydrated by biological fluids with or without the reducing agent AnaeroGen to obtain hypoxic condition or normoxic condition; respectively. The relative yield of 3γ-to-2γ annihilation photons was determined using the positron emitter, Na-22, with a lanthanum bromide:Cerium ($LaBr_3$:Ce[5 %]), scintillation detector. The peak-to-peak method was used to calculate the ratio of the full-energy photopeak area of the 511 keV annihilation obtained in the sample and the aluminium reference material. The Na-22 source used has a positron yield of 90.4 % and a gamma-ray energy at 1274 keV of relative intensity 99.9 %, emitted almost simultaneously. The energy resolution and the intrinsic photopeak efficiency figures for $LaBr_3$:Ce were (3.37±0.08) % and (29.1±0.8) %, respectively for the 511 keV annihilation energy. The relative yield of 3γ-to-2γ annihilation photons was calculated and discussed in different hydrophilic co-polymers.

NAM-P31, (Id: 298)

DEVELOPMENT OF AN IN-SITU RADIOTRACER METHOD TO MEASURE THE ADSORPTION PHENOMENA OF DIFFERENT ALPHA-EMITTERS

Dávid Horváth, Tibor Kovács

University of Pannonia, Institute of Radiochemistry and Radioecology
namthar@gmail.com

The so called in-situ radiotracer methods are widely used for the determination of charge- and mass transport on the liquid-solid interfaces. With these methods different phenomena can be investigated, such as adsorption, corrosion, contamination or decontamination. Each technique is based on the thin layer principle of Aniansson, which claims, that the adsorbed amount of a radioactive isotope with soft radiation can be measured with low background noise in case of proper cell arrangement.

In the past decades several methods were developed to measure the adsorption phenomena of different beta and soft gamma emitting isotopes in-situ (^{36}Cl, ^{35}S, ^{32}P, ^{51}Cr, ^{110}mAg, etc.), but none for the alpha emitters.

The alpha radiation measurement technique is extensive, several measurement methods have been developed to measure both intensity and spectroscopic parameters. However, the existing methods are not capable to measure under in-situ conditions, most of them are presume vacuum technique, in which case a continuous contact with the solution is not possible.

To determine the adsorption of alpha emitters under in-situ conditions on compact surfaces development of a new technique is necessary, which is the aim of this work.

The main steps of the research and development project are:

- Selection of the proper detection technique
- Design a cell construction, which fits the Aniansson principle
- Preparation of a high activity pure alpha source
- Calibration of the cell
- Determine the main equations
- Measure the adsorption phenomena of different alpha emitting isotopes

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NAM-P32, (Id: 300)

DETERMINATION OF DISTRIBUTION COEFFICIENTS OF ^{134}Cs FROM BALTIC SEA WATER USING Cs-SELECTIVE SORBENTS.

Krzysztof Borowik[a], Halina Polkowska-Motrenko[a], Jaroław Ostrowski[b]

[a]*Institute of Nuclear Chemistry and Technology*
[b]*Fertilizer Research Institute*
k.borowik@ichtj.waw.pl

Radiocaesium is one of the most important radionuclides introduced into natural environment by human activity. In spite of its small concentration ^{137}Cs and ^{134}Cs may cause serious hazard in case of spread of fission products in the air or contamination water reservoirs. This risk is a result of high radioactivity and long decay time of mentioned radioisotopes. Decontamination of fresh or salty water needs special handling as a result of specific properties of caesium ions. Unlike to transition metals, caesium does not create insoluble precipitates and is weakly sorbed onto conventional cationic ion exchangers. Highly selective sorbents are used for that purposes. The most frequently used sorbents are titanates and silicotitanes, transition metal(II) hexacyanoferrates(II) and heteropolyacid salts. The minor role plays zeolites and natural organic sorbents.

According to the Polish energy policy for the next two decades commissioning of two nuclear power plants is expected. In this poster a results of the determination of distribution coefficients of ^{134}Cs from Baltic Sea water using commercially available and synthesised in a laboratory scale Cs-selective sorbents are presented. Comparison of these values may be important not only as an analytical purposes of radionuclide preconcentration, but also simulates decontamination of large volume salty water as a potential result of radioactive leakage. The research has been executed as a part of research task No. 8 „Study of processes occurring under regular operation of water circulation systems in nuclear power plants with suggested actions aimed at upgrade of nuclear safety" financed by the National Research and Development Centre in the framework of the strategic research project entitled „Technologies Supporting Development of Safe Nuclear Power Engineering”.

NAM-P33, (Id: 308)

ON THE DEVELOPMENT OF A RAPID METHOD FOR THE DETERMINATION OF Pb-210 IN WATER SAMPLES BASED ON TK100 RESIN

Carina Dirks[a], **Jake Surman**[b], **Jackie Pates**[b], **Steffen Happel**[c]

[a]*Radiochemistry, Department of Chemistry, Philipps-University Marburg*
[b]*Lancester Environmental Center, Lancaster University*
[c]*TrisKem International*
carina.dirks@chemie.uni

The crown-ether based SR Resin is frequently used for the separation and determination of Pb-210 in aqueous samples via liquid scintillation (LSC) or gas proportional counting (GPC). The resin only shows significant Pb (and Sr) retention at moderate to high acid concentrations; it does thus not allow for direct loading of Pb from acidified or raw water samples, making the additional use of pre-concentration steps such as ion exchange or co-precipitation necessary.

In order to simplify and quicken the Pb-210 determination an extraction chromatographic resin (TK100 Resin) allowing the direct load of Pb from water samples and its subsequent purification on the same resin has been developed and characterized.

The TK100 Resin is based on the crown-ether also used in the SR Resin; accordingly its selectivity and robustness against interferences from common matrix elements, such as e.g. Ca and Mg, are similar to that of the SR Resin. However, by including HDEHP into its composition Pb can now be extracted at a much wider range of pH conditions, i.e. pH £8. Conditions allowing the removal of other beta emitters (e.g. Sr-90, Bi-210, Y-90) from the resin, and for the final elution of Pb from the resin, have been identified.

Elution studies have been performed with the resin in column form as well as in disc form, the latter having the advantage of allowing higher flow rates. It could be shown that Pb uptake was very high even at elevated flow rates (e.g. 10 mL/min for columns and 30 mL/min for discs). The new rapid method was tested on spiked tap water samples. Samples of up to 5 L were directly loaded onto the resin in column or filter geometry at elevated flow rates; Pb was retained on the resin, purified and finally eluted with high chemical yield and purity.

The direct measurement of Pb-210 loaded discs by liquid scintillation counting is being evaluated in order to further speed up the method.

NAM-P34, (Id: 315)

FAST PROCEDURE FOR SELF-ABSORPTION CORRECTION FOR LOW Γ ENERGY RADIONUCLIDE Pb-210 DETERMINATION IN SOLID ENVIRONMENTAL SAMPLES

Magdalena Długosz-Lisiecka

Technical University of Lodz, Faculty of Chemistry
mdlugosz@mitr.p.lodz.pl

Low-energy X and γ radiations (for example of ^{210}Pb: E $\gamma = 46.5$ keV) are effectively self-absorbed even in thin environmental samples, including air filters with captured dust or contaminated soil, as well as in bottom sediment matrixes with limited quantities of the samples. In this paper, a simple method for the direct analysis of ^{210}Pb ($T_{1/2} = 22.3$ years) by gamma-ray spectrometry in environmental samples with self-absorption correction is described. The method is based on the comparison of two γ peak activities coming from other natural radionuclides, usually present in environmental samples. The analysis the dependence of the self-absorption correction factor for the ^{210}Pb activity on the activity ratios of 911 and 209 keV peaks and 609 and 295 keV peaks coming from nuclides of ^{238}U or ^{232}Th rows, present in typical environmental samples was done. Instrumental gamma spectrometry with HPGe detectors is usually applied for environmental radioactivity monitoring. The preferred method for the correcting of this effect is to use spiked or natural matrix reference materials.

Commercially available radioactive standards allow us to establish the dependence of the detection efficiency versus the energy of c-photons in the wide energy range from 40 to 2,000 keV, for the fixed geometry (for example: cylindrical or Marinelli beaker and known chemical composition of the sample. However, several very important primordial and anthropogenic radionuclides occurring in the environmental samples emit low-energy photons in the range up to 200 keV, particularly: ^{210}Pb—46.5 keV, ^{241}Am—59 keV, ^{234}Th (^{238}U)—63.3 and 92.6 keV, ^{228}Th—84.8 keV,^{235}U—140, 163 and 186 keV and ^{226}Ra—186 keV. For these radionuclides one should take into account the occurrence of the self-absorption of soft c radiation in the measured samples, which strongly depends on the density, resultant atomic number—Z and geometry of the samples. Therefore, instrumental gamma ray spectrometry may require additional corrections for self-absorption of gamma rays, as environmental samples often differ in densities and composition from each other, and the offered calibration standard reference materials may have slightly different chemical compositions. Generally, two basic approaches have been applied for solving the problem of self-attenuation in volume samples: experimental and mathematical— using Monte Carlo simulations. Finally, a few computer programs have been developed for calculating the corrected detection efficiency for samples with a normalized shape with a known chemical composition (e.g. LabSOCS).

In all solid environmental samples together with the very important ^{210}Pb radionuclide there are other natural radionuclides. Some of them emmit at least one of the pair of photons with different energies. Simultaneous determination of the ratios of their c-line activities can be a valuable method for searching for small chemical changes in the examined matrixes. We have proved this for at least following radionuclides: ^{228}Ac emitting with sufficient efficiency photons with energies 209 and 911 keV, or a pair of ^{214}Pb–^{214}Bi with gamma-ray energies of 252 and 609 keV can be used for simultaneous self-absorption correction in the determination of the another soft-gamma emitter—^{210}Pb.

NAM-P35, (Id: 335)

NATURAL RADIONUCLIDE EXTRACTION FROM AQUEOUS SOLUTIONS BY IONIC LIQUIDS

Gabriele Wallner, Orhan Sap, Regina Krachler

Institut für Anorganische Chemie, Universität Wien
gabriele.wallner@univie.ac.at

Ionic liquids (ILs) are salts with a low melting point (below 100 °C) and they are composed of completely dissociated ions. ILs have many advantages and they are of growing interest in the field of green chemistry. Most of the commonly used ILs are composed of large organic cations and the basic compounds consist of e.g. imidazolium, pyridinium, pyrrolidinium, ammonium and phosphonium(1).

Some of the unique properties of the most widely studied ILs include the large liquid temperature range, high thermal stability, electrical conductivity, and tunable physical properties. Especially the extraction of uranium by using ILs is of enduring interest in the literature as it may also be relevant to spent fuel reprocessing.(4,5)

The presented work is part of a project dealing with purification processes for drinking water. The aim of our work was the extraction of Uranium, Radium and Polonium from aqueous solutions with an IL as well as its back extraction (Pb-^{210} has not been taken into account here as it is removed together with stable lead). Especially the conventional anion exchange step for uranium separation from water (or other sample matrices) is very time consuming (pre-concentration and column chromatography), while the liquid-liquid extraction into an IL also takes its time, but can be done by automated systems. Investigations in our laboratory a few years ago demonstrated that extraction of uranium from water is possible with [A336][TS]2,3, tricaprylmethylammonium thiosalicylate. The ILs under investigation now are [A336][MTBA], tricaprylmethylammonium 2-(methylthio)benzoate, as well as [Mal][A336], [Thiom.][A336], [Mal][Cyphos], [Thiom.][Cyphos], [A336][Ant], [PR4][Ant], [A336][DBA], [PR4][DBA].

Investigations were performed with an artificial uranyl nitrate solution of a known amount of uranium (e.g. a few µg U in 10 ml diluted nitric acid) and mixed with the respective ILs. After centrifugation the phases were separated and the aqueous phase was analysed by liquid scintillation counting (LSC) to ensure that the uranium was removed. Afterwards acids of different molarity or EDTA solutions were used for back extraction of uranium from the organic phase.

For the investigation of the other nuclides, water samples with known amounts of Ra and Po were used (reference samples or mineral waters). For application in the field of drinking water purification we searched also for immobilisation of the ILs on a suitable backing material.

Our goal is to find a new method to shorten and simplify the chemical procedure for the determination of radionuclides (especially uranium) in natural (water) samples as well as to look for a new purification method for drinking water supplies.

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NAM-P36, (Id: 338)

DETERMINATION OF STRONTIUM RADIONUCLIDE USING FLOW-INJECTION ANALYSIS WITH ICP-MS DETECTION

Kamila Kołacińska, Anna Bojanowska-Czajka, Marek Trojanowicz

Institute of nuclear chemistry and technology
k.kolacinska@ichtj.waw.pl

Flow analysis is considered an efficient and universal technique of analytical science. Its wide range of advantages as compared to other known techniques is the argument for its increasing use. Thus, there may be distinguished a simple apparatus construction, which provides low sample use, together with an opportunity to implement many measurement concepts which are not always possible to achieve with common laboratory methods. Generally, this is understood as a variety of system constructions which are adapted to the analysts' ideas and can assure that a sample in the flow is processed chemically i.e. by derivatization, even by multistage reactions, and also physically, for example by sample preconcentration. Another facility of the flow analysis is its automation ability, which means a full control over the fluid flow, its volumes, flow rates and timing.

The main objective of the study is to develop and apply flow systems based on MSFIA - LOV (Multi-syringe flow injection analysis—Lab-on-Valve) to radioanalysis of strontium-90 in reactor coolant samples. The initial stage of research is to optimize the method of mechanized processing of samples. What is worth to remark, is that the construction of the system has been miniaturized enough to allow all the processes of sample preparation to take place in a several centimeters big reaction valve (LOV). The analytical procedure included a couple of stages—firstly, the column in the LOV was loaded with Sr-resinTM and conditioned. In the further stages, a sample was injected and its proceeding—the separation and concentration—took place in the LOV. The proposed analytical procedure included also the elimination of interferences from the elements disturbing detection (with similar affinity to Sr-resin i.e. Ba and isobaric interferences of ^{90}Sr) as well as from the elements present in the coolant (boric acid). The optimization of the process included: selection of the solution and its volume to elute the retained strontium on a column with Sr-resin, the selection and optimization of the solution volume for the elution of interfering elements. The results of optimization were checked by using inductively coupled plasma mass spectrometry (ICP MS).

The wide scale of implementation of this technique to monitoring and determination of radionuclides is a promising idea esspecialy for continuous monitoring of radionuclides in the reactor coolant.

NAM-P37, (Id: 376)

AMERICIUM WINNING FOR ITS DETERMINATION IN BORIC-ACID CONTAINING NPP EVAPORATOR CONCENTRATE

Pavel Bartl, Jana Šuľaková, Jan John, Mojmír Němec

FNSPE-CTU in Prague
pavelbartl80@gmail.com

The aim of this research was to develop a method for pre-concentration of americium from operational radioactive waste for its determination. In these experiments, the attention was paid to separation of americium from boric acid containing evaporator concentrate coming from the Dukovany Nuclear Power Plant by an extraction chromatographic system, where extraction agent used was N,N,N',N'-Tetraoctyl Diglycolamide (TODGA) incorporated in polyacrylonitrile (PAN) matrix. For the elution of retained americium, the oxalic acid solution was chosen. Eluted americium has been, subsequently, determined by alpha spectrometry. Alpha samples were prepared using constant current electrodeposition technique from oxalate-sulfate electrolyte.

The system characterization consisted of several experiments. At first, the dependence of americium weight distribution ratios on pH (ranging between 1.5 and 5.5; adjusted with nitric acid solutions) for four different dilutions of evaporator concentrate was studied, as well as blank experiments where americium weight distribution ratios dependences on pH for every dilution curve were determined for sorption on polyacrylonitrile matrix itself. Next, kinetics of this process, capacity of the used solid phase extractant, and elution profile of americium stripped by oxalic acid and loaded from various solutions were determined. Also the extraction behavior of americium in presence of various anions (namely nitrates, sulfates, oxalates, citrates and chlorides) in scale which can occur in real samples was investigated. The parameters of the electrodeposition process were optimized in an independent series of experiments; the most effective parameters were applied for the alpha samples preparation. Effectiveness of the electrodeposition method was monitored by comparing with simultaneously used liquid scintillation counting (LSC) method.

As a result of a kinetics study, it was found out that about 97 % of americium uptake has been reached after half an hour of phase contact. The study of americium elution from TODGA-PAN resin filled column of bed volume equal to 0.24 mL, after its loading from the boric acid containing evaporator concentrate, revealed that almost all of the approximately 6 kBq of Am-241 loaded (97.43 ± 0.97 % or 98.26 ± 1.77 %, depending on the detection method used) could be eluted by about 1.7 mL of 0.25M oxalic acid solution.

NAM-P38, (Id: 379)

^{90}Y CHERENKOV RADIATION MEASUREMENT FOR ^{90}Sr DETERMINATION

Soběslav Neufuss, Mojmír Němec

CTU in Prague
neufuss@fjfi.cvut.cz

Isotope of strontium ^{90}Sr (one of the nuclear fission products with half-life 28.9 years) is well known for its biochemical similarity with calcium and possible consequent incorporation into human body. Main risk presents its daughter product ^{90}Y (half-life 64.1 hours), which is a high energy β-emitter ($E_{\beta,max} = 2.28$ MeV). That is why the development of fast and effective method of ^{90}Sr determination or monitoring is ongoing last 50 years and it is still one of the important topics. Hence, current demands call for advanced and less time-consuming methods for ^{90}Sr determination. Main aim of this research was focused on the 90Sr determination in simulant solutions of environmental samples without the necessity to wait for the equilibrium with ^{90}Y. This approach is crucial for the development of rapid method of ^{90}Sr determination in environmental samples. Activity of ^{90}Sr was measured through its daughter product ^{90}Y using Cherenkov counting on HIDEX 300 SL and TRIATHLER (both Hidex Oy, Finland) liquid scintillation counters. Two type of samples were used for measurement. The Cherenkov radiation was measured from samples containing equilibrium amount of ^{90}Y or from samples where ^{90}Y growth is observed. A set of solutions with different diffraction indexes and set with different wavelength shifters for increasing Cherenkov radiation yield/detection was studied. It was find out that composition of the solution strongly affects measured background and hence further optimization of the sample content and parameters measurement is necessary. The activity obtained via Cherenkov counting were compared and verified using liquid scintillation counting of ^{90}Sr, similar comparison was done between Triathler (1-photomultiplier) and HIDEX 300 SL (3-photomultipliers, TDCR) measurements.

NAM-P39, (Id: 393)

NUCLEAR ANALYTICAL MERTHODS FOR STUDYING ELEMENTAL COMPOSITION OF CALCIOFIED TISSUERS

Mohammad Anwar Chaudhri[a], **M. Nasir Chaudhri**[b]

[a]*Institute of Biopphysics, Center for Medical Physics and Technology, University of Erlangen-Nuernberg, Erlangen, Germanyrnberg, Germany*
[b]*Pakistan Council of Scientific & Industrial Research, Lahore*
anwar.chaudhri@gmx.net

Various nuclear activation techniques have been developed and applied to determine the elemental composition of calcified tissues (teeth and bones). Fluorine was determined by prompt gamma activation analysis through the ^{19}F(p,a)^{16}O reaction. Carbon was measured by activation analysis with He-3 ions, and the technique of Proton-Induced X-¬ray Emission (PIXE) was applied to simultaneously determine Ca, P, and trace elements in well-documented teeth. Dental hard tissues: enamel, dentine, cementum, and their junctions, as well as different parts of the same tissue, were examined separately. Furthermore, using a Proton Micro-probe, we measured the surface distribution of F and other elements on and around carious lesions on the enamel. The depth profiles of F, and other elements, were also measured right up to the amelo-dentin junction. A new technique has been developed for studying the depth profiles of F in teeth, non-destructively, to larger depths than hitherto known. It is further shown that using this technique depth profile of any element/isotope can be determined non-destructively as long as the reaction cross sections of the particular nuclear reaction are available.

Some results on the microscopic spatial distributions of various elements in kidney stones, using the powerful technique of Laser-Ablation Inductively-Coupled Plasma Mass Spectrometry (La-ICP-MS) are also presented.

NAM-P40, (Id: 411)

APPLICATION OF ICP-MS FOR THE DETERMINATION OF ^{99}Tc AND ^{90}Sr IN PRIMARY COOLANT WATER. OPTIMALIZATION OF MEASUREMENTS AND ANALYSIS OF POTENTIAL INTERFERENCES.

Ewelina Chajduk, Iwona Bartosiewicz, Anna Bojanowska-Czajka, Halina Polkowska-Motrenko

Institute of Nuclear Chemistry and Technology
e.chajduk@ichtj.waw.pl

Sr-90 and Tc-99 are produced by the fission of U-235. Information on Sr, Tc and other fission and activation product content in the primary coolant and at various locations in the purification system can be of considerable value in assessing fuel integrity and performance of purification system component. Using inductively coupled plasma mass spectrometry (ICP-MS) for long-lived radionuclides improves detection limit and accuracy. However, in accurate measurements by ICP-MS method, the contribution of isobaric interferences from atomic- and molecular ions created by plasma gas and/or solvent used should be defined and appropriate ways of their elimination should be introduced. Also, to obtain accurate results in trace and ultra-trace analysis of Tc-99 and Sr-90, optimatization of measurements is necessary. In this work, the influence of different parameters (eg. sample flow rate, nebulizer type) on the strontium and technetium measurements have been taken into account. Acknowledgments:

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NAM-P41, (Id: 413)

ANALYSIS OF HG AND PB BY ICP-MS FOR THE STUDY OF PHYTOREMEDIATION OF Pb AND Hg BY SCIRPUS MUCRONATUS

Ainon Hamzah, Nur Idaya Yatim, Sukiman Sarmani

[a]*Universiti Kebangsaan Malaysia*
ainonh@gmail.com

Phytoremediation is a procedure that uses plants to remove contaminants from the environment and it is a better option of recovery technique because of its cost-effectiveness and environmentally friendly especially for hyperaccumulator plants. Since heavy metals such as lead (Pb) and mercury (Hg) have limited bioavailability in the soil, methods to facilitate their transport to the shoots and roots of plant are required for efficient phytoremediation. The objective of this study was to investigate the effects of adding different heavy metal-tolerant bacterial inoculums (Brevundimonas diminuta SF-S1-5 and Alcaligenes faecalis SF-S1-60) on Pb and Hg accumulation in the shoots and roots of Scirpus mucronatus. The experiment was done in a greenhouse by planting acclimatized S. mucronatus in crates (52 cm length × 30 cm width × 25 cm height) with 30 kg sand and spiked with 100 ppm Pb and 1 ppm Hg, separately. The bacterial inoculums were added into the soil and the plants were watered using tap water to ensure the growth. The plants and sand samples were collected on day 1, 7, 14, 28 and 42, and the heavy metals in plant samples were extracted by using wet digestion method. The total concentration of Pb and Hg in samples was analyzed using Inductively Coupled Plasma-Mass Spectrometry(ICP-MS) and Atomic Absorption Spectrometer (AAS), respectively, and the phytoextraction ability was assessed in terms of its metal transfer factors; bioaccumulation factor (BAC), bioconcentration factor (BCF) and translocation factor (TF). Experimental results showed that after 42 days of treatment, the highest accumulation of Pb in shoot (265.8 ± 47.3 mg/kg^{-1} dryweight) was found in control plant (no addition of bacteria), while in root (697.2 ± 8.5 mg/kg^{-1}dryweight) was found in plant inoculated with A. faecalis SF-S1-60. On the other hand, the highest accumulation of Hg (2.21 ± 0.08 and 5.71 ± 0.31 mg/kg-1 dryweight in plant shoot and root, respectively) were obtained in plant inoculated with A. faecalis SF-S1-60. In addition, plant inoculated with A. faecalis SF-60 showed the highest BAC and BCF values, and the lowest TF value compared to plant inoculated with B. diminuta SF-S1-5 and the control plant. This suggests that A. faecalis SF-60 can be utilized as an enhancer for accumulation of Pb and Hg in soil by S. mucronatus.

NAM-P42, (Id: 431)

DETERMINATION OF URANIUM ISOTOPES COMPOSITION USING LSC

Mojmír Němec, Kateřina Čubová

Department of Nuclear Chemistry, Faculty of Nuclear Sciences and Physical Engineering, CTU in Prague
mojmir.nemec@fjfi.cvut.cz

Fast, simple and effective method for determination of enrichment/depletion of uranium samples that can be used not only in the laboratory but also for unknown samples at inspections outdoors, it is for longer time in insistent demand of specialists. The technique of liquid scintillation counting (LSC) in the mobile mode represented by Triathler LSC Counter (Hidex Oy) could be a valuable tool for this type of measurement. Application (usage) of this equipment allows several advantages: determination of enrichment/depletion under off-road conditions, combination of alpha, beta and Cherenkov counting (gives a complete picture required), milligram or even sub-milligram amounts of the sample (comparing e.g. to gamma-ray spectrometry), and easy preparation of the sample by mixing of U-salt with scintillation cocktail (comparing to e.g. alfa-spectrometry).

The method can be used as the final step of suitable separation/concentration method. The method was also adjusted as a task for students in “Practical exercises in radiochemistry techniques” in the educational programme “BSc in Nuclear Chemical Engineering”.

NAM-P44, (Id: 437)

A COMPARISON OF EXPANDED UNCERTAINTIES FOR MEASURING IODINE LEVELS IN NUTRITIONAL MATERIALS BY PSEUDO-CYCLIC EPITHERMAL INAA-AC USING SINGLE COMPARATOR AND K_0 METHODS

Amares Chatt[a], B.J.B. Nyarko[b], E.H.K. Akaho[b], J.J. Fletcher[b]

[a] *Dalhousie University*
[b] *Ghana Atomic Energy Commission*
a.chatt@dal.ca

A combination of different types of instrumental neutron activation analysis (INAA) technique was developed for the determination of iodine in various food items from Ghana [1]. The methods involved conventional INAA, epithermal INAA (EINAA), pseudo-cyclic INAA (PC-INAA) and pseudo-cyclic EINAA (PC-EINAA) in conjunction with conventional and anti-coincidence (AC) gamma-ray spectrometry using both single comparator and k_0 standardization methods. The uncertainties associated with these methods were evaluated following ISO GUM procedures. The trueness of the methods were checked by analyzing several reference materials (RM) and standard reference materials (SRM) provided by the U.S. National Institute of Standards and Technology (NIST). Our results were in good agreement with the certified values. The expanded uncertainties associated with the measurement of iodine levels in NIST RM 8415 Whole Egg Powder by a PC-EINAA-AC method using the single comparator and k_0 standardization procedures will be presented. The expanded uncertainty ($\kappa = 2$, ~95 % CL) of 1.81 ±0.48 was obtained for the k_0 procedure compared to that of 1.85 ±0.22 for the single comparator procedure. The value for the k0 procedure appears to be slightly influenced by the uncertainties in the nuclear constants and detector full photopeak efficiency determination.

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NAM-P45, (Id: 444)

ELEMENTAL DETERMINATIONS IN BIOLOGICAL AND ENVIRONMENTAL SAMPLE USING PGNAA FACILITY AT DALAT NUCLEAR RESEARCH INSTITUTE

Canh Hai Nguyen[a], Huu Tan Vuong[b], Tuan Anh Tran[a]

[a]*Nuclear Research Institutey*
[b]*Viet Nam Agency for Radiation and Nuclear Safety*
nchai@hcm.vnn.vn

In this paper we present the results of determination of element concentrations in biological, environmental samples by using PGNAA facility which was installed at channel No. 4 of Dalat research reactor. The biological standard samples, Bovine Liver NBS 1577a and Rye Grass BCR 281 and environmental standard samples, Coal Fly Ash NBS 1633a were analyzed to verify the analytical ability of the facility. After that, the concentrations of C, N, S, K, Cl in biological samples and concentration of Al, K, Ti, Mn, Fe, Ca, Gd, Sm, Cd and Si in environmental samples were determined. The detection limits of the above elements were also investigated.

Chemistry of Actinide and Trans-actinide Elements (TAN)

Verbal presentations

TAN-I01, (Id: 92)

GAS PHASE CHEMISTRY OF SUPERHEAVY ELEMENTS

Alexander Yakushev

GSI Helmholtzzentrum für Schwerionenforschung GmbH
a.yakushev@gsi.de

Long-lived isotopes of superheavy elements (SHE) beyond Rf, i.e., with atomic number $Z \geq 104$ can be produced via fusion reactions between heavy actinide targets and neutron-rich projectiles at a rate of only single atoms per minute ($Z = 104$) or per week ($Z = 114$). Investigating these neutron-rich SHE nuclei using rapid gas-chemical separation and subsequent on-line detection provides an independent chemical characterization and an alternative separation technique to electromagnetic recoil separators. Approaching the heaviest elements, the coupling of chemistry setups to a recoil separator promises extremely high sensitivity due to strong suppression of background from unwanted species. The use of a combination of two separation techniques, physical pre-separation and gas phase chemistry opens the possibility for investigating new compound classes of superheavy elements [1,2].

Electron shells of SHE are influenced by strong relativistic effects caused by the high value of Z. The lighter transactinides with $Z = 104$-108 were experimentally shown to be members of groups 4 through 8 of the Periodic Table of the elements [3]. Early atomic calculations predicted copernicium (Cn, element 112) and flerovium (Fl, element 114) to be noble gas-like due to the strong relativistic stabilization of the closed-shell configuration $6d^{10}7s^2$ in Cn, and the very large spin-orbit splitting in 7p AOs resulting in the quasi-closed-shell configuration $7s^27p_{1/2}^2$ in Fl [4]. Recent fully relativistic calculations studying Cn and Fl in different environments suggest those to be less reactive compared to their lighter homologues in the group, but still exhibiting metallic character [5]. The dilemma whether Cn and Fl are noble gases or rather noble metals calls for experiments. Experimental gas-chromatography studies on Cn have, indeed, revealed a metal-metal bond formation with gold [6]. In contrast to this, for Fl, the unexpected formation of a weak physisorption bond upon adsorption on gold was inferred from first experiments [7]. The recent gas chromatography study on Fl upon the adsorption on gold was performed exploiting clean Fl samples, provided after the pre-separation with the gas-filled separator TASCA [8]. Two Fl decay chains were detected under background-free conditions. The observed behavior of Fl in the chromatography column is indicative of Fl being less reactive than the nearest homolog Pb. The evaluated lower limit of the adsorption enthalpy $-\Delta H_{ads(Fl)} > 48$ kJ/mol (95 % confidence level) reveals the formation of a metal-metal bond with Au, which is at least as strong as that of Cn, and thus demonstrates the metallic character of Fl [9].

In other experiments, a first molecule of a compound class, which was previously inaccessible for superheavy elements, was recently investigated. The adsorption behavior of $Sg(CO)_6$ was studied by gas-solid chromatography in comparison with that of its nearest homologs in the group, Mo and W [10-12].

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TAN-V02, (Id: 167)

DECOMPOSITION STUDIES OF W AND MO CARBONYL COMPLEXES AND THEIR IMPLICATIONS FOR FUTURE EXPERIMENTS WITH $Sg(CO)_6$

Ilya Usoltsev[a], Robert Eichler[a], Antonio Di Nitto[b], Christoph Düllmann[c], Fan Fangli[d], Willi Hartmann[e], Minqhiu Huang[f], Egon Jäger[e], Daiya Kaji[f], Jumpei Kanaya[f], Yusuke Kaneya[g], Jadambaa Khuyagbaatar[c], Andreas Türler[a], Birgit Kindler[e], Jens Kratz[b], Joerg Krier[e], Yuki Kudou[f], Nikolaus Kurz[e], Bettina Lommel[e], Sunao Miyashita[g], Kouji Morimoto[f], Kosuke Morita[f], Masashi Murakami[f], Yang Wang[d], Yuichiro Nagame[g], Heino Nitsche[h], Katsuhiro Ooe[i], Matthias Schädel[g], Jutta Steiner[e], T. Sumita[f], Mirei Takeyama[f], Kengo Tanaka[f], Atsushi Toyoshima[g], Kazuaki Tsukada[g], Julia Even[c], yasuo Wakabayashi[f], Norbert Wiehl[c], Sayaka Yamaki[f], Qin Zhi[d], Alexander Yakushev[e], Hiro Haba[f], Masato Asai[g], Tetsuya Sato[g], Holger Brand[e]

[a]*Paul Scherrer Institut*
[b]*Johannes Gutenberg-Universität Mainz*
[c]*Helmholtz-Insitut Mainz*
[d]*Institute of Modern Physics Lanzhou*
[e]*GSI Helmholtzzentrum für Schwerionenforschung GmbH*
[f]*Nishina Center for Accelerator-Based Science, RIKEN*
[g]*Advanced Science Research Center, Japan Atomic Energy Agency*
[h]*University of California, Berkeley*
[i]*Niigata University, Niigata, Niigata*
ilya.usoltsev@psi.ch

Recent experiments at RIKEN (Japan) showed that Sg carbonyl ($Sg(CO)_6$) can be produced with yields high enough for experimental investigation of its chemical properties [1]. According to theoretical calculations [2], which include so-called relativistic effects, $Sg(CO)_6$ is expected to be slightly more stable than $W(CO)_6$. In this work we aimed at designing an experimental setup for testing this theoretical prediction.

Carbonyl complexes of W and Mo, as lighter homologues of Sg, were chosen for testing the setup. Gas-jet systems as well as the detection system used in our work are described in [1]. Two alpha-active tungsten isotopes were produced in fusion-evaporation reactions $^{144}Sm(^{24}Mg,xn)163\text{-}164W$, while $^{nat}Zn(^{24}Mg,xn)87\text{-}88W$ allowed for formation of β+-decaying molybdenum. The Gas-filled Recoil Ion Separator (GARIS) provided an effective separation of evaporation residues from the beam and from multinucleon transfer reaction products. Evaporation residues were thermalized in a recoil transfer chamber [3], flushed by a He/CO gas mixture. Formed carbonyl products [4] were transported to a decomposition column, held at different temperatures, and bypassed by a column of the same size made of PFA Teflon. Complexes transported through this bypass or the decomposition column were deposited at the low-temperature end of the COMPACT detector [1] according to their adsorption enthalpy and thus provided quantitative information about the production and the decomposition rates, respectively. Obtained results are discussed in the light of future experiments with $Sg(CO)_6$.

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TAN-V03, (Id: 93)

TOWARDS SELENIDES OF THE SUPERHEAVY ELEMENTS COPERNICIUM AND FLEROVIUM

Nadine Mariel Chiera, Robert Eichler,Andreas Türler

Paul Scherrer Institute, University of Bern
nadine-mariel.chiera@psi.ch

Transactinide's chemical behavior is similar to their lighter homologues in the corresponding group of the periodic table. However, with increasing nuclear charges, superheavy elements (SHE) show deviations from the periodicity of chemical properties [1]. An experimentally exceptionally favourable case for comparative studies is the possibility of a simultaneous production of Cn (Z = 112) and Fl (Z = 114) in Ca-48 induced nuclear fusion reactions with Pu-242 / Pu-244 [2]. Since these superheavy elements are characterized by short half-lives and low production rates, their chemical behavior has to be explored on a single atomic scale. For this purpose gas chromatography is used, allowing for efficient studies of the interaction of volatile gas-phase species with stationary surfaces [1]. Sulphur was chosen as stationary chromatography material for such a comparative studies. In fact, extrapolative predictions, in which thermochemical state functions are correlated mutually, showed that both Cn and Fl may form stable sulfides, and since the stability trends of sulfides formation in group 12 and 14 were predicted to be opposite, FlS was expected to be more stable than CnS. In preparation of the chemical investigations of these superheavy elements, isothermal model experiments with Hg (copernicium homologue) and sulfur surfaces were conducted. Although the formation of HgS(s) is thermodynamically favored (ΔH_{ads}Hg(S) < -75 kJ/mol), it was difficult to obtain reproducible results due to the slow interaction kinetics between the sulfur S8 rings (dominant sulfur allotrope at room temperature), and Hg.

Recent studies reported amorphous nano-selenium as an efficient mercury sorbent, due to the high affinity of Se towards Hg and the high surface-to-mass ratios of the nanoparticles [3]. Hence, extrapolative predictions for the group 12 and 14 selenide formation were done. Again, stability trends in group 12 and 14 are predicted to be opposite: the formation of FlSe is expected to be favored or at least similar to the homologue selenides, while the interaction between Cn and selenium is expected to be a weak physisorption. The chemical system Hg / Se is an ideal model system to investigate the kinetics and thermodynamics of the adsorption and reaction of a volatile noble metal with selenium surfaces. Hence, first model experiments on the interaction of elemental Hg with red amorphous selenium surfaces, obtained through supercooling of high temperature Se vapors on quartz tubes, were performed.

Here, first results from these investigations will be presented. Some conclusions will be drawn, which are important for the preparation of further chemical investigations of Cn and Fl.

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TAN-V04, (Id: 220)

PRODUCTION OF ^{261}Rf, ^{262}Db, AND ^{265}Sg FOR CHEMICAL STUDIES USING GARIS AT RIKEN

Hiromitsu Haba[a], Daiya Kaji[a], Yoshitaka Kasamatsu[b], Hidetoshi Kikunaga[c], Yukiko Komori[b], Hisaaki Kudo[d], Kouji Morimoto[a], Kosuke Morita[a], Masashi Murakami[a], Katsuhisa Nishio[e], Kazuhiro Ooe[d], Atsushi Shinohara[b], Atsushi Toyoshima[e], Kazuaki Tsukada[e],Yasuo Wakabayashi[a]

[a]*RIKEN*
[b]*Osaka University*
[c]*Tohoku University*
[d]*Niigata University*
[e]*Japan Atomic Energy Agency*
haba@riken.jp

Recently, chemical characterization of superheavy elements (SHEs) with atomic numbers $Z \geq 104$ is an extremely interesting and challenging research subject in modern nuclear and radiochemistry [1,2]. At RIKEN, we have been developing a gas-jet transport system coupled to the RIKEN gas-filled recoil ion separator GARIS as a novel technique for SHE chemistry [3–5]. This system is a promising approach for exploring new frontiers in SHE chemistry; (i) background radioactivities originating from unwanted by-products are strongly suppressed, (ii) an intense primary heavy-ion beam is absent in the gas-jet chamber and hence a high gas-jet yield is achieved, and (iii) the beam-free conditions also make it possible to investigate new chemical reactions. In this work, we investigated production and decay properties of long-lived radioisotopes of Rf ($Z = 104$), Db ($Z = 105$), and Sg ($Z = 106$) available for chemical studies [6–9]. Oxygen-18, ^{19}F, and ^{22}Ne beams were extracted from the RIKEN linear accelerator. The isotopes of ^{261}Rfa,b, ^{262}Db, and ^{265}Sga,b were produced in the reactions of ^{248}Cm(^{18}O,5n)^{261}Rfa,b, ^{248}Cm(^{19}F,5n)^{262}Db, and ^{248}Cm(^{22}Ne,5n)^{265}Sga,b, respectively. The evaporation residues of interest were separated in flight from the beam particles and the majority of the nuclear transfer products by GARIS and were guided to a gas-jet chamber at the focal plane of GARIS. The evaporation residues were then thermalized in He gas, attached to KCl aerosol particles, and were extracted through a Teflon capillary to the chemistry laboratory. Alpha and spontaneous fission (SF) decays of ^{261}Rfa,b, ^{262}Db, and ^{265}Sga,b were measured with the rotating wheel apparatus MANON under low background conditions. In the conference, perspectives of the next-generation SHE chemistry opened by GARIS will be also presented.

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TAN-V05, (Id: 267)

EXCITATION FUNCTIONS FOR PRODUCTION OF RUTHERFORDIUM ISOTOPES IN THE ^{248}Cm + ^{18}O REACTION

Masashi Murakami[a], Shin-ichi Goto[b], Hirohumi Murayama[b], Takayuki Kojima[b], Daiya Kaji[a], Kouji Morimoto[a], Hiromitsu Haba[a], Yuki Kudou[a], Takayuki Sumita[a], Ryutaro Sakai[a], Akira Yoneda[a], Kosuke Morita[a], Yoshitaka Kasamatsu[c], Hidetoshi Kikunaga[d], Tetsuya Sato[e], Hisaaki Kudo[b]

[a]*Nishina Center, RIKEN*
[b]*Niigata University*
[c]*Osaka University*
[d]*Tohoku University*
[e]*Japan Atomic Energy Agency*
masashi.murakami@riken.jp

Rutherfordium-261 (^{261a}Rf; $T_{1/2} = 68$s) has been used in chemical studies of element 104, Rf [1]. In recent years, it was reported that there exists a spontaneously-fissioning (SF) isomer (^{261b}Rf; $T_{1/2} = 2.6$ s) in ^{261}Rf [2-6]. On the other hand, a SF isomer with the similar half-life of 2.1 s also had been reported as ^{262}Rf ($T_{1/2} = 47$ ms) [7,8]. It is possible that these two SF isomers are the same and one of these is misassigned. In this work, the excitation functions of Rf isotopes in the ^{248}Cm + ^{18}O reaction were measured to clarify the ambiguity on the assignment of the fissioning isomers in ^{261,262}Rf [9]. Rutherfordium isotopes were produced by bombarding the ^{248}Cm target with an ^{18}O beam supplied from the RIKEN linear accelerator. The beam energies were 88.2, 90.2, 94.8, and 101.3 MeV at the center of the target. A gas-filled recoil ion separator (GARIS) was used to separate the evaporation residues (ERs) in-flight from the incident particles and majority of by-products. ERs were then implanted into a position-sensitive Si strip detector mounted at the focal plane of GARIS. The beam on-off method was applied to measure the decay events of Rf isotopes under low background conditions. At each beam energy, beam on-off periods were set to 6 s-6 s and 0.1 s-0.1 s. The shape of the measured excitation function of ^{261a}Rf agreed with the previously reported one [10]. The excitation function of a-few-second SF nuclide exhibited the maximum cross section at 94.8MeV, and the shape of the excitation function was almost the same as that of ^{261a}Rf. On the other hand, short-lived SF decays were observed at 88.2 MeV and 101.3 MeV, and they were assigned to ^{262}Rf and ^{260}Rf, respectively. Such the short-lived SF decay was not observed at 94.8 MeV. Therefore, we concluded that a-few-second SF nuclide previously assigned to both ^{261}bRf and ^{262}Rf is not ^{262}Rf but ^{261b}Rf.

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TAN-V06, (Id: 324)

GAS CHROMATOGRAPHY OF ELEMENT 113

Yury Albin, Nikolay Aksenov, Sergei Dmitriev, Gospodin Bozhikov, Aleksey Sabelnikov, Lidia Sokolova, Oleg Petrushkin, Alexander Yeremin, Viktor Chepigin, Oleg Malyshev, Aleksandr Svirihin, Andrew Isaev, Vyacheslav Lebdev, Genndiy Starodub

Jlint Institute for Nuclear Research
albin@jinr.ru

The discovery of new superheavy elements with Z = 113-118 in ^{48}Ca induced nuclear reactions was one of the most outstanding scientific achievement of the last decade. The long halflives of radionuclides of these elements extend the application of radiochemical techniques to their chemical characterization and to test the hypothesis about the impact of so-called "relativistic effects" on the chemical properties of superheavy elements [1]. According to Periodic Table element 113 belongs to group 13and its ground state electronic structure is $[Rn]5f^{14}6d^{10}7s^{2}7p^{1}$ (i.e. homolog of Tl). Modern relativistic calculations predict weak adsorption on inert surfaces due to strong contraction and stabilization of surface 7 $p_{1/2}$ orbital(adsorption enthalpy on Teflon is 14 kJ/mol, and on polyethylene 16 kJ/mol) [2]. At the same time due to relativistic stabilization $7p_{1/2}$ and high spin-orbital splitting of 7p element 113 has to easily be adsorbed (in H_2/He) on Au surface (adsorption enthalpy is - 158.6 kJ/mol) [1]. Taking this into consideration we studied a gas chromatography of the given upwards theoretical predictions of element 113 properties, its adsorption of element 113 on a Au surface was studied compared to Hg and At (similar as in the case of Cn and Fl [3, 4]).

The reaction ^{4}8Ca + ^{243}Am was used to produce nuclides 288115 and its daughter 284113 [5]. Nuclear reaction products were stopped in a He / Ar gas mixture and atoms of volatile elements were transported by the gas jet through a Teflon capillary to chromatography column. Gas chromatographic column is a two-detector system consisting of Si detectors covered with gold. First detector operated at room temperature (20 °C) and the second one with a temperature gradient from +20 °C to -60 °C. A total of five chains of 284113 was detected in the first isothermal detector. Adsorption enthalpy of element 113 on gold surfaces is comparable with that of mercury, which indicates that element 113 is a volatile metal and weakly interacts with inert surfaces. The probabilities for a random origin are $7.6\times10e^{-3}$, $6.6\times10e^{-5}$, $2\times10e^{-4}$, $6.7\times10e^{-10}$, $5.7\times10e^{-6}$ calculated using Poisson distribution [6].Direct formation of nuclide 284113 in irradiation of 243Am with 48Ca in multi-nucleon transfer reactions (18 protons and 23 neutrons) is virtually impossible. From this we can deduce that isotopes of 113-111-109-107-105 elements detected in the experiment are daughters of mother nuclide 288115 synthesized in a reaction ^{243}Am(^{48}Ca,3n). The work was supported by Russian Foundation for Fundamental Research (project code 13-03-12205 ofi-m).

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TAN-V07, (Id: 350)

ADSORPTION BEHAVIOR OF SUPER-HEAVY ELEMENTS (Z ≥ 112) ON METAL AND INERT SURFACES

Josef Anton

University of Ulm
josef.anton@uni-ulm.de

Investigation of chemical and physical properties of the heaviest elements (those beyond Lr) is a hot topic since several decades. In this time period, many new elements were discovered and after a proper characterization were added to the Periodic Table of the elements. The main problem of such investigations, however, is the rather short half-life of these elements, which requires the development of innovative experimental techniques. Nowadays the research focusses on the chemical properties of the element 114. So far, two gas chromatography experiments to study the interaction strength of element 114 with a gold surface have been performed with conflicting results. One experiment [1] reported a weak interaction of element 114 with a gold surface, leading to adsorption only at very low temperatures of approximately -90 °C, while in the second experiment [2] adsorption on gold has been observed at the room temperature, indicating a much stronger bond between element 114 and gold. To resolve this conflict, further experiments on chemical properties of the element 114 will be performed at GSI and PSI/JINR in the next two years. For theoretical studies, standard quantum-mechanical packages that treat a system mostly non- or only scalar-relativistically are not satisfactory: Due to rather significant relativistic effects on the electron shells of the heaviest elements a fully-relativistic four-component description is required.

Recently, we have studied the adsorption behavior of elements 112, Cn, and 114 and their lighter homologues Hg and Pb, respectively, on gold surfaces [3] by using a cluster-approach [4]. We found that Hg/Cn and Pb/114 prefer different adsorption sites. Also, the adsorption energies of elements 112 and 114 are related to those of their lighter homologues in a different way. Thus, Eb(Cn) is only slightly (0.1-0.2 eV) lower than Eb(Hg), while Eb(114) is much lower (1.4 eV) than Eb(Pb). This is due to the fact, that in element 112 both the relativistically stabilized 7s and destabilized 6d AOs take part in the binding, while for element 114 binding is mostly determined by the relativistically stabilized $7p_{1/2}$ orbital. In contrast to Pb, where $6p_{3/2}$ strongly contributes to the surface bond, the $7p_{3/2}$ participate much less due to its large relativistic destabilization (the spin-orbit splitting between $7p_{1/2}$ and 7p372 is about 3.5 eV). Furthermore, binding of element 114 to gold is similar to that of Cn, however, about 0.2 eV stronger. Our predicted sequence in the Eb values is Cn < Hg < E114 << Pb. Thus, we predicted that in the thermochromatography experiments, element 114 will adsorb right at the beginning of the chromatography column with the hot end of 35 °C, at the position of Hg. This prediction was recently confirmed experimentally [2].

In this talk we will present theoretical results on adsorption energies and distances of the elements from 112 to 114 and their homologues on metal (gold) and inert (SiO_2) surfaces.

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TAN-V08, (Id: 264)

HIGHER OXIDES, PEROXIDES, AND SUPEROXIDES OF EARLY TRANSURANIUM ELEMENTS: A RELATIVISTIC DENSITY FUNCTIONAL STUDY

Andrei Zaitsevskii[a], Nikolai S. Mosyagin[b], Anatoly V. Titov[b], W. H. Eugen Schwarz[c]

[a]Petersburg Nuclear Physics Institute / NRC Kurchatov Institute
[b]Petersburg Nuclear Physics Institute
[c]Department of Chemistry, Tsinghua University, Beijing / Theoretical Chemistry, University Siegen
azaitsevskii@pnpi.spb.ru

The results of relativistic electronic structure calculations on simple molecules of higher oxides (actinide oxidation state VI through VIII), peroxides, and superoxides of Pu, Am, and Cm are reported. The calculations employed accurate "small-core" two-component pseudopotentials derived from the outer (valence) shell solutions of the atomic Dirac–Fock–Breit equations with the Fermi nuclear model; the optimal description of the valence (rather than semicore) shells appears essential for reproducing the chemical properties. The molecular semicore/valence many-electron problem was solved by the two-component non-collinear relativistic DFT technique with the fully unrestricted optimization of Kohn–Sham one-electron spinors expanded in weakly contracted Gaussian basis sets; the bases were optimized for spin-orbit-coupled calculations. Ground-state equilibrium structures, vibrational frequencies and charge and spin magnetization density distributions were analyzed in order to characterize the different isomers in chemical terms.

The stability of higher oxidation states in oxygen compounds rapidly decreases from Pu to Am and further to Cm. All "true" An tetroxides (An = Pu, Am, Cm), were predicted to be thermodynamically unstable in realistic gas-phase conditions with respect to the decay into lower oxides (An_2O_6 or An_2O_7) and molecular oxygen as well as to the conversion into dioxosuperoxides $[AnO_2](O_2)$ which appear to be the most stable $An{\cdot}4O$ species in all cases. Structural and magnetization-density features of the tetroxides indicate that Pu and Am are octavalent while Cm is only hexavalent. No structural similarities between higher oxides of Pu-Am and Os-Ir was found. A variety of bis-dioxygen species of different nature ($An(O_2)_2$, $[AnO_2](O_2)_2$) is discussed. The stability of some heterooxide molecules ($PuAmO_6$ and especially $PuAmO_7$) with respect to the transformation to the mixture of the corresponding pure oxides is noticed. Implications for the chemistry of the transuranium element – oxygen systems and the identification of volatile An-oxygen compounds are discussed.

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TAN-V09, (Id: 205)

COMPLEXATION AND EXTRACTION STUDIES OF HIGH VALENCY ACTINIDES BY SALICYLIDENEIMINE-BASED LIGANDS

Christian Bustillos, Mikael Nilsson, Cory Hawkins

University of California Irvine Department of Chemical Engineering
bustillos.christian@gmail.com

Increased knowledge of actinide coordination chemistry and the development of advanced actinide separation processes are essential to reducing the radiotoxicity of used nuclear fuel. Commercial separation techniques for nuclear fuel (i.e. PUREX) selectively remove U(VI) and Pu(IV) from the other components, while the minor actinides, e.g. Np and Am, are not extracted. However, these four mid-actinides (U, Np, Pu, Am) all have highly accessible oxidation states (+V, +VI) at which they exist as linear dioxo actinyl ions $[AnO_2]^{n+}$. The An = O bonds are incredibly stable, permitting ligand coordination in the equatorial plane of the metal ion center and affording a geometry for unique bonding characteristics. Tetradentate Schiff bases can be prepared with synthetic ease and have been used extensively in the area of metal ion coordination chemistry. These ligands have rather planar structures that chelate around the equatorial plane of actinyl ions through their N(2)O(2) binding site, presenting the possibility that this distinct coordination environment may facilitate the selective solvent extraction or aqueous retention of pentavalent and hexavalent actinides. We have synthesized multiple organic and water soluble Schiff base ligands, of the salen and salophen type, and have conducted complexation and solvent extraction experiments with UO_2^{2+} and NpO^{2+}, as representative actinyl ions. Preliminary results indicate that salen-based ligands show promise for extracting uranium from nitrate media, while a water soluble salen and a lipophilic di-t-butyl-salophen are the most promising in providing crystallized structures with UO_2^{2+} and NpO^{2+}. Ongoing studies of these ligands in our laboratories will help to further define possible methods for used nuclear fuel separations.

TAN-V10, (Id: 136)

COMPLEXATION OF ACTINIDES BY RAMIFIED N-MACROCYCLE DOTA

Matthieu Audras[a], Laurence Berthon[a], Nicole Zorz[a], Claude Berthon[a], Dominique Guillaumont[a], Thomas Dumas[a], Philippe Moisy[a], Christoph Hennig[b], Pier Lorenzo Solari[c]

[a]*CEA Marcoule, France*
[b]*ESRF*
[c]*SOLEIL, France*
matthieu.audras@cea.fr

The comprehension of the actinides affinity for interest ligands has been a pivotal issue since the beginning of the nuclear fuel reprocessing. The difference in interaction between N-donors ligands and O-donor ligands is a hint on the selectivity difference between trivalent and tetravalent actinides(1). The study of molecules featuring both N and O-donor functions may be a way to reach a better understanding. Thus, the poly-amino-carboxylate ligands form an interesting family of f-element cations chelating agents. One specific ligand has been selected for this study: the DOTA macrocycle (1,4,7,10-tetraazacyclododecane-tetraacetic acid).

This molecule has been widely studied with lanthanides(2), but few investigations have been carried out with actinides. The main goal of this work is to extend the investigations to the complexing behavior of DOTA with An(III) and An(IV) in aqueous solution. In order to achieve it our methodology will consist in a twofold approach, combining experimental studies with modeling calculations. Americium(III) and plutonium(III) have been selected to represent the An(III) series, while thorium(IV) and neptunium(IV) have been chosen to represent the An(IV) series. Besides the conventional analytical techniques (UV-Vis spectrophotometry, NMR and ESI-MS), the systems have been monitored with X-ray absorption spectroscopy (EXAFS) to determine the stoichiometry of the complexes, identify the ligand complexing sites and probe the coordination sphere of the cation.

The experimental EXAFS spectra are compared to models obtained thanks to quantum chemistry calculations. The experiments proved DOTA forms complexes with both An(III) and An(IV). Complexation of An(III) is similar to what has been observed with Ln(III) i.e. the slow formation of a (1:1) complex(2,3). At $t_0+\varepsilon$, the reaction first leads to the formation of an intermediate species where the cation is complexed by the carboxylate arms only. Then, the system slowly evolves towards the final species and the cation eventually gets inside the cage formed by the N-cycle and the carboxylate arms.

In equivalent chemical conditions, Np(IV) behaves as the An(III): the cation also ends up inside the cage. However, Th(IV) does not present the same behavior, as we see no significant participation of the N-ring in the coordination sphere (no intense signal on the EXAFS spectrum of an M-N bond at ca. 2.4 Å.

The differences in coordination mode regarding the An(III)-DOTA and An(IV)-DOTA systems will be discussed: stoichiometry, participation of the complexing sites and distances to the metallic center. The evolution over time of the formed species will be considered.

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TAN-V11, (Id: 337)

ON THE ORIGIN OF SELECTIVITY OF BIS-TRIAZINYL BIPYRIDINE LIGANDS FOR COMPLEXATION OF AMERICIUM(III) OVER LANTHANIDES. QUANTUM MECHANICAL ANALYSIS OF M–N BONDS

Jerzy Narbutt[a], **Artur Wodynski**[b], **Magdalena Pecul**[b]

[a] *Institute of Nuclear Chemistry and Technology*
[b] *Department of Chemistry, University of Warsaw, 02-093 Warsaw, Poland*
j.narbutt@ichtj.waw.pl

Selective separation of actinide elements from highly radioactive nuclear waste is the key issue for modern technologies of nuclear waste reprocessing. Partitioning of long-lived minor actinides, in particular americium, followed by their transmutation into short-lived and stable nuclides would lead to a significant reduction of long-term environmental hazard from this radiotoxic waste, and contribute to the development of safe nuclear power. Derivatives of 6,6'-bis([1,2,4]-triazin-3-yl)-2,2'-bipyridine (BTBP), the tetra-N-dentate lipophilic ligands which selectively extract trivalent actinides (An) over lanthanide fission products (Ln) from nitric acid solutions (modeling PUREX raffinate) to organic solvents (SANEX process), have been considered the most promising species for partitioning the minor actinides from high-level nuclear waste.

Recent theoretical studies, carried out on two pairs of americium and europium complexes formed by the BTBP ligands, neutral $[ML(NO_3)_3]$ and cationic $[ML_2]^{3+}$ where M = AmIII or EuIII, and L = 6,6'-bis-(5,6-diethyl-1,2,4-triazin-3-yl)-2,2'-bipyridine (C2-BTBP) [J. Narbutt, W.P. Oziminski, Dalton Trans. 41, 14416 (2012)], have shown that greater thermodynamic stability (in water) of the Am-L complexes than that of the analogous Eu species, caused by greater covalencies of the Am–N than Eu–N bonds, is the main reason of BTBP selectivity in the separation of these metal ions.

Theoretical analysis of Am–N and Eu–N bonds in the BTBP complexes was carried out in this work, with the use of one-component Zeroth Order Regular Approximation (ZORA) Hamiltonian and Kohn-Sham density functional theory. Kohn-Sham orbitals were analyzed with Natural Population Analysis (NPA), Mulliken Population Analysis, Second Order Perturbation Theory (SOPT) implemented for Natural Bond Orbitals (NBO) and Symetrized Fragments Orbitals (SFO) with overlap populations density-of-states (OPDOS). Electron density was analyzed with The Quantum Theory of Atoms in Molecules (QTAIM). The QTAIM analysis for the bond critical points (BCP) confirms mostly ionic character of M-N bonds with slightly bigger covalent contribution for the Am-N than Eu-N bonds. This is due to a bigger charge transfer from the ligand to the Am than Eu ion, in particular to the 6d(Am) and 5d(Eu) orbitals. The results of the SOPT method show that the greater shift of electron density on the 6d(Am) orbitals is due to the large overlap integrals of 6d(Am) with the ligand donor orbitals, not to the smaller energy gap. This is in line with the calculated greater radial expansion of the 6d(Am) than 5d(Eu). The OPDOS coupled with the SFOs has shown that outermost occupied MOs as well as inner MOs are involved in the M-N interactions.

This work was financed from the National Centre for Research and Development through the Strategic Program Technologies Supporting Development of Safe Nuclear Power Engineering, task 4: Development of spent nuclear fuel and radioactive waste management techniques and technologies.

TAN-I12, (Id: 364)

UTILIZATION OF TECHNETIUM AND ACTINIDE COMPOUND SYNTHESIS AND COORDINATION CHEMISTRY FOR THE NUCLEAR FUEL CYCLE: EXPLORING SEPARATIONS, FUELS, AND WASTE FORMS

Kenneth Czerwinski, William Kerlin, Erik Johnstone, Frederic Poineau

University of Nevada, Las Vegas
czerwin2@unlv.nevada.edu

Compared to other elements on the periodic table, technetium and the actinides are less explored, especially in areas of compound synthesis and coordination chemistry. The nuclear fuel cycle offers opportunities to investigate fundamental and applied technetium and actinide chemistry in more detail, with fundamental complexation chemistry providing insight into waste forms, fuels, and separations. Examples are given for technetium and actinide solution and solid phases, with the coordination chemistry explored by spectroscopy and diffraction. An overview on technetium waste forms is provided, highlighting the need for fundamental information on this element to improved synthetic routes and understand resulting behavior. The thermal and hydrothemal based synthesis of technetium compounds is described. Spectroscopic and diffraction results are provided. Trends in the products from computation [1] and experiment are discussed, emphasizing the role of technetium-technetium interaction with oxidation state change. For waste forms, low valent or metallic phase formation demonstrates enhanced inter-technetium interactions which grants the resulting compounds resistance to corrosion or limits solubility.

Development of advanced fuels can leverage innovative synthetic techniques that are utilized in the laboratory and non-nuclear industry. In particular methods that use novel reactions with common starting materials can be applied to produce fuels with suitable attributes for advanced fuel cycles. An example is provided based on the formation of uranium mononitride from dinitride starting material [2]. Uranium dinitride is air stable and can be produced from oxide starting material. Uranium dinitride pellets can be formed in air and then sintered under inert atmosphere to produce uranium mononitride. The unique method for the nitride synthesis can be coupled with established sintering techniques to produce fuel. These waste form and fuel illustrations exemplify the utility synthesis reactions can play in the future fuel cycles. Solution based separation of trivalent lanthanides from Am and Cm is also provided as an example of the utility of speciation and coordination chemistry in the nuclear fuel cycle. Soft donor ligands such as dithiophosphinic acids and bis-1,2,4-triazinylpyridine/bipyridine (BTP/BTBP) derivatives show significant separation selectivity. Many of these ligands are limited by poor stability, constrained working pH range, solubility in suitable solvents, and competition from counter anions. Various triazinyl and bis-triazinylpridine (H, Methyl, Ethyl, Pyridyl and Phenyl) derivatives have been synthesized and their complexation with Eu^{3+}, Tb^{3+} and Cm^{3+} by time resolved laser fluorescence spectroscopy presented. The solvent is found to play a significant role in the complexation behavior and resulting speciation and coordination. In the acetonitrile medium, the complexes contain one ligand molecule per metal ion. Spectroscopic signatures change to ML3 species in methanol medium. For hard acceptors acetonitrile is known to be less solvating as compared to methanol. The Eu^{3+} ion, being a hard cation, is less solvated by acetonitrile and the nitrate counter anion strongly binds with it and the BTP molecules. When the Eu(III) complex of Py-BTP was prepared in acetonitrile medium, the single crystal XRD result shows that it acts as a tetra-dentate ligand with the stoichiometry $Eu(Py\text{-}BTP)(NO_3)_3$ resulting in 10 coordinated Eu(III) ion. The overall results show the utility of radioelement speciation, compound synthesis, and coordination chemistry in expanding general chemistry knowledge and the development of applications exploiting radionuclide synthesis, speciation, and coordination chemistry.

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TAN-V13, (Id: 279)

SOLID STATE DIFFUSION INTERACTIONS OF METALLIC URANIUM WITH TECHNETIUM

Daniel Koury, Frederic Poineau, Ken Czerwinski, Erik Johnstone

University of Nevada, Las Vegas, United States
dan@physics.unlv.edu

In metallic nuclear fuels, uranium will interact with fission products formed at higher burn-ups. Understanding the binary interactions between components is helpful in building a description of the overall system consisting of fuel and fission products. Many of the fission product metals are easy to obtain and study in reactions with metallic depleted uranium to simulate conditions in an active metallic nuclear fuel. Technetium is a major fission product (~ 6 % from ^{235}U) and very little is known about its interaction with uranium: only one phase has been identified (i.e., U_2Tc) and no Tc-U binary phase diagram is reported. In this study, the interaction between metallic uranium and technetium at elevated temperature has been investigated. Discs of uranium and technetium were prepared into a couple and heat treated at 1023 K for 120 h. After treatment, the couple was analyzed by Electron Microscopy and the U_2Tc phase was identified. In order to better understand the physico-chemistry of binary alloys of uranium with transition metals, discs consisting of uranium with molybdenum, rhenium and ruthenium were prepared, heat treated at 1023 K and analyzed by Electron Microscopy.

TAN-V14, (Id: 29)

APPLICATION OF MULTI-STEP EXCITATION SCHEMES FOR DETECTION OF ACTINIDES AND LANTHANIDES IN SOLUTIONS BY LASER SPECROSCOPY

Igor Izosimov

JINR
izig@mail.ru

Development of laser spectroscopy with tunable lasers gives rise to new procedures for detection of trace amounts of various substances in various media. A possibility to tune a wavelength of laser radiation allows selective action on certain atoms and molecules and, hence, selective detection of these species [1]. The practical application of laser spectroscopy to analysis of different samples is confronted with one essential difficulty, namely the element to be detected must be permanently located in the area of interaction with laser radiation. Therefore the use of solutions of the substances to be analyzed is the most attractive from the practical standpoint. When the pulse (1ns) UV radiation produced by nitrogen laser is used for lanthanide and actinide excitation in solutions the UV radiation is absorbed with different impurity molecules and as a consequence the background radiation is increased. Using short laser pulses for excitation of molecules and ions in liquids and time resolution for registration of luminescence or chemiluminescence produced by actinide and lanthanide ions we can separate target signals from short-lived background luminescence [1]. Selective excitation of detectable molecules can additionally decrease the intensity of background radiation.

In addition, UV radiation is absorbed with chemiluminogen (luminol in our experiments) molecules, which makes difficult interpretation of the results. Therefore a key problem of chemiluminescence application to detection of lanthanides and actinides in solutions is an increase in the selectivity of detection. Appropriate selectivity of lanthanide or actinide excitation can be reached by initiation of transitions within 4f- or 5f-electron shell, which correspond to visible spectral range of absorbed laser radiation. Since the energy of one-quantum excitation in visible range may be insufficient for initiation of chemiluminescence it was proposed to excite lanthanide and actinide ion by multi-quantum absorption of visible light [1-3].

The use of laser radiation with tunable wavelength allows selective excitation of actinide or lanthanide species with subsequent registration of luminescence or chemiluminescence. The details of multi-step luminescence/chemiluminescence excitation in solutions are considered. It is shown that a multi-step scheme of luminescence/chemiluminescence excitation increase both the sensitivity and selectivity of lanthanide and actinide detection.

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TAN-V15, (Id: 108)

INVERSE QUENCHING EFFECT OF EXCITED U(VI) IONS BY EU(III) IONS IN AQUEOUS SOLUTIONS

Euo Chang Jung, Kyoung Kyun Park, Hye-Ryun Cho, Wansik Cha

Korea Atomic Energy Reserach Institute
ecjung@kaeri.re.kr

This talk will focus on energy transfer phenomena between hexavalent uranium (U) ions (U(VI)) and trivalent europium ions (Eu(III)). In the literature on this subject [1-3], the interaction between U(VI) and Eu(III) was explained as intramolecular energy transfer from excited U(VI) to Eu(III), and thus, the strong quenching of the luminescence of excited U(VI) by Eu(III) was observed. Because these earlier works were performed at relatively high U(VI) concentrations on the order of a few tens mM using conventional spectrofluorimetry, the precipitation of U(VI) at high pH values and the inner filter effect may interrupt the measurement of luminescence of U(VI).

In this work, the time-resolved laser luminescence spectroscopy was adopted to verify the quenching effect of excited U(VI) by Eu(III) at relatively low U concentrations on the order of a few microM. Two types of uranium materials, dissolved U species in aqueous solutions and adsorbed U species onto a silica surface, were prepared with a solution pH range of 4-7. For both U materials, it is apparent that energy transfer between U(VI) and Eu(III) involves the formation of a hetero-polynuclear complex between the hydrolytic U(VI) and Eu(III) species. The new results observed in this work are as follows: (1) the $(UO_2)_3(OH)^{5+}$ hydrolytic compound is the major species taking part in the energy transfer process, (2) the first rising part appeared in the luminescence signal waveform of Eu(III) implies direct evidence of energy transfer process from U(VI) to Eu(III), and (3) the negative quenching effect of U(VI) by Eu(III) ions, which represents the enhancement of luminescence of U(VI) with increasing Eu(III) concentration, was observed in aqueous solutions and the reason can be understood in terms of enhanced absorbance of U(VI) for a hetero-polynuclear complex. A similar negative quenching effect of U(VI) by trivalent terbium ions was observed in acidic solutions [4]. Characteristic features on the luminescence and absorption spectra for this complex will be discussed.

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TAN-V16, (Id: 150)

SPECTROPHOTOMETRIC AND TRLFS SPECIATION STUDY OF $UO_2^{(2+)}$ - $CHO_4^{(2-)}$ – H_2O (Ch = S, Se) SYSTEM

Jakub Visnak, Jakub Kuba

Department of Nuclear Chemistry, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague
jvisnak@gmail.com

This experimental study seeks for stability constants β_m, absorption $Z_m\lambda$ and fluorescence $Z_m\lambda$ spectra (including fluorescence lifetimes τ_m) for the individual species of the general formula $[UO_2(ChO_4)_n]^{2-2n}$ ($n \in \{0; 1; 2; 3\}$), specific ion interaction theory parameters $\varepsilon_{(i,j)}$ between uran-containing species and the most dominantly present ions (Na^+, ClO_4^-, ChO_4^{2-}, $HChO_4^-$) and their temperature dependence (for which the $\Delta H°$ for all present complex species is derived). Our study was done by preparing of several series of solutions (solutions differing by total sulfate/selenate concentration within the series and by total uranium concentration, pH and ionic strength between different series), measurement of the spectra (UV-VIS abs., TRLFS) and subsequent multilinear analysis (based on Singular Value Decomposition, Parallel Factor Analysis, …). The obtained results are compared with the previously measured data (our TRLFS spectra for uranyl-selenate complex species were, however, in the time of the abstract submission novel) and quantum chemical (ab initio and DFT) study, which part is presented on RadChem 2014 as well.

Chemistry of Actinide and Trans-actinide Elements (TAN)

Posters

TAN-P01, (Id: 4)

UO_2, NpO_2 AND PuO_2 PREPARATION IN AQUEOUS NITRATE SOLUTIONS IN THE PRESENCE OF HYDRAZINE HYDRATE

Yury Kulyako, Sergey Perevalov, Trofim Trofimov, Dmitriy Malikov, Sergey Vinokurov, Maxim Samsonov, Boris Myasoedov

Vernadsky Institute RAS
kulyako@geokhi.ru

Modern nuclear power engineering is focused on the use of fast neutron reactors (FNR). These reactors run on the mixed uranium-plutonium oxide fuel (MOX) and allow one both to use weapon-grade plutonium as a fuel and to transmute formed long-lived actinide isotopes. In this connection there arises the problem of a creation of economically effective and environmentally acceptable technology of the MOX fuel production. The separation technologies of U and Pu from spent nuclear fuel (SNF) complete nitrates forms of these elements. As a rule, uranium and plutonium are isolated from the solutions by ammonia and oxalate precipitation, respectively. Isolated compounds are used for the production of powders of uranium and plutonium dioxides or nitrides for MOX fuel synthesis. For example powders of the mixed oxides are produced by precipitation from the solutions of mixtures of ammonium diuranate and plutonium hydroxide or by combined co-precipitation ammonium uranylplutonyl carbonates followed by filtration, drying and ignition of the compounds obtained at 800 °C under reducing conditions of argon-hydrogen atmosphere. The disadvantages are obvious - the complexity of the implementation and the multi-stage processes. The development of new technologies for MOX fuel involves fixing the problem of denitration of actinides aqueous solutions. There exist the methods of direct denitration and by using reagents. Gaseous hydrogen, formaldehyde, formic acid, urea, sugar, ethyl alcohol et al. are used in the methods of reagent denitration.

This work presents data on thermal denitration of U, Np, Pu solutions by hydrazine hydrate to produce individual and mixed oxides of these elements. Simple and effective method of preparation of homogeneously mixed U, Np and Pu dioxides from aqueous nitrate solutions containing a mixture of the actinides was developed. The method is to use a thermal denitration of solutions of U, Np and Pu nitrates in the presence of hydrazine hydrate to obtain hydrated dioxides of these elements. It was established that the $UO_2.nH_2O$ calcination results:

- crystalline UO_2 under inert or reducing conditions in the range of 280-800 °C;
- UO_3 in air atmosphere at 440 °C;
- U_3O_8 at 570-800 °C.

It was shown that thermolysis of the solution containing a mixture of uranium, neptunium and plutonium nitrates at 90 °C in the presence of hydrazine hydrate allows one to prepare hydrated dioxides (U, Np, Pu)$O_2.nH_2O$ which on heating to ~300 °C transmogrify into crystalline (U, Np, Pu)O_2 solid solution.

TAN-P02, (Id: 31)

A QUANTUM CHEMICAL STUDY ON THE ACTINIDES TRIFLATES An(OTf)n WHERE (An = Th, U, Np, Pu, Am, Cm, Bk AND No); n = (3, 4)

Nadia Ouddai

univ Hadj-Lakhdar batna Algeria
ouddai_nadia@yahoo.fr

The actinides triflates are formed from a central metal that relates to the ligands ($CF_3SO_3^-$). The transition metal triflates (trifluoromethanesulfonates) are much considered as Lewis acid catalysts in a variety of organic reactions, as well as precursors in inorganic and organometallic synthesis. In coordination chemistry, the selective complexation of actinides (ш) over lanthanides (ш) with efficient extractant molecules is an important problem for both its fundamental aspects and its applications, in particular in the partitioning of spent nuclear fuels.

We carry out a quantum calculation based on the density functional theory (DFT) of the actinide triflates complexes. Our aim is to study the structural proprieties changes of these complexes geometries. Furthermore we report the computational study on An(OTf)n where (An = Th, U, Np, Pu, Am, Cm, Bk and No); n = (3, 4).

The quantum calculation DFT proved that the trigonal prismatic geometry is favored for all the studied actinide complexes of the general formula $An(OTf)_3$ where (An = Th, U, Np, Pu, Am, Cm, Bk and No) so as by the lanthanide triflate complexes; where the trigonal prismatic geometry is most distorted in the case of triflate thorium $Th(OTf)_3$ and almost perfect in the case of $U(OTf)_3$. The OTf group is bonded to the central metal An as a bidentate ligand with a number of coordination equal to six.

For the $An(OTF)_4$ where (An = Th, U and Pu), the optimized geometry results showed a dodecahedron geometry. Differences in the structural parameters (bond, lengths and angles) can be attributed partly to the nature of the metal atoms and the structural arrangement of the studied compounds. Keywords: actinide- triflate- catalyst- DFT- trigonal prismatic.

TAN-P03, (Id: 38)

THE REDUCTION OF Pu(IV) BY CARBOHYDRAZIDE IN AQUEOUS SOLUTIONS AND IN TWO-PHASE SYSTEM WITH TRIBUTYL PHOSPHATE

Konstantin Dvoeglazov[a], Vladimir Alekseenko[b], Valeriy Marchenko[a], Sergey Alekseenko[c], Vladimir Volk[a], Lyubov Podrezova[a]

[a]*JSC "VNIINM"*
[b]*Federal Centre for Nuclear and Radiation Safety*
[c]*Mining & Chemical Combine*
knd2002@mail.ru

At present, as one of the promising methods of preparation Pu and Np ions valences in aqueous SNF reprocessing technology, a method using organic reagents (substituted hydrazine, hydroxylamine and carbamide, oximes, etc.) is considered. Many of these compounds reduce Pu (IV) and Np (VI) ions quickly and also are effective stabilizers of formed Pu (III) and Np (V) ions in a nitric acid solution, thus eliminating the use of traditional antinitrite reagent - salt forming hydrazine nitrate. The report the results of applying one of these compounds - carbohydrazide ($CO(N_2H_3)_2$) for Pu (IV) ions reduction.

The kinetics of Pu (IV) reduction by carbohydrazide in aqueous nitric acid solution was investigated using UV-Vis spectrophotometry. It is found that within the concentration range of $[HNO_3]$ = 0,5-2,0 mol/l and $[CO(N_2H_3)_2]$ = 0,05-0,2 mol/l the reaction rate is proportional to the concentration of Pu (IV) and carbohydrazide. The reaction rate decreases with increasing of HNO_3 concentration and increases with the growth of the solution temperature. Activation energy of the reaction was calculated 78,7 kJ/mole. Based on the kinetic data, assumptions were made concerning the possible mechanism of the reaction under investigation. The specific reaction rate and the activation energy of the studied reaction were compared with the same values for the reactions of between Pu (IV) and other organic hydrazine substituted. Reduction of Pu(IV) by carbohydrazide in two-phase system (30 % TBP in isopar-M / aqueous nitric acid solution containing Pu(IV)) was studied. It is shown that the efficiencies of plutonium back-extraction from the TBP solution increases with the presence of aminoacetic acid (glycine, NH_2CH_2COOH) in the stripping solution, and under optimum conditions exceeds 99 %.

The possibility of carbohydrazide and glycine mixture applying for concentrating back-extraction of plutonium demonstrates the experiment performed on the laboratory facility of centrifugal extractors using a synthetic solution under conditions of the 1st extraction cycle of the irradiated nuclear fuel VVER-1000 reprocessing.

TAN-P04, (Id: 39)

MECHANISM OF ADDITION-FRAGMENTATION REACTION OF THIOCARBONYLS COMPOUNDS IN FREE RADICAL POLYMERIZATION. A DFT STUDY

Nadjia Latelli

latellinadjia@yahoo.fr

In the present study we analyze the reaction mechanisms involved by Xanthates (SA(C@S)AO) and Thiocarbonates (OA(C@S)AO) compounds in a reversible addition fragmentation chain transfer (RAFT) polymerization. For the purpose, theoretical calculations have been performed by means of density functional theory (DFT), using the B3LYP, M06, CAM-B3LYP, LC-xPBE exchange correlation functionals and 6-31G⁄ basis sets. Thanks to the transition state theory, the rates of addition and fragmentation reactions were obtained. It is shown that, for these systems, the fragmentation step is more selective than the addition step, and that the range-separated functionals give results close to the experimental trends.

TAN-P05, (Id: 53)

SYNTHESIS AND STUDY OF LITHIUM TRIURANATE $Li_2U_3O_{10}.6H_2O$

Elena Kostrova, Nicholay Chernorukov, Oxana Nipruk, Kseniya Chaplieva

kostrova90@inbox.ru

In this work, a method of synthesis of lithium triuranate hexahydrate $Li_2U_3O_{10} \cdot 6H_2O$ is described. The chemical and functional composition of this compound has been investigated; its crystallographic characteristics have been determined; the state of H_2O and its role in the formation of the structure have been studied. Synthesis of the investigated compound is a reaction of shoepita UO_3•$2.25H_2O$ with aqueous solution of lithium nitrate under hydrothermal conditions at 200 °C. The synthesized lithium triuranate hexahydrate is an easily reproducible individual crystalline compound. The X-ray diffraction picture contains a series of reflections from planes with indices which, in combination with an intense reflection peak at $2\theta = 12.04°$, indicate a typical layered structure of the triuranate. For evaluation of its functional composition of $Li_2U_3O_{10} \cdot 6H_2O$, we have performed the IR spectroscopic research. The spectrum contains two groups of vibrations associated with H_2O and uranyl group. The vibrations of H_2O are very characteristic. The band of $\delta(H_2O)$ vibrations at 1620 cm^{-1} is not split. Due to the participation of H_2O molecules in the formation of the branched system of H-bonds, the bands of vibrations νs and νas represented in the spectra by a broad and intense band with faint maxima at 3511 and 3414 cm^{-1} . On the whole, all H_2O molecules in the IR spectrum of $Li_2U_3O_{10}$. $6H_2O$ retain their vibrational identity. The vibrations of the uranyl group are represented in the spectrum by the only band νas at 917 cm^{-1}, which is typical for the seven-fold coordination of uranium(VI) in its uranium–oxygen polyhedron. The absence of the band allows us to consider the uranyl group as having a linear and the equal-shoulder configuration. To specify the state of H_2O in $Li_2U_3O_{10} \cdot 6H_2O$ and to estimate its position in the structure, we have performed thermographic study. According to the first effect in the DTA curve at 162°C, the elimination of four H_2O molecules per $Li_2U_3O_{10}$•$6H_2O$ formula unit proceeds in a single stage. The elimination of the two additional H_2O molecules also proceeds in a single stage, but at a higher temperature 393°C. The dehydration process is completed at 393°C by the total destruction of the crystal structure and the transition into the amorphous state. The crystallization of $Li_2U_3O_{10}$ over wide time and temperature ranges occurs above 393 °C.

TAN-P06, (Id: 56)

SYNTHESIS AND RESEARCH OF THE HYDRATED OXIDE U(VI) WITH GENERAL FORMULA UO_3•2.25H_2O

Kseniya Chaplieva, Nicholay Chernorukov, Oxana Nipruk, Elena Kostrova

kseniyachaplieva@yandex.ru

A new method of synthesis of schoepite $[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}(UO_3{\bullet}2.25H_2O)$ has been proposed in this work. Dehydration process of the synthesized compound has been studied, the state and role of H2O in the structure has been established by mean of high-temperature X-ray diffraction, IR spectroscopy and thermography. The transformation processes of schoepite in other forms of the hydrated oxide U(VI) have been investigated.

The individual crystalline phases of schoepite were synthesized by the two stages process. Earlier $UO_4{\bullet}2H_2O$ was prepared and decomposed into UO_3 at 200°C. Thereafter this freshly obtained uranium (VI) oxide was hydrated by water vapor at 100°C.

An IR spectroscopic study was carried out in order to evaluate the functional group composition, the state of H_2O molecules and the state hydroxide groups in the structure of schoepite. The IR spectrum of $UO_3{\bullet}2.25H_2O$ contains three groups of absorption bands. Among these bands there are vibrations of H_2O molecules, UO-H group and uranyl bonds. In schoepite all H_2O molecules forms two types of H-bonds. First type of bonds is formed by the interaction of H_2O molecules with each other. Interlayer H_2O molecules and hydroxide groups, which are included in the structure of layer, interact and form other type of H-bond. The average intensity pick of ν (UO-H) appears in the spectrums at 3356 cm^{-1}. Corresponding bands of δ (U-O-H) vibrations are intensive ones at 997 cm^{-1}.

For detailed determination of the schoepite structure and its resistance to high temperatures, a thermographic investigation has been carried out. Two H_2O molecules is removed $[(UO_2)_8O_2(OH)_{12}](H2O)_{12}$ in one stage according to the first endotherm effect at 80–116°C. A new crystalline phase of meta-schoepite $[(UO_2)_8O_2(OH)_{12}]{\bullet}(H_2O)_{10}$ is formed as a result of these processes. This compound is stable at room temperature. The process of the meta-schoepite thermal decomposition occurs in one stage according to the second endotherm effect in the temperature range of 118–156°C. The dehydration product $([(UO_2)_8O_2{\bullet}(OH)_{12}](H_2O)_2)$ could not be obtained as the individual phase, because two H_2O molecules per formula unit of the compound are insufficiently for binding of the layers in the stable formation. At intermediate values of from 2 to 10 compound $[(UO_2)_8{\bullet}O_2(OH)_{12}](H_2O)_n$ should be regarded as a crystalline phase of variable composition, related to the class of solid solutions with different content of molecular water. The dehydration product with formula $[(UO_2)_8O_2(OH)_{12}](H_2O)_2$ $(UO_3{\bullet}H_2O)$ isomerizes in to α-modification of uranyl hydroxide α-$UO_2(OH)_2$. The condensation of hydroxide groups in α-$UO_2(OH)_2$ and formation UO_3 occurs at the third endotherm effect at 289–361°C. This oxide decomposes to U_3O_8 at 500°C.

Thus schoepite, meta-schoepite and uranyl hydroxide contain the similar structure units such as H_2O molecules, uranyl and hydroxide groups. Different combination of these structural units is a reason of existence of a variety of chemical forms of $UO_3{\bullet}nH_2O$.

TAN-P07, (Id: 59)

THE INVESTIGATION OF URANYL VANADATES STATE IN THE SATURATED AQUEOUS SOLUTIONS

Anna Eremina, Oxana Nipruk, Nikolay Chernorukov

ereminaanna89@yandex.ru

The state of uranyl vanadates with formula $Ak(VUO_6)k.H_2O$ (Ak –elements of the I-III groups of Periodic system) was investigated in aqueous solutions. The study of these compounds are interested because of their low soluble in aqueous solutions and the compounds are likely to form at the contact with the nuclear waste in the environment, therefore $Ak(VUO_6)k.nH_2O$ can be used to bind uranium. Thereby it is necessary to investigate the state, stability, solubility, conversion of uranyl vanadates in aqueous solutions.

It is shown that pH has the most significant impact on the state of uranyl vanadates in heterogeneous water-salt systems. The pH of the aqueous solution defines the range pH of uranium existence, the type and solubility of the secondary phases. On the whole, it was established that uranyl vanadates are inconvertible at the contact with the aqueous solutions in the wide acid-base range. Their structure and composition preserve in heterogeneous water-salt systems at pH from 1-2 to 11-12. Out of the pointed interval the structure of uranyl vanadates destructs and compounds with another composition and structure form and are in the equilibrium to the aqueous solution. A type of formed compounds depends on pH. In acidic media at $pH \leq 1$-2 initial compounds convert into the amorphous V_2O_5. At $pH >$ 11-12 the equilibrium solid do not contain $Ak(VUO_6)k.nH_2O$ and consist of the $Ak(OH)_2$ and $Na_2U_2O_7$ mixture.

The solubility products were calculated using the solubility data of the system for the pH intervals, where uranyl vanadates saved their composition and structure. The type of interlayer atom do not significant influence on the solubility of compounds. The solubility of $Ak(VUO_6)_k.nH_2O$ has been determined, it changes on the several orders from 10^{-6} – 10^{-8}M in the subalkali solutions to 10^{-2} - 10^{-3}M in the acid and the strongly alkaline media. It was established that the solubility products values for all investigated compounds decrease according to the interlayer atoms radius increasing. The solubility products allow to calculate the thermodynamic functions of the heterogeneous system components, to plot speciation diagrams of uranium (VI) and vanadium (V) in the aqueous solution and solid phases. The solid phase and aqueous solutions diagrams and solubility curves of uranyl vanadates at the range pH 0-14 were plotted. This research makes it possible to use experimental data to solve practical problems, and allows to obtain the important information about the state of the saturated aqueous solutions and the secondary phases of studied heterogeneous systems in the isobaric-isothermal conditions.

TAN-P08, (Id: 74)

THEORETICAL CHEMISTRY STUDY OF URANYL (VI)-SULPHATE COMPLEX SPECIES

Jakub Visnak, Lukas Sobek

Department of Nuclear Chemistry, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague
jvisnak@gmail.com

This theoretical study of several possible complex species of the general formula ($[UO_2(H_2O)_a(\varepsilon^1\text{-}SO_4)_b(\varepsilon^2\text{-}SO_4)_c]^{2-2(b+c)}$, $0 \leq b + c \leq 4$, $5 \leq a + b + 2c \leq 6$, $[UO_2(H_2O)_2(\varepsilon^1\text{-}SO_4)(\varepsilon^2\text{-}SO_4)]^{2-}$ depicted at the Fig. 1.) aspires to the theoretical prediction of stability constants β°, thermodynamical properties (i.e. ΔG° and ΔH°) and their dependance on the temperature. Equilibrium geometries in the ground state and several excited electronic states, vibrational modes and frequencies, moments of inertia, vertical transition energies important to the UV-VIS absorption, excitation and emission/fluorescence spectra were calculated as well. Our study is also the first step towards the molecular-dynamical study searching seeking for another approach to predict ΔG°, ΔH° and log β° and, more importantly, to predict the fluorescence lifetimes (or more generaly - the TRLFS spectra) and their dependance on the temperature and ionic strength (or, more generaly - the solution composition). The comparison of all of the ab initio predicted and experimentally obtained quantities is included. Both, the purely ab initio methods based on the Dirac(-Breit) equation (DHF, MCDHF, KRCI, CCSD) and the density functional methods (DFT (b3-lyp/def-SVP), TDDFT (bh-lyp/def-SVP)) were used. This work tries to reproduce and further develop the study of uranyl-sulfates done by Jakub Šebera [1].

TAN-P09, (Id: 118)

PRELIMINARY INVESTIGATIONS TOWARDS THE SEPARATION OF HEXAVALENT AND TETRAVALENT SEABORGIUM - EXTRACTION OF HOMOLOGS

Mohamed F. Attallah[a], H. V. Lerum[a], Atsushi Toyoshima[c], Kazuhiro Ooe[d], Sunao Miyashita[e], Masato Asai[c], Naoya Goto[d], Nalinava S. Gupta[b], Hiromitsu Haba[f], Minghui Huang[f], Jumpei Kanaya[f], Yusuke Kaneya[c], Yoshitaka Kasamatsu[g], Yoshihiro Kitatsuji[c], Yuta Kitayama[h], Kazuki Koga[e], Yukiko Komori[g], Takumi Koyama[d], Jens V., Kratz[i], Yoshinari Oshimi[d], Valeria Pershina[j], Daisuke Sato[d], Tetsuya K. Sato[c], Yudai Shigekawa[g], Atsushi Shinohara[g], Akira Tanaka[d], Kazuaki Tsukada[c], Shohei Tsuto[d], Takuya Yokokita[g], Akihiko Yokoyama[h], Yuichiro Nagame[c], Matthias Schädel[c], Jon Petter Omtvedt[a]

[a]*Chemistry Department, University of Oslo, Norway*
[b]*Chemistry Department - University of Oslo*
[c]*Japan Atomic Energy Agency*
[d]*Niigata University, Japan*
[e]*Hiroshima University, Japan*
[f]*RIKEN, Japan*
[g]*Osaka University, Japan*
[h]*Kanazawa University, Japan*
[i]*Universität Mainz, Germany*
[j]*GSI Helmholtzzentrum für Schwerionenforschung GmbH, Germany*
dr.m.f.attallah@gmail.com

Element 106, seaborgium (Sg) is a group-6 element with the lighter homologs tungsten (W) and molybdenum (Mo). The homologs have several stable oxidation states in aqueous solutions. Therefore, one can empirically expect that Sg should exhibit similar properties. In addition, theoretical estimates of redox potentials of group-6 elements show that Sg can be reduced from the most stable hexavalent state to a lower oxidation state [1]. The aim of the present study is to find a suitable chemical extraction and separation system to be applied in future reduction studies of Sg [2] to distinguish and isolate reduced species from Sg(VI) by its different extraction behavior in a subsequent liquid-liquid extraction stage. Our strategy to achieve this is to identify a chemical system where the reduced and non-reduced species in solution have opposite charge. It should then be possible to distinguish between them by simply using a cation or anion extraction agent. Details of the strategy and overall system for performing liquid-phase redox studies on seaborgium will be presented in a separate contribution to this RadChem conference [3]. The extraction behavior of Mo(VI) and W(VI) from HCl with Hinokitol in toluene has been investigated in our previous work [4]. In the present work, we have focused our investigation towards systems where reduced species are anionic and hexavalent ions are cationic. Radiotracers of ^{89}Zr and ^{93m}Mo was used to represent reduced species of Sg(IV) and non-oxidized Sg(VI), respectively. 0.1 M solutions of H_2SO_4, HCl, and $HClO_4$ with and without 0.01 M HF were investigated. Di-(2-ethylhexyl)phosphoric acid (HDEHP) and Tri-n-octylamine (TOA) dissolved in toluene were used as extraction agents.

The Oslo Cyclotron Laboratory's (OCL) MC35 Scanditronix Cyclotron was used for producing the ^{89}Zr and ^{93m}Mo radiotracer. While all these experiments were performed as discontinuous "batch" extractions, in the future, on-line studies will have to be performed using the full on-line and automated system (SISAK with a redox cell, see [3] for details) to test realistic conditions for a Sg experiment. 30 MeV $4He_2^+$ ions, delivered with an intensity of ~350 nA (electrical), were used for the nuclear reactions ^{nat}Zr(α,x)9^{3m}Mo and ^{nat}Sr(α,x)^{89}Zr. The activity was then transported in a KCl gas-jet and was deposited on a filter paper. This was gently washed off using the desired aqueous solution. The solution was mixed with an organic extractant dissolved in toluene and was violently shaken for 5 min using a Vortex shaker. Using H_2SO_4 + 0.01 M HF with either 0.1 M HDEHP or 0.1 M TOA gave the best separation between Mo and Zr. The obtained results indicate that a solution of 0.1 M H_2SO_4 + 0.01 M HF with 0.1M HDEHP provided the best separation: 88 % Mo(VI) and 12 % Zr(IV) were extracted. This is a promising start to develop suitable conditions for a future element 106 (Sg) experiment. These experiments will be presented in more detail. Preliminary data of the reduction of Mo(VI) to Mo(IV) using a Flow Electrolytic Column (FEC) [5] in combination with a promising extraction system will be presented by Toyoshima et al. in a parallel contribution to this conference [2].

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TAN-P10, (Id: 152)

ELECTROLYTIC REDUCTION STUDIES OF MO AND W TOWARDS THE REDUCTION OF SEABORGIUM

Atsushi Toyoshima[a], Masato Asai[a], Mohamed F. Attallah[b], Naoya Goto[c], Nalinava S. Gupta[b], Hiromitsu Haba[d], Minghui Huang[d], Jumpei Kanaya[d], Yusuke Kaneya[a], Yoshitaka Kasamatsu[e], Yoshihiro Kitatsuji[a], Yuta Kitayama[f], Kazuki Koga[g], Yukiko Komori[e], Takumi Koyama[c], Jens V. Kratz[h], Hans V. Lerum[b], Sunao Miyashita[g], Kazuhiro Ooe[c], Yoshinari Oshimi[c], Valeria Pershina[i], Daisuke Sato[c], Tetsuya K. Sato[a], Yudai Shigekawa[e], Atsushi Shinohara[e], Akira Tanaka[c], Kazuaki Tsukada[a], Shohei Tsuto[c], Takuya Yokokita[e], Akihiko Yokoyama[f], Jon Petter Omtvedt[b], Yuichiro Nagame[a], Matthias Schädel[a]

[a]*Japan Atomic Energy Agency*
[b]*University of Oslo*
[c]*Niigata University*
[d]*RIKEN*
[e]*Osaka University*
[f]*Kanazawa University*
[g]*Hiroshima University*
[h]*University Mainz*
[i]*GSI Helmholtzzentrum für Schwerionenforschung GmbH*
a.atsushi@jaea.go.jp

Seaborgium (Sg), element 106, is the third transactinide element placed at the 7th row of the Periodic Table. Similar to its lighter group-6 homologs, Mo and W, Sg is expected to be redox-active in aqueous solutions. Pershina et al. [1] theoretically calculated the redox potentials of various couples of Sg on the basis of its multiple ionization-potentials [2]. They predicted that the redox couples of Sg such as Sg(VI)/Sg(V) and Sg(VI)/Sg(IV) have a more negative redox potentials than those of the corresponding Cr, Mo, and W ones in acidic solutions [1]. This is because the reduction processes of Sg are associated with its lower ionization potentials due to the large destabilization of 6d atomic orbitals [1]. Experimental determinations of redox potentials of Sg, therefore, provide tests of these theoretical predictions and yield information on the stability of the valence 6d orbital.

The best Sg isotope for chemical investigation is ^{265a,b}Sg (a and b denote the ground and isomeric state) produced in the ^{248}Cm(^{22}Ne, 5n)^{265a,b}Sg reaction. Because of low production rates of ^{265a,b}Sg and their short half-live of 8.5 s and 14.4 s [3], respectively, only single atoms of Sg are present during an experiment. Standard electrochemical techniques are, thus, not applicable to reduction studies of Sg. Furthermore, continuously rapid experiments are required to efficiently separate reduced and non-reduced species and to measure the alpha decay of ^{265a,b}Sg within its lifetimes. We are, therefore, developing a novel chemistry assembly consisting of a membrane degasser, a flow electrolytic column (FEC) [4], and the continuous liquid-liquid extraction apparatus SISAK coupled with a liquid scintillation counting system [5] to carry out a continuous reduction experiment of Sg. The development of suitable liquid-liquid extraction schemes are described in a separate contribution [6].

In this contribution, electrolytic reduction of Mo and W using a FEC to prepare the reduction experiment of Sg is presented. We carried out batch-wise electrolytic reduction of carrier-free ^{93m}Mo and ^{176,181}W radiotracers using a FEC. The electrolyzed samples from a FEC were chemically analyzed by solvent extraction with TOA and HDEHP to separate and identify reduced species from the stable Mo(VI) and W(VI) ones based on their different extraction behavior. ^{93m}Mo and $^{176,\ 181}$W were applied as radiotracers. We also performed cyclic voltammetry and UV/Vis absorption spectrometry of macro amounts of Mo and W in acidic solutions to obtain information on redox reactions of these elements under given conditions. In this conference, the present status of the preparatory reduction experiments with Mo and W will be presented.

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TAN-P11, (Id: 193)

CALCULATION OF BOILING TEMPERATURE OF SEABORGIUM HEXAFLUORIDE

Oleg Gromov

ollgromov@mail.ru

The formulation of the Mendeleyev's Periodic law says: "Properties of chemical elements and their connections are in periodic dependence..." Therefore, it is possible to define evaluate unknown or by practical consideration inaccessible constants of some connections operating with various constants of similar substances in chemical behavior [1].

Chemical similar substances are connections with a close factor of intermolecular interaction (ψ-factor). They possess the actual identical chemical properties. For calculation and an assessment of unknown physical and chemical constants, in particular, boiling temperatures widely use methods of comparative calculation if temperatures of boiling of similar connections are known, for example. A boiling temperature is one of the main characteristic constants of any substance. For molecular connections there is the following dependence:

(Tb•M) 0, 5 = f (M) (1)

them Tb – a boiling temperature, K; M – molecular mass of substance, g-mol.

Dependence (1) is a straight line for similar in the chemical relation of hexafluorides of the chrome, the molybdenum and the tungsten, and also uranium.

According to works [2-4] character of a chemical bond in CrF_6 molecules ($\psi = < 0, 05$), UF6 ($\psi = 0{,}028$), MoF_6 ($\psi = 0{,}038$) and WF_6 ($\psi = 0{,}028$) is mainly covalent, i.e. these connections define as molecular. Chemical element No 106 which has the name "seaborgium", is chemical analog of elements of a chrome subgroup. It is possible to tell surely that seaborgium forms molecular hexafluoride, though possessing considerably smaller oxidizing ability in comparison with MoF_6 and even with WF_6 [4].

Function (1) was applied to calculation of boiling temperature of seaborgium hexafluoride, it was equal 355 K.

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TAN-P12, (Id: 261)

SUPERHEAVY ELEMENT CHEMISTRY THROUGH HIGHLY ACCURATE SMALL-CORE PSEUDOPOTENTIAL MODEL

Yuriy Demidov[a], Nikolay Mosyagin[a], Andrei Zaitsevskii[b]

[a]*PNPI*
[b]*NRC "Kurchatov Institute", PNPI*
iurii.demidov@gmail.com

Recent advances in first-principle based studies of superheavy element (SHE) chemistry using the new accurate small-core pseudopotential model are summarized. This model accounts for the finite nuclear size and effectively incorporates most relativistic effects described by the all-electron Dirac—Coulomb—Breit model (including the bulk of Breit interactions) and enables explicit correlation of both valence and subvalence electrons. It provides thus a good basis for attaining optimal accuracy/cost ratio in the cases of large and strongly interfering relativistic and correlation effects characteristic for the SHE compounds. Depending on the size of systems under study and required accuracy, high-level relativistic wavefunction theory (mainly coupled-cluster) and density functional theory methods or their combinations were used to solve the electron correlation problem.

Synthesis and chemical identification of new superheavy elements is of top interest during the last decade. Since the thermochromatography on gold has been proved to be a unique method of chemical detection of heaviest elements, main attention was paid to the description of the SHEs – gold interactions. Adsorption energies of SHEs on gold surface were estimated using the cluster model. Its reliability was improved by monitoring charge distributions in the vicinity of the adsorption site and taking into account the effects of relaxation of the cluster compatible with its embedding into the crystal. In some cases the results differ significantly from those of previous theoretical studies. For instance, the new estimates of element 113 and element 120 on gold adsorption energies (1.0-1.2 eV and 2.5-2.7 eV respectively [1, 2]) are recommended.

Further development of the SHE "chemical" identification techniques may benefit from having a broader view of their chemical properties. We performed systematical relativistic calculations of molecular structures and energetics of presumably stable binary compounds of SHEs with the most common light elements. We focus on the properties of element 120, copernicium (E112) and flerovium (E114) which are expected to display particularly strong relativistic contraction and stabilization of the filled s or $p_{1/2}$ subshells. The obtained results along with the similar data for the homologues of SHEs were visualized through the "chemical graphs" which reflect the main trends in changing basic gas-phase chemical properties of the elements in the given group of the Periodic table and demonstrate the specificity of SHEs [3]. The work is partially supported by the RFBR (grants # 13-03-01234, # 13-03-01307 and # 13-03-12252-ofi_m-2013). Thanks are due to Prof. C. van Wüllen for supplying us with his relativistic DFT code. The calculations were performed at MCC NRC "Kurchatov Institute" (http://computing.kiae.ru/).

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TAN-P13, (Id: 281)

MEASUREMENT OF THE FIRST IONIZATION POTENTIALS OF SHORT-LIVED LANTHANIDES USING A SURFACE IONIZATION METHOD

Yusuke Kaneya[a], Tetsuya Sato[b], Osa Akihiko[b], Ichikawa Shinichi[c], Stora Thierry[d], V. Kratz Jens[e], Asai Masato[b], Tsukada Kazuaki[b], Toyoshima Atsushi[b], Nagame Yuichiro[b], Schädel Matthias[b], Sato Nozomi[b], Ooe Kazuhiro[f], Miyashita Sunao[g]

[a]*Graduate School of Science and Engineering, Ibaraki University / Japan Atomic Energy Agency*
[b]*Japan Atomic Energy Agency*
[c]*Nishina Center for Accelerator Based Science, RIKEN*
[d]*ISOLDE, CERN*
[e]*Institut für Kernchemie, Universität Mainz*
[f]*Institute of Science and Technology, Niigata University*
[g]*Graduate school of Science, Hiroshima University*
kaneya.yusuke@jaea.go.jp

The first ionization potential (IP) directly reflects a valence electronic configuration influenced by relativistic effects which are significantly noticeable for heavy elements. Information on IP of heavy elements, therefore, gives us a better understanding of relativistic effects. IPs of heavy actinides with atomic number $Z > 100$, however, have not been measured by conventional techniques, such as resonance ionization mass spectrometry (RIMS), because these elements are only available in non-weighable quantities down to the one-atom-at-a-time scale. This condition forces us to call for a different experimental approach.

Here, we have focused on a surface ionization process. Since the surface ionization process takes place between an atom and a metal surface, this method is applicable to one-atom-at-a-time scale experiments. In fact, we ionized and mass-separated short-lived isotopes using the surface ionization method installed in the JAEA-ISOL system [1]. Further improvement of the surface ionization type ion-source has been recently applied to measure the IP of lawrencium (Lr, $Z = 103$). 27-s ^{256}Lr produced in the ^{249}Cf +^{11}B reaction was successfully ionized [2]. The IP measurement of Lr is now under way. In this work, we measured ionization efficiencies of various short-lived lanthanides and evaluated their IPs, as a test experiment for measurement of IPs of heavy actinides. Short-lived lanthanides, ^{143m}Sm, ^{143}Eu, ^{148m}Tb, ^{154}Ho, ^{157}Er, and ^{165}Yb, were produced by the irradiation of a 67.9- MeV $^{11}B^{4+}$ beam delivered from the JAEA tandem accelerator on ^{136}Ce / ^{141}Pr / ^{159}Tb and ^{142}Nd / ^{147}Sm / natEu targets.

Short-lived ^{168}Lu was also produced in the reaction of ^{162}Dy with a $^{11}B^{4+}$ beam. Nuclear reaction products recoiling from the targets were transported to the ion-source of the JAEA-ISOL set up by a He/CdI_2 gas-jet transport system. The products were ionized in the ion-source, accelerated with 30 kV, mass-separated, and collected on an aluminized Mylar tape. The amounts of the collected ions were determined by gamma-ray measurement with a HP-Ge detector. To calculate ionization efficiencies, the amounts of the transported products were also determined by direct collection using a separate catcher system.

IPs of various short-lived lanthanides are evaluated based on the following Saha-Langmuir equation: $\alpha = n_i/n_0 = \exp((\varphi\text{-IP})/kT)$, where n_i and n_0 indicate the number of ions and that of atoms on a metal surface, respectively. T, k, and φ are the absolute temperature of the metal surface, the Boltzmann constant, and the work function of the specific metal surface, respectively. The experimental ionization efficiency β is expressed by using the α as follows: $\beta = n_i/(n_0+n_i\ ) = \alpha/(\alpha+1)$. Obtained IP values of short-lived lanthanides with tracer scale atoms were compared with literature values measured with macro-scale amounts of these elements.

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TAN-P14, (Id: 336)

STUDY OF N_P(V) COMPLEXATION WITH PROPIONATE AND LACTATE AT ROOM TEMPERATURE

Aleksandr Vasiliev[a,b], Nidhu Banik[b], Remi Marsac[b], Christian Marquardt[b], Stepan Kalmykov[a]

[a] Moscow State University, Department of Chemistry, 119991 Moscow, Russia
[b]Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, 76021 Karlsruhe, Germany y
stavrogin.aleksandr@yandex.ru

Np-237 is one of the important contributors to the radiation inventory of nuclear waste repositories over a very long time period, because of its long half-life ($2.14•10^6$ y). Natural clay rocks are considered as potential host rocks for deep geological disposal of nuclear waste, because of their low permeability and high retention properties for radionuclides via sorption processes. However, small organic molecules, such as lactate and propionate exist in clay rock pore water and they might enhance Np mobility. The understanding of the complexation of Np with these ligands and reliable complex formation data are required in the frame of safety assessment of a nuclear waste repository.

Two methods were applied and compared for the determination of Np(V) (NpO^{2+}) complexation with propionate ([Prop] = 0-0.30 mol/L) and lactate ([Lact] = 0-0.33 mol/L), namely UV-Vis/NIR spectroscopy and liquid-liquid extraction (LLE) technique with isoamyl alcohol solution containing 10^{-3} M TTA and $5•10^{-4}$ M 1,10-phenanthroline [1]. All measurements were performed at 0.5 M ionic strength of NaCl solution at room temperature (22±1 °C). The concentration of ^{237}Np(V) in LLE experiments was $1·10^{-6}$ - $3·10^{-6}$ M at pH 7. Liquid scintillation counting was used for the determination of the neptunium concentration in aqueous and organic phases after the extraction. UV-Vis/NIR spectroscopy measurements in the wavelength range of 950-1030 nm were carried out at pH 4, 5 and 7 with ^{237}Np(V) concentrations of $2·10^{-5}$ - $6·10^{-5}$ M. The maximum of the absorption band of the neptunyl aqua ion (NpO^{2+}) at 980 nm shifts with increasing ligand concentration to 983 nm (NpO_2Prop) and 986 nm (NpO_2Lact) while its absorption intensity decreases. Slope analysis of the results yields a 1:1 Np(V) complex formation for propionate and lactate at the given pH values. In the extraction experiment, the distribution ratio of [Np-org]/[Np-aq] decreases with increasing ligand concentration. Both methods provided similar conditional complexation constants at ionic strength of 0.5 M NaCl: log Kc (spec) = 1.09±0.1 and log Kc (LLE) = 1.04±0.02 for NpO_2Prop; log Kc (spec) = 1.75±0.1 and log Kc (LLE) = 1.85±0.01 for NpO_2Lact. The value for the lactate complex is comparable with a value from literature: log Kc (spec) = 1.78±0.03 for NpO_2Lact I = 0.3 M [2]. The complexation strength of propionate is similar to the acetate complexation expressed in a similar complex formation constant of log Kc (spec) = 1.05±0.04 for NpO_2Acet at I = 0.3 M [2]. The work will be extended to different ionic strengths and elevated temperatures in the near future.

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TAN-P15, (Id: 439)

GAS PHASE CHEMISTRY OF THE VOLATILE CHLORIDE COMPOUND OF HF ISOTOPES

Hisaaki Kudo, Shin'ichi Goto, Masashi Murakami

Niigata University
hkudo@sc.niigata-u.ac.jp

Gas-phase chemistry is one of the most utilized techniques to study chemical properties of superheavy elements. An adsorption enthalpy of volatile compounds of these elements can be determined with their adsorption-desorption processes on a gas chromatographic column surface. The gas phase chemistry for group 4 elements, Zr, Hf, and Rf has been performed by several groups, and it is reported that the order of the volatility of their tetrachlorides is Zr$\geqq$Rf>Hf [1, 2] and Zr~Hf~Rf [3]. However, in macro-scale, tetrachloride of Hf is known to be more volatile than that of Hf. Until now, we have investigated gas chromatographic behavior of volatile chloride compounds of Zr and Hf, and the transfer process in the column using Hf radioisotopes of various half-lives. The results show a similar behavior with nonvolatile compound, oxychloride which is formed by oxygen in a system [1]. Therefore, we investigated in detail oxygen effects on a gas chromatographic behavior.

Hf isotopes were produced in the ^{nat}Eu(^{19}F,xn) and ^{152}Gd(^{18}O,xn) reactions using 20 MV tandem accelerator at Japan Atomic Energy Agency (JAEA). The beam energy of ^{19}F and ^{18}O were 122 and 108 MeV, respectively. Produced Hf isotopes were ^{165}Hf (76 s), ^{166}Hf (6.8 min), ^{167}Hf (2.05 min). To compare volatility with a Zr compound, ^{85}Zr (7.9 min) was also produced in the ^{nat}Ga(^{19}F,xn) and ^{nat}Ge(^{18}O,xn) reaction. Nuclear reaction products were transported to the gas chromatographic apparatus with a carbon cluster in a helium gas flow. The transported products were collected on quartz wool plugged in a quartz tube where HCl gas added to form volatile chloride compounds. Oxygen gas was also introduced in order to examine an oxygen effect on a gas chromatographic behavior. The volatile compounds through the isothermal column were re-transported using a He/KCl gas-jet system, and collected in a cold trap where gamma-rays were measured to obtain the yield of each Hf isotope which passed through the column.

The relative yields for ^{165,166,167}Hf and ^{85}Zr are regarded as 100 % at the column temperature of 450 °C. In the condition of oxygen free, the yields of all nuclides increased with the temperature of the column from 200 °C up to 300 °C. When oxygen was added into the system, the yields at 300 °C were very low and the temperature to which the yield reaches to 100 % was 400 °C. Since this result agrees with our previous results, it is found that oxygen had actually influenced the chromatographic behavior reported until now. In the model generally used for analysis of the gas-phase chemistry, it is explained that the yield of the volatile compound changes according to the half-life of the nuclide used. But our experimental results show that nuclides of different half-lives exhibit almost the same breakthrough curves in an isothermal chromatography. The detailed reason is under investigation.

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Radiation Chemistry (RCH)

Verbal presentations

RCH-I01, (Id: 448)

RADIATION CHEMICAL PROCESSES IN PREBIOTIC CHEMISTRY: AN OVERVIEW

Alicia Negron-Mendoza , Maria Colin-Garcia, Alejandro Heredia

[a]*Instituto de Ciencias Nucleares, Universidad Nacional Autonoma de Mexico*
negron@nucleares.unam.mx

Scientists have long made efforts to understand the origin of life; and several hypotheses about early life have been proposed and coexist today. Among them, the framework laid out by Alexander Oparin and John Haldane who postulated the chemical evolution theory for the origin of life. According to them, a physical and chemical process took place on the early Earth named chemical evolution, which led to the formation of biologically relevant molecules, starting from simple inorganic compounds and under the influence of natural energy sources; later these molecules organized into the first molecular system. After this process, the initiation of biological evolution took place, which led to the first cells. The accumulation of organic matter on the primitive Earth and the generation of replicating molecules are two factors of prime importance in chemical evolution.

The exact sequence of chemical events that led to the living beings is not known; however, a chemical approach is used to study this process in the laboratory (named prebiotic chemistry), by simulating the synthesis of compounds through a recreation of the inferred possible conditions that prevailed on the early Earth. Many prebiotic reactions are not spontaneous and require the input of energy. UV light from the sun is the most important source of free energy, due to its abundance. Another important aspect for an efficient chemical synthesis is the specific action of a given type of energy, and not only its abundance. In this regard, ionizing radiation was a minor energy source among the others available on the primitive Earth. However, radioactivity -from radioactive elements, must be important because it was present since the Solar System formation, and therefore, our planet has been permanently exposed to ionizing radiation of both terrestrial and extraterrestrial origin. In this context, ionizing radiation can be considered a very efficient source of energy for prebiotic synthesis due to its unique qualities, like its way of energy deposition, its omnipresence, and the effectiveness of its reactions via free radicals. The use of this source is substantiated by calculations of the energy available for the decay of the main contributors, i.e., radioactive elements with half-lives longer than 1 million years, such as postassium-40, uranium-235, uranium-238, and thorium-232. An external source of energy is cosmic radiation, which consists of electromagnetic radiations and charged particles, especially high-energy protons, which also could have contributed to chemical evolution processes. For these reasons, in the context of chemical evolution, radiation chemistry can be a very precise and useful tool to simulate the changes that suffered organic molecules exposed to high-energy radiation in a prebiotic scenario.

This work analyzes the results of laboratory-simulated experiments, which are being performed with low concentration water solutions of compounds of biological importance, and on irradiated frozen solutions, which reproduce terrestrial and extraterrestrial environments, such as a nucleus comet irradiated with cosmic rays. In addition, the importance of radiations in prebiotic chemical reactions is highlighted.

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RCH-V02, (Id: 427)

CHEMICAL AND HEAVY ION IRRADIATION INDUCTION OF HPRT MUTATIONS IN V79 CELLS

Pavel Bláha[a,b], Igor Koshlan[b], Natalia Koshlan[b], Raisa Govorun[b], Daria Elsha[b], Viliam Múčka[a]

[a]*CTU in Prague*
[b]*JINR*
[c]*CTU in Prague*
pavel.blahax@gmail.com

Induction of mutations has been observed in the HPRT locus of the Chinese hamster cells (line V79) after irradiation with accelerated heavy ions and also after the action of chemical agent. The mutant fractions were measured after exposure to two types of accelerated ions: ^{18}O and ^{20}Ne, under three different irradiation conditions. The linear energy transfer (LET) values ranged from 115 to 153 keV/μm. As a chemical agent, the ethanol was used. The dependence of the mutant fraction on expression time (the incubation period of the cells from termination of the irradiation until reseeding on a selective medium containing 6-thioguanine for the isolation of HPRT mutants) was measured for the doses of 0.5, 1, and 2 Gy; and for 1.65 M (10 vol. %) ethanol. The dependence was non-linear for all irradiation conditions. The mutant fraction increased with expression time, reached a maximum, and fell back to the starting level. It was found that after approximately 40 – 45 days (80 – 90 cell generations), mutant fraction returned to the levels typical for spontaneous mutants. The maximum of the mutant fraction on expression time relation was reached in different expression times under various irradiation conditions. The position of this peak was moving with the LET value of the used radiation. The observations were compared to the mutagenic actions of ethanol, which is a potent scavenger of hydroxyl radicals and it will be used in the upcoming research simultaneously with irradiation to observe its protective (or synergistic) effects.

RCH-V03, (Id: 397)

PHOTO- AND RADIATION-INDUCED SYNTHESIS OF (NI,ZN)O OR MIXED NIO-ZNO OXIDES

Tereza Pavelková[a], Lenka Procházková[a], Václav Čuba[a], Viliam Múčka[a], Milan Pospíšil[a], Ivo Jakubec[b]

[a]CTU in Prague, Czech Republic
[b]Institute of Inorganic Chemistry, AS CR, Czech Republic
tereza.pavelkova@fjfi.cvut.cz

Set of mixed oxide samples containing crystalline NiO-ZnO with variable composition was prepared by simple irradiation of aqueous solutions containing nickel and/or zinc nitrate hexahydrate, with subsequent annealing. Effects of various types of radiation were studied - solutions were irradiated either by accelerated electrons or UV light. Due to irradiation, weakly crystalline solid precursor was formed. After annealing at 200-300 °C, nanocrystalline (Ni,Zn)O or a mixture of NiO-ZnO oxides were formed, with different amounts of nickel or zinc, depending on the composition of initial solution. Due to high level of interaction between nickel and zinc compounds achieved, formation of solid solution was frequently observed even in the NiO-ZnO mixture. The size of the crystallites was calculated from XRPD spectra to be in order of tens of nm. Photo- or radiation- induced synthesis yields material with quality nanocrystals and very high specific surface area.

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RCH-V04, (Id: 396)

THERMAL CONDITION MONITORING METHODS APPLIED TO DEGRADED CABLE INSULATIONS AND JACKETS

Grazyna Przybytniak, Jacek Boguski

Institute of Nuclear Chemistry and Technology
g.przybytniak@ichtj.waw.pl

Selection of condition monitoring (CM) method is an important aspect of cable ageing management for Nuclear Power Plants (NPP). The current status of cables might be inter alia assess by various thermal methods based either on Differential Scanning Calorimetry (DSC) or on Thermogravimetric (TG) analysis. The techniques might be used to determine the extent of cable damage caused either by degrading stressors occurring in a hot spot of NPP or by accelerated thermal and/or radiation aging performed in the laboratory. Using DSC apparatus Oxidation Induction Time (OIT) and Oxidation Induction Temperature (OITp) measurements might be carried out and the data obtained dependents on the remaining upon degradation content of antioxidants and the extent of oxidation. On the other hand, TG dynamic tests which theoretically might follow the changes in chemical structure of polymeric matrix are usually insufficiently sensitive to monitor progress of cable aging. Thus, finding other opportunities for such applications is currently a challenge.

Our TG studies confirmed that for the cable insulations/jackets made of some polymers (EPR, EVA) tests conducted via an isothermal mode seem to be promising manner allowing for the diagnosis of gradual radiation aging. Variations in the TG thermograms for polymers degraded to different extents are substantial only if the experiments are performed in the aerobic atmosphere, whereas under nitrogen the changes are insignificant and can not be used for the evaluation of cable aging. During the first stage of tests the specimens were fast heated to 400 °C, i.e. to the temperature throughout which the thermal decay of hydrocarbon macromolecules starts. In the second step the samples were kept at 400 °C until the thermal decomposition of polymer. Functions of mass loss versus time for specimens irradiated to various doses were analyzed and compared. Surprisingly, the data confirmed that the more degraded insulations the higher thermal stability of the polymeric matrix measured as the time required to achieve assumed mass loss. The thermo-oxidation effects detected by the isothermal TG analysis are the consequences of chemical and physical changes occurring during radiation aging in the aerobic environment, such as oxidative degradation, formation of double bonds in the main chains improving thermal resistance, saturation of oxygen sensitive sites, barrier effects caused by flame retardant transformations, etc. It was also found that initial crosslinking of the polymers influences their thermo-oxidative stability. The effect was attributed to the raise of the rate of oxidation due to chain branching and increasing population of the labile bonds between third order carbon and hydrogen atoms.

The method may not be considered as a condition indicator or an acceptance criterion but can provide information about the state of cable. Contrary to OIT and OITp measurements, the isothermal characteristic is not associated with the antioxidant content but rather with the extent of polymeric matrix degradation. The time necessary for achieving the selected ratio of mass loss might be confronted with other data characterizing progress of insulation/jacket aging, e.g. elongation at break, degree of swelling or density.

RCH-V05, (Id: 268)

INFLUENCE OF DOSE RATE IRRADIATION ON POLYMERS PROPERTIES

Martin Cabalka, Bohumil Bartoníček

ÚJV Řež, a. s.
cab@ujv.cz

Influence of dose rate irradiation on elongation at break, strength at break and density was evaluated on insulation of cables NSKFA, NSKA and CXFE-V. It was applied gamma irradiation and reactor ïrradiation. It was performed a experimental comparison among three dosimetry systems (alanine, oxalic acid, PFMCH) for reactor irradiation to evaluate the total dose and parts of neutrons and gamma.

RCH-I06, (Id: 436)

IONIZING AND NON-IONIZING RADIATION IN NANOPARTICLE SYNTHESIS

Václav Čuba

CTU in Prague - FNSPE, Department of Nuclear Chemistry
vaclav.cuba@fjfi.cvut.cz

Materials consisting of nanometer-sized particles have drawn substantial attention in wide range of research fields, mostly for their various unique properties originating from their small size or related high specific surface area. For this reason, the nanoscale materials have been considered for many applications (e.g. as phosphors, catalysts or sorbents). This talk covers brief history and recent development of nanoparticle synthesis using various types of ionizing (IR) and UV radiations. The synthesis of various inorganic compounds using IR or UV light represents very promising research and technological field. Radiation-induced processes have some advantages over common chemical methods: they are mostly independent of temperature and they yield material of high purity, with narrow size distribution of particles. The radiation methods has been successfully tested for preparation of variety of nano-scale compounds, namely metals, metal alloys and core-shell systems, metal oxides, garnets, various heterostructures and nanocomposites.

RCH-V07, (Id: 103)

PRIMARY RADIOLYTIC PROCESSES STUDIED BY POSITRON ANNIHILATION AND EMISSION MOESSBAUER SPECTROSCOPY

Sergey Stepanov[a], Vsevolod Byakov[a], Gilles Duplatre[b], Dmitriy Zvezhinskiy[a], Yurii Perfiliev[c], Kulikov Leonid[c]

[a]*Institute of Theoretical and Experimental Physics*
[b]*Pluridisciplinaire Hubert Curien, CNRS/IN2P3, BP 28 67037 Strasbourg*
[c]*Moscow State University*
stepanov@itep.ru

The e+ fate since its injection into a liquid until its annihilation is described. There are several steps of the e+ evolution [1]:

1) energy deposition and track structure of fast positrons: ionization slowing down, thermalization, track structure, terminal positron blob, electrostatic interaction between e+ and radiolytic products in its blob, effect of local heating;

2) positronium formation in aqueous solutions and other molecular condensed media: the Ore model, quasifree Ps state, intratrack mechanism of Ps formation. Ps bubble models. “Non-point” positronium: wave function, energy contributions, relationship between the pick-off annihilation rate and the bubble radius;

3) fast intratrack diffusion-controlled reactions: Ps oxidation and ortho-para conversion by radiolytic products, reaction rate constants, interpretation of the PAL spectra in water at different temperatures.

Intratrack radiation chemical reactions in frozen solutions can be studied by means of the emission Moesbauer spectroscopy. Radioactive transformation of ^{57}Co into ^{57}Fe (E-capture by ^{57}Co nucleolus) is accompanied by emission of several Auger-electrons having total kinetic energy about 6 keV. Emission of these energized electrons leads to formation of a cloud around Moessbauer ^{57}Fe ion with a radius of about 100 Å containing (200-300) ion-electron pairs (H_2O^+, e^- in case of aqueous solutions). Such a cloud (the Auger-blob [2]) is formed within 0.1 ps. Further fast intrablob processes (ion-electron recombination, electron localization and scavenging) can be observed experimentally via measuring of the yields of final chemically stable ions $^{57}Fe^{3+}$ and $^{57}Fe^{2+}$ by means of EMS. Observation of these processes is terminated by the lifetime of the excited Moessbauer nuclei ^{57}Fe, which is about 100 ns. We have studied experimentally reaction ability of NO_3^- cations towards quasifree track electrons in frozen aqueous solutions of acids and salts [2]. It was shown that NO_3^- scavenges track electron more efficiently than H_3O^+, but only by a factor of 3. It is in a drastic contradiction with known behavior of nitrite ions in liquid water, where they are very efficient electron scavenger.

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RCH-V08, (Id: 314)

APPLICATION OF RARE EARTH DOPED PHOSPHATE GLASSES IN RADIATION DOSIMETRY

Piotr Szajerski, Andrzej Gasiorowski, Malgorzata Jakubowska

Institute of Applied Radiation Chemistry, Lodz University of Technology, Wroblewskiego 15, Lodz, Poland
szajer@mitr.p.lodz.pl

Presently ionizing radiation and radioactive isotopes are used in many fields of life, technology and medicine. Radiation and nuclear technologies are used for food and materials sterilization, radiation induced polymerization, materials modification, medical diagnostics and cancer therapies. In order to assure safe application of these technologies and to control radiation exposure to humans and natural environment radiation doses must be strictly controlled. For these reasons many techniques have been developed, which allow for radiation doses measurements. Currently many of these methods are used for particular dosimetric purposes. One of the most common in radiation dosimetry is method based on the themoluminescence properties of solid state materials. Thermoluminescence dosimetry (TLD) is based on the signal originating from electron-hole pairs recombination during heating of irradiated previously dosimeter. TL signal intensity is proportional to the dose absorbed within the material. The most often used materials in TL dosimetry are inorganic dosimeters based on the lithium fluoride (MTS-N, MCP-N).

However, preparation techniques of the presently used TLD dosimeters is difficult and their application for high doses and high dose rates measurements is problematic. Our studies were dedicated to evaluation of rare earth elements (REE) doped phosphate glasses for application in high dose dosimeters.

A series of phosphate glass (PPG) samples doped with 0.5-1.5 % of Eu_2O_3, Gd_2O_3 and CeO_2 REE oxides were prepared by quench-melt technique. The initial phosphate glass matrix composition used was based on the P2O5, Na_2O and Al_2O_3 oxides in amounts of 56, 32 and 12 % (w/w) respectively. The starting materials used for synthesis were ammonium dihydrogen phosphate ($NH_4H_2PO_4$), sodium carbonate (Na_2CO_3), aluminum oxide and respective REE oxide. Before synthesis batch components were grinded in an agate mortar and next melted in Al_2O_3/ZrO_2 95/5 composite crucible. For decomposition of batch components, $NH_4H_2PO_4$ and Na_2CO_3, batch was heated to and maintained in 800-900 °C for 3 hours and subsequently heated to 1200 °C. After 3 hours melt were poured on a stainless steel plate preheated to 400 °C. To assure homogenous distribution of all glass components, especially REE, after cooling and crushing, samples were grinded in ZrO_2 planetary ball mill and subsequently melted in 1000 °C and finally poured again on the stainless steel plate. Dosimetric experiments were carried out in IARC using installed radiation sources. Glass samples in the form of small pieces (ca. 20 mg each) were irradiated with electron beam (linear electron accelerator ELU-6E, 6 MeV) or with Co-60 gamma source. Radiation doses varied from a few Gy up to 1 Mgy. TLD measurements were performed with TL RA-94 thermoluminescence reader.

As a results of our studies, it has been found, that for investigated glasses within the doses ranges of 50-100 kGy the most intense TL signal was observed for 1.5 % CeO_2 doped PPG glass. The best linearity of the TL signal vs. absorbed dose was found for 1.5 % Gd_2O_3 doped glass. Pure, undoped PPG matrix was not as effective as REE PPG glasses taking into account both their sensitivity and response linerity. Proposed glasses can be considered as prospective materials for radiation dosimetry unless optimization of the glass composition and improvement of the preparation methods leading to the final dosimeters forms. Acknowledgements.

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RCH-V09, (Id: 420)

APPLICATION OF AB-INITIO MOLECULAR ELECTRONIC STRUCTURE CALCULATIONS OF RADIOLYTIC AND HYDROLYTIC STABILITIES OF PROSPECTIVE EXTRACTANTS

Tomas Koubsky, Ladislav Kalvoda

Czech Technical University in Prague, Faculty of Nuclear Sciences and Physical Engineering
tkoubsky@gmail.com

Many proposed sustainable nuclear fuel cycles include coextraction of minor actinides together with lanthanides from the high level liquid waste. The extraction of minor actinides is of particular importance due to their responsibility for the long-term radiotoxicity of the waste. For the trivalent actinides and lanthanides ions extraction, the diglycolamide (DGA) family of organic extractants is being used, among others. Since it is well known that the degradation of the extractants in the highly acidic and active environment leads to undesirable effects, it is necessary to demonstrate their hydrolytic and radiolytic stability.

For theoretical estimation of the general as well as the local chemical stability of the particular extractant's structure, the ab-initio calculations of some DGA extractants and their degradation products were performed. For the geometry optimization and electronic structure calculations, the Gaussian and DMol3 codes were used on the DFT level of theory (BLYP, B3LYP functionals / 6-31G**, DNP basis sets). The chemical stability was assessed according to various theoretical general and local stability indicators – electrostatic potential, HOMO-LUMO gap, spatial localization of HOMO, atomic charges, and bond orders. The results of local and general stability of the investigated extractants and their degradation products is in good agreement with the published experimental stability studies. The results for different computational codes and methods (exchange-correlation functionals, basis function types) were compared and found to be in good mutual agreement. Thus, such theoretical chemical stability predictions can provide a valuable support to experimental scientists in development of novel, more stable organic extractants and extraction methods.

RCH-V10, (Id: 408)

EFFECTS OF DOSE RATE ON THE RESPONSE OF A FLUORESCENCE CHEMICAL DOSIMETER FOR ULTRA-FAST PULSE RADIOLYSIS

Martin Precek[a], Petr Kubelik[a], Libor Juha[a], Ulrich Schmidhammer[b], Mehran Mostafavi[b]

[a]*Institute of Physics AS CR*
[b]*Université Paris-Sud*
precek@fzu.cz

Recent developments in the utilization of high-power femtosecond lasers for generation of X-ray and particle radiation sources as well as the on-going deployment of the first multi-keV X-ray free-electron laser facilities (such as are the LCLS, SACLA and the European XFEL) have opened an opportunity for application of these ultrashort pulsed radiation sources to study radiation chemistry with truly femtosecond temporal resolution that has so far not been accessible to experimental observation.

In the study of radiolytic processes in condensed liquids on femtosecond time-scales a serious challenge is the effect of the group velocity mismatch between the pulses of ionizing radiation and the probing light. A feasible solution is to use very thin renewable windowless targets based on liquid jets of 10 - 100 micrometers in diameter. On the other hand, determination of the delivered final radiation doses might be complicated in these liquid-jet systems, especially if these doses are small. Several suitable fluorescence dosimeters based on hydroxyl-radical scavenging aromatic carboxylic acids were developed in the past for use in aqueous solutions and are particularly useful for determination of doses down to 0.1 Gy. A system based on fast on-line detection of fluorescence from their fluorescent radiolytic products would be capable of measuring the dose delivered by each radiation pulse.

An important issue in the development of such a fluorescence-based dosimetry system for use in ultra-fast pulse radiolysis is to identify any potential dose rate effects resulting from the vastly increased dose rates (over 15 orders of magnitude) compared to standard radiation sources that have been used in the past to calibrate their response (e.g., cobalt-60 radionuclide sources or X-ray tubes). Preliminary experiments revealing observable differences in these fluorescence yields at different dose rates were performed with a fluorescent dosimeter based on trimesic acid at the picosecond pulse radiolysis facility ELYSE of the Laboratoire de Chimie Physique at Université Paris-Sud in France.

Radiation Chemistry (RCH)

Posters

RCH-P01, (Id: 13)

RADIATION STABILITY OF HYDROCARBON DILUENTS OF TBP IN TWO PHASE SYSTEM USED IN SNF REPROCESSING

Elena Belova, Zayana Dzivanova, Alexsey Rodin

Russian academy of sciences A.N. Frumkin Institute of Physical chemistry and Electrochemistry RAS
bl174@bk.ru

The modern technology of reprocessing of irradiated fuel nuclear power plants (NPP SNF) is based on the Purex process, which uses a solution of tributylphosphate (TBP) in an inert dilu-ent as extractant. There are most commonly used aliphatic hydrocarbons with straight chain and mixtures thereof (a mixture of n-paraffins) or mixtures of iso-paraffins (tetrapropylene) or a mixture of n-paraffins with iso-paraffins and naphthenes (dearomatised kerosene). High ra-diation and chemical exposure faced by the extractant lead to the formation and accumulation of impurities, which affect its hydrodynamic and selective properties. Therefore the extractant is constantly regenerated in the extraction cycle by soda washing but a part of the degradation products is not removed by this treatment and gradually accumulates. The basic role in dete-rioration of hydrodynamical characteristics of the extractant is played by the products of ra-diation-chemical decomposition of hydrocarbon diluents among which the main contribution is from the products of nitration, oxidations and the mixed products of interaction with TBF.

The purpose of the given work is comparison of radiation stability of branched diluent Isopar-M, mixtures of i-paraffins C13 (C11- 7,11 %, C12 - 17,25 %, C13 - 72,15 %, C14 and above - less 2.9 %) and comparison to data on destructions of RED-1, and also substantiation of choice of both high boiling diluent, and the recycling solution allowing to wash away organic ligands and admixed elements from the extractant thus not creating difficultly separable emul-sions and deposits, formed, first of all, by sodium salts VKK.

After each cycle of irradiation a reextraction was performed, an organic phase was halved: one half was recycled with Na2CO3, and another half was recycled with $NaHCO_3$ for com-parison. After each contact the speed of aliquation and after each cycle in both variants the size of an interphase tension were determined. The latter was determined by modified Re-binder's device by method of detection of the maximal pressure in a bubble of an organic phase.

Comparing data on an irradiation of studied diluents with investigated earlier RED-1 and RJ-13, it could be noted, that a superficial tension on soda regeneration at irradiated C13 and Isopar-M is a little bit higher, than at irradiated RED-1 and RJ-13. Thus speeds of aliquation of emulsions at soda processing at C13 and Isopar-M have close values and since a doze of an irradiation of 200 kGy practically does not change up to a doze 500 kGy, keeping value within the limits of 0,2-0,3 of mm/s while for RJ-13 speed of aliquation monotonously de-creases and at a doze 550 kGy is 0,1 mm/s, and RED-1 at dozes more 200 kGy does not un-dergo aliquation.

Thus, newly examined diluents are characterized by more stable properties at an irradiation in comparison with studied earlier. Thus, Isopar-M has appreciable advantage over C13 at the stage of regeneration, especially at use of 1 M solution of $NaHCO_3$ increasing in the irradiation process. For a choice of a spe-cific diluent for radiochemical plant it is necessary to consider both individual dissolving abil-ity, including propensity of formation of the 2nd organic phase, and specificity of production.

RCH-P02, (Id: 176)

NATURAL METAMICT MINERALS AS ANALOGUES OF AGED NUCLEAR CERAMIC WASTE FORMS

Qiuxiang Cao[a], Sergey V. Krivovichev[b], Xiaodong Liu[a], Boris E. Burakov[b]

[a]*East China Institute of Technology, Guanglan Road, 418, 330013, Nanchang, Jiangxi*
[b]*Saint-Petersburg State University, Universitetskaya emb. 7/9, 199034, St.-Petersburg, Russia*
qiuxiangcao@126.com

Natural metamict U-Th-containing minerals are well known analogues of aged nuclear ceramic waste forms, which were affected by self-irradiation and chemical alteration under the conditions of geological environment. Main concern related to the behavior of radioactive ceramics during their long-term storage is the stability of radionuclide solid solution in the crystalline structure of durable host-phases. Self-irradiation may cause not only damage of crystalline structure of host-phase (its amorphization or metamictization) but also destruction of solid-solution and release of radionuclides in separate chemically mobile forms. We have studied two large (1^{-3} cm in size) and relatively homogeneous samples of natural fully metamict minerals: Y-Fe-niobate, (Y,Fe,U,Th)x(Nb,Ti,Ta)yOz (containing 1.0 wt. % ThO_2 and 4.2 wt. % UO_2) and lovchorrite, $Na(Ca,Na)_2(Ca,Ce)_4TiO_2F_2(Si_2O_7)_2$ (containing 1.1 wt. % ThO_2). No evidences of solid solution destruction as a result of metamictization were observed in these samples. Both samples: untreated and annealed at different temperatures in order to initiate recrystallization were analyzed in comparison by precise X-ray powder diffraction, electron microprobe (EMPA) and scanning electron spectroscopy (SEM). It was observed that annealing caused not only recrystallization of both samples but also destruction of initially homogeneous solid solutions with partial release of U or Th in the forms of separate phases. It was proposed that recrystallization of aged nuclear ceramic waste forms as a result of any possible natural process is not positive phenomenon as it was assumed before. Recovery of crystalline structure can be accompanied by essential release of radionuclides.

RCH-P03, (Id: 196)

THIACALIX[4]ARENES: RADIATION STABILITY AND EU/AM EXTRACTION IN SYNERGISTIC SYSTEMS WITH COSANS

Irena Špendlíková[a], Jan John[a], Václav Čuba[a], Pavel Lhoták[b]

[a]*Department of Nuclear Chemistry, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University, 115 19 Prague, Czech Republic*
[b]*Department of Inorganic Chemistry, ICT Prague, Technická 5, 166 28 Praha 6*
spendlikovairena@gmail.com

This study deals with the effects of irradiation on the stability and extraction properties of thiacalixarenes1, the prospective liquid-liquid extractants for the extraction of actinides and lanthanides from aqueous solutions. Thiacalixarenes (T1, T2) dissolved in cyclohexanone and 1,2-dichloroethane were irradiated with ^{60}Co gamma rays or accelerated electrons with energy of 4.5 MeV. The absorbed doses ranged from 0 to 100 kGy.

The extraction properties towards europium and americium, as lanthanide and actinide representatives, were studied in synergistic systems. The combinations of two thiacalixarene extracting agents, three COSAN molecules and three diluents (chlorobenzene, nitrobenzene and 1,2-dichloroethane) were evaluated.

For the determination of residual concentration, the HPLC method was used and compared with the assessment of the change of the D(Am) and D(Eu) values in solvent extraction experiments. The aqueous phase consisted of a solution of COSAN (chloro-protected bis(1,2-dicarbollide) cobaltic acid) in 0.1 mol/l nitric acid; solutions of thiacalixarene T2 in 1,2-dichlorethane were used as the organic phase. Distribution ratios D for ^{152}Eu and ^{241}Am and their mutual separation factors were evaluated. The activity of aqueous and organic phase was measured via gamma spectrometer with HPGe detector.

The results obtained from both methods correspond to each other and the decline in the extraction behaviour can be derived from the residual concentration determination and otherwise. Both thiacalixarenes seem to be more stable in the irradiated cyclohexanone samples than in the 1,2-dichloroethane samples which is in good agreement with the state that during cyclohexanone radiolysis less aggressive intermediates are produced comparing with the latter case.

This work was performed under the auspices of Czech Science Foundation grant GACR 104-07-1242 and Ministry of the Interior of the Czech Republic grant VG20132015132.

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RCH-P04, (Id: 224)

CONTAINMENT SURFACE INTERACTIONS OF GASEOUS ELEMENTAL IODINE AND RUTHENIUM TETROXIDE DURING SEVERE NUCLEAR ACCIDENTS IN LWRS

Ivan Kajan, Sabrina Tietze

[a]*Chalmers University of Technology*
kajan@chalmers.se

During severe nuclear accidents in LWRs several hazardous and radiotoxic gaseous fission products will be released from damaged UO_2 fuel. Volatile iodine species (CsI, IOx, I2, org. iodides such as MeI) will be released and formed already in an early stage of a severe accident, while the release of volatile oxides of ruthenium (RuO_3, RuO_4) will require a rupture of the containment with a significant air ingress.

Considerable amounts of released CsI and elemental iodine will dissolve in the water pools and steam. Remaining gaseous elemental iodine can be partly immobilized by sorption on the containment surface and structural materials (paint, Al, Cu, Zn).

A fraction of the iodine will be physisorbed and thus can be rather quickly revaporised or washed off from the surfaces. Some of the iodine will be chemisorbed, like on copper and epoxy paint surfaces (Teknopox Aqua VA).

Ruthenium tetroxide has a high affinity to deposit on all the available surface materials. It is a strong oxidizing agent and thus possibly affects the volatile iodine source term. Differences of the sorption behavior of RuO_4 on plane and iodine covered surfaces have been investigated qualitatively and quantitatively, as well as the effects on the iodine revaporisation behavior.

RCH-P05, (Id: 248)

APPROACH OF EVALUATION OF INFLUENCE OF GAMMA AND UV RADIATION ON MICROORGANISMS IN PRESENCE OF SOME SCAVENGERS OF OH RADICALS.

Jaroslav Červenák, Viliam Múčka, Václav Čuba

Department of Nuclear Chemistry, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University, 115 19 Prague, Czech Republic
yaro.cervenak@gmail.com

During irradiation of microorganisms in liquid media by gamma radiation, hydroxyl radicals are considered as one of the most dangerous agents. Elimination of these radicals by their scavengers (ethanol, methanol and potassium formate) should protect the cells. Comparison of two ways of interpretation of acquired data was performed. Dependencies of σ ($= (\ln(s0))/(\ln(s))$, where s0 is fraction of cells surviving in suspension with no scavenger added and s is fraction of cells surviving in suspension with one of OH scavengers) and α (increase of survival) on scavenging efficiency (Q) were evaluated and compared. Besides, a method that allows to compare effects of gamma and UV radiation was developed. This procedure, permitting to determine the dose of UV light, is based on constant absorbance and continuous stirring of the sample during irradiation.

RCH-P06, (Id: 283)

CHEMICAL EVOLUTION STUDIES: THE RADIATION CHEMISTRY AND THERMAL DECOMPOSITION OF MALONIC ACID

Alicia Negron-Mendoza[a], Jorge Cruz-Castañeda[b], Diego Frias-Suarez[c], Alejandro Herediab, Saul Villafañe[b]

[a]*Instituto de Ciencias Nucleares, UNAM*
[b]*Instituto de Ciencias Nucleares, Universidad Nacional Autonoma de Mexico*
[c]*Universidad del Estado de Bahía, Brasil*
negron@nucleares.unam.mx

A cornerstone of modern biology is Darwinian evolution. By accepting the Darwinian evolution, we must postulate another form of evolution before this, and it is called chemical evolution. Thus, chemical evolution encompasses the study of physical and chemical events leading the formation of biological relevant molecules for the probiotic milieu. This process is considered a necessity for the emergence of recognizable living forms. Early Earth was extremely dynamic and chemically complex because the existence of different environments (atmosphere, lithosphere and hydrosphere, and the interfaces among them) where chemical evolution proceeded complicating the scenario. For the chemical processes a source of energy was also necessary.

Several sources of energy have been proposed to contribute for the chemical evolution; among them are high-energy radiation and thermal energy. Several environments on Earth have temperature gradients. These gradients chemical reactions, for example, in volcanic hot springs, and especially in hydrothermal vents on the bottom of the ocean (some at moderately high temperatures). In these environments, the presence of radionuclides was also important for the synthesis or degradation of the present chemical compounds. Thus, radioactivity must be important because it has been present since the formation of the planet. During the supernova explosion, many of the chemical elements were synthesized, many of them with radioactive nature, allowing the synthesis /decomposition of organic molecules.

In this context, the radiolysis and thermolysis of malonic acid in aqueous solution has been studied. The importance of this compound is because it might play a dual role as intermediate in the synthesis of other polycarboxylic acids and inhibiting important metabolic processes such as the Kreb's cycle.

In our experiments, malonic acid was irradiated with gamma rays in oxygen-free aqueous solutions. The thermal decomposition was studied in a static system at temperatures from room temperature up to 90 °C simulating a hydrothermal vent. The main products obtained by the thermal treatment were acetic acid and CO_2. The radiolysis of malonic acid yields carbon dioxide, acetic acid and di and tricarboxylic acids such as succinic, carboxy- succinic tricarballylic and citric acids. A numerical simulation of the chemical process taking place under irradiation was developed and it was being able to reproduce the time evolution of the products of irradiation and the consumption of the malonic acid. Finding these compounds are very important in chemical evolution studies as they are the source of the important building blocks of metabolic pathways. We experimentally identified the products by gas chromatography, and gas chromatography coupled to mass spectroscopy.

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RCH-P07, (Id: 285)

RADIOLYSIS OF FROZEN AQUEOUS SOLUTION OF METHANOL

Sergio Ramos-Bernal[a], Adriana Melendez[a], Maria Colin-Garcia[b], Diana Vazquez[a]

[a]*Instituto de Ciencias Nucleares, Universidad Nacional Autonoma de Mexico*
[b]*Instituto de Geologia, Universidad Nacional Autonoma de Mexico*
paninegron@gmail.com

Comets contain a silicate core, an organic refractory inner mantle and an outer mantle, predominantly of water ices in which are embedded small particles. The spectroscopic analyses suggest the presence of molecules, such as ammonia (NH_3), methane (CH_4), formaldehyde (H_2CO), methanol (CH_3OH) and hydrogen cyanide (HCN). The possibility that comets collide with planets delivering such compounds made those bodies very attractive, connecting them with chemical evolution and the origin of life on Earth.

Comets, since their formation, have been exposed, besides ultraviolet radiation, to high levels of ionizing radiation due to cosmic rays and decays of imbedded radionuclei. The bombardment by energetic particles profoundly affects the nuclei composition, and new chemical species are produced by radiolysis. Therefore, the radiation-induced reactions are very important when consider the evolution of the cometary material. The estimate of the total absorbed dose accumulated -from the internal radionuclides and external radiation- over a comet life-time is nearly 3000 MGy at the surface. For that reason, radiation chemistry can be a very precise and useful tool to simulate the evolution of organic molecules exposed to high-energy radiation during the life-time of a comet.

In this work, we analyzed the results on irradiated frozen dilute solutions of methanol, as one of the components of a nucleus comet. As a result of the radiolysis at 77 K, the active radical species form the dimeric product, glycol. The irradiation was carried out in a 60-cobalt gamma source and the irradiation doses were from 2.5 kGy to 3000 kGy.

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RCH-P08, (Id: 365)

STABILITY UNDER IRRADIATION OF SOME AMINOACIDS

Alicia Negron-Mendoza, Ellen Aguilar-Ovando

Instituto de Ciencias Nucleares, Universidad Nacional Autonoma de Mexico (UNAM)
negron@nucleares.unam.mx

Homochirality of certain organic molecules essential for all living organisms, such as the L-amino acids and the D-sugars, has made the search for its origin an important issue in studies of the origin of life and evolution.

Comets and asteroids are thought to include organic compounds imbibed in ices, rocks, and have been proposed as carrier of those compounds to the early Earth. Among the products detected in meteorites (carbonaceus condrites) are amino acids, which are key compounds for chemical evolution studies. The meteoritic amino acids are of the D and L optical isomers types with a lightly enantiomeric excess. The mechanism involved for this excess is still a debate. One theory involves the irradiation with high energy on racemic mixtures. The purpose of this work is to study the stability under irradiation of some amino acids (in solid state and in aqueous solutions). For this purpose, individual amino acids (L, D and D,L alanine, L, D and D,L serine and L, D and D,L phenylalanine) were exposed to different irradiation doses up to 90 MGy that is a dose higher than the calculated total dose that received a comet since it formation.

The analysis of the samples was made by high performance liquid chromatography with a quiral column. The results show that the molecules under study presented great stability under gamma irradiation and the recovery is more than 60 %.

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RCH-P09, (Id: 423)

TIME PROGRAMMING OF MECHANICAL AND ELECTRONIC PROPERTIES OF MATERIALS VIA SELF-IRRADIATION PHENOMENA: A THEORETICAL STUDY

Valeriy Luchnikov

Institut de Science des Matériaux de Mulhouse CNRS
valeriy.luchnikov@uha.fr

Structure transformations owing to self-irradiation of materials by fission products of unstable isotopes constitute a special case of ageing phenomena. For instance, radio-decay of uranium and thorium atoms substituting zirconium atoms in the crystal lattice of zircon causes radiation damage and gradual amorphization of the mineral's structure. This process called metamictization leads to negating of birefringence, lowering of the mineral's refractive index, hardness and specific gravity.

In our work, we consider theoretically intentional induction of ageing processes in materials via the introduction of small quantities of unstable nuclei in materials structure. It is argued that both mechanical and electronic properties of materials can be programmed over relatively large time intervals by the use of radioisotopes. The approach can open the route to novel materials with time-dependent functionalities. For example, radio-decay of unstable nuclei embedded in conductive polymers and dielectrics will enable the design of electrical resistors and capacitors with well-defined time-dependent characteristics. Such electronic elements can be explored for creation of electronic circuits which self-activate or self-desactivate after a certain time interval. Incorporation of minuscule amounts of radio-active species (e.g. carbon-14, tritium) in the structure of polymers, such as polytetrafluoroethylene, can be investigated for presetting self-decomposition of plastic products to a certain term. Relaxation of internal mechanical stresses, amorphization and swelling driven by self-irradiation can be used for programming the configurations of mechanical systems (e.g. bending/unbending of bimetal films) over large terms.

Possible implementations of the time-programmed materials and their perspective applications are discussed, as well as the radiation safety concerns and the choice of suitable radio-isotopes. V. Luchnikov, J Mater Sci (2009) 44:6294–6301

RCH-P10, (Id: 429)

RADIATION STABILITY OF CyMe$_4$-BTBP AND CyMe$_4$-BTPHEN IN THEIR SOLUTIONS IN CYCLOHEXANONE-BASED DILUENTS

Bohumír Grüner[a], Jaroslav Švehla[a], Zuzana Hájková[a], Jana Sočuvková[b], Petr Distler[b], Jan John[b], Christian Ekberg[c], Elin Löfström Engdahl[c]

[a]*Institute of Inorganic Chemistry, AS CR, Řež*
[b]*CTU in Prague, FNSPE, Department of Nuclear Chemistry, Prague*
[c]*Chalmers University of Technology, Gothenburg*
gruner@iic.cas.cz

CyMe$_4$--BTBP and CyMe$_4$--BTPhen are two prospective extractants for the European SANEX and/or GANEX processes for the recovery of minor actinides from a genuine spent nuclear fuel solution.[1] In such applications, radiation stability of the extractants and the influence of solvent irradiation on its extraction properties is one of the key factors determining feasibility of the extractant use in a process. [2]

In this study, radiation stability of CyMe$_4$-BTBP or CyMe$_4$--BTPhen was examined in systems with series of cyclohexanone-based diluents. In addition to following the degradation of the extractant, major degradation products were identified and the impact of irradiation of CyMe$_4$- BTPhen-based solvent on its extraction properties was followed.

Cyclohexanone and a series of different alkylated cyclohexanone derivatives were used as diluents. Two sources of ionizing radiation were used – in one part of the study CyMe$_4$--BTBP solutions were irradiated by accelerated electrons up to the absorbed dose 100 kGy; in the second part of the study both, the CyMe$_4$--BTBP or CyMe$_4$--BTPhen solutions were irradiated by gamma radiation up to the absorbed dose 400 kGy. Identifications and characterizations of the degradation products were performed by HPLC and MS analyses. Residual concentrations of both ligands were determined. The effect of the presence of HNO_3 during the irradiation was studied for 2 selected solvents. Moreover, extraction properties of the irradiated CyMe$_4$--BTPhen solvents were compared with the extraction properties of non-irradiated solvents to estimate the influence of the degradation products in the organic phase.

In case of CyMe$_4$--BTBP in absence of the acid, a visible increase of stability was observed for systems containing 2-Me-cyclohexanone or 2,6-di-Me-cyclohexanone diluents. However, preliminary results indicate that this protective action is probably lost in presence of the acid. From this point, the system containing 3-Me-cyclohexanone seems better due to uniform stability in presence/absence of the acid. Composition of main degradation products corresponds to reactions with particular solvent molecules and oxygen or water. From these results, it could be concluded that the main issue of stability of the extraction system is apparently connected with reactivity of the carbonyl function (or other highly polarized bonds) present in the solvent, which leads either to nucleophilic reactions of BTBP with the solvent or radical reactions proceeding apparently also at the same sites of the solvent molecule.

The results of the study of extraction properties of the irradiated CyMe$_4$--BTPhen solvents revealed that the decrease in D(Am) is slower in 3-methylcyclohexanone at lover doses, but at the dose of 400 kGy 2,6-dimethylcyclohexanone seems to prevent the extractant degradation better.

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RCH-P11, (Id: 449)

REDOX BEHAVIOR OF NEPTUNIUM IN IRRADIATED AQUEOUS SOLUTIONS OF NITRIC ACID IN PRESENCE OF AN EXTRACTING ORGANIC PHASE

Martin Precek[a], Bruce Mincher[b], Stephen Mezyk[c], Alena Paulenova[c]

[a]*Institute of Physics AS CR*
[b]*Idaho National Laboratory*
[c]*California State University - Long Beach*
[d]*Oregon State University*
precek@fzu.cz

A reliable solvent extraction process for separation of neptunium from irradiated nuclear fuels depends upon the maintenance of a valence state amenable to complexation by tributylphosphate (TBP). However, radiolytic generation of nitrous acid in irradiated nitric acid solution may reduce extractable Np(VI) into non-extractable Np(V). One complicating factor that has so far not been well investigated is the influence of the presence of an extracting organic phase on the redox speciation and extraction of neptunium during radiolysis; hence, the rates and total yields of radiolytic reduction of neptunium were measured in varying concentrations of nitric acid, both in the presence and absence of a 30% TBP/dodecane organic phase. In the aqueous solution, greater concentrations of nitrous acid were produced at higher nitric acid, although this did not necessarily result in faster reduction rates for Np(VI). This is likely because of oxidation of Np(V) directly by nitric acid and by oxidizing radicals produced by radiolysis of aqueous nitric acid. The presence of the organic phase appeared to protect Np(VI) from reduction, perhaps due to complexation by TBP

RCH-P12, (Id: 412)

COMPUTER SIMULATION OF DIFFUSION, ADSORPTION, DESORPTION , AND β – DECEAY OF ^{89}Br ON THE TUNGSTEN SURFACE

Andei Androsov, Dimitry Lyubimov

andorosow@gmail.com

In course of construction of thermionic converter it is necessary to solve the problem of electrodes metal surface [1].

This paper presents the method and results of computer simulation of surface diffusion, adsorption, desorption, and β-decay of ^{89}Br on the surface of single-crystal tungsten, in both case at the presence, and at the absence of ^{133}Cs on it.

The simulation of all the mentioned processes was carried out by solving the system of partial differential equation with the appropriate boundary and initial conditions.

As a result of this simulation it was shown that: - principal amount of 89Sr hits the surface of the tungsten collector by direct adsorption from the gas phase and not at the expense of β-decay of ^{88}Kr, ^{89}Kr, ^{89}Rb, ^{89m}Y and ^{89}Y in the adsorption layer. - joint diffusion and desorption of ^{89}Sr with the presence on the surface of ^{133}Cs is faster than a single ^{89}Sr.

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Production and Application of Radionuclides (PAR)

Verbal Presentations

PAR-V01, (Id: 266)

PRODUCTION CROSS SECTIONS OF Nb AND TA ISOTOPES IN THE (p,x) AND (d,x) REACTIONS ON ^{nat}Zr AND ^{nat}Hf

Masashi Murakami[a], Hiromitsu Haba[a], Shin-ichi Goto[b], Hisaaki Kudo[b]

[a]*Nishina Center, RIKEN*
[b]*Niigata University*
masashi.murakami@riken.jp

To perform chemical experiments of superheavy elements (SHEs) on a single-atom scale, it is important to investigate the optimal experimental conditions in advance using long-lived and carrier-free radiotracers of their homologue elements. The isotopes ^{95g}Nb ($T_{1/2}$ = 34.991 d) and ^{179}Ta ($T_{1/2}$ = 1.82 y) are the useful radiotracers for the basic studies of element 105, Db [1,2]. In this work, we measured the excitation functions for production of ^{95g}Nb and ^{179}Ta as well as other isotopes in the proton- and deuteron-induced reactions on ^{nat}Zr and ^{nat}Hf for application studies. Experiments were performed with the AVF cyclotron at the RI Beam Factory in RIKEN, Japan. A well-established stacked-foil technique was used for measurements of the excitation functions. The stacks of ^{nat}Zr/^{nat}Cu and ^{nat}Hf/^{nat}Cu were irradiated by the 14-MeV proton beam, while those of ^{nat}Zr/^{nat}Ti/^{nat}Ta and ^{nat}Hf/^{nat}Ti were irradiated by the 24-MeV deuteron beam. After the irradiation, gamma and X rays of each metallic foil were measured by Ge detectors to determine the activities of the produced nuclides. The cross sections of ^{90g,91m,92m,95m,95g,96}Nb, ^{95}Zr, ^{87g,88}Y, 1^{75,176,177,178a,179}Ta, and ^{175}Hf were measured in the (p,x) reactions, whereas those of ^{90g,91m,92m,95m,95g,96}Nb, ^{95,97}Zr, ^{87m,87g,88}Y, ^{175,176,178a,179,180g}Ta, and ^{175,179m2,180m,181}Hf were measured in the (d,x) reactions. The excitation function of the ^{nat}Hf(d,x)^{179}Ta reaction was measured for the first time. The obtained cross sections were compared with the data in the literatures and with the theoretical cross sections calculated by the TALYS code [3]. In the proton-induced reactions, the calculation reproduced well the measured production cross sections except for some nuclides which have isomeric states. On the other hand, only the partial agreements among the measured cross sections and predicted ones were found in the deuteron-induced reactions. Thick-target yields of the observed nuclides were deduced from the measured production cross sections.

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PAR-V02, (Id: 110)

PRODUCTION OF ^{236g}Np AND ^{236}Pu IN PROTON INDUCED NUCLEAR REACTIONS ON NATU

Peter Ivanov, Cyrus Larijani, Simon Jerome, Patrick Regan

National Physical Laboratory
peter.ivanov@npl.co.uk

Radiochemical analysis of ^{237}Np is important in a number of fields, such as nuclear forensics, environmental analysis and measurements throughout the nuclear fuel cycle. However analysis is complicated by the lack of a stable isotope of neptunium. Although various tracers have been used, including ^{235}Np, ^{239}Np and even ^{236}Pu, none are entirely satisfactory. However, ^{236g}Np would be a better candidate for a neptunium yield tracer, as its long half-life means that it is useable as both a radiometric and mass spectrometric measurements. ^{236}Pu is a valuable radionuclide itseld and has been routinely used as a yield tracer for analysis of plutonium in environmental and technological samples.

Current study investigates the feasibility of ^{236}Np and ^{236}Pu production by (p,3n) reaction on natural uranium. The targets– either metallic uranium, U_3O_8 or uranyl nitrate– were prepared by compaction into copper or aluminium substrates, with a thin aluminium or titanium cover foil and irradiated with 25 MeV protons on the cyclotron at the University of Birmingham. Targets were cooled for 20 days to allow the short lived fission products to decay away and than chemically processed to separate Np and Pu fraction by solvent extraction, ion-exchange and extraction chromatography. The neptunium and plutonium fractions were assayed by γ- and α-spectrometry and the production yields were determined and discussed.

PAR-V03, (Id: 35)

SYNTHESIS OF THE RADIOISOTOPE Mn-56@SiO_2, Sm-153@SiO_2, AND Dy-165@SiO_2 HYBRID NANOPARTICLES FOR RADIOTRACER

Sung-Hee Jung[a], Sang-Ei Seo[b], Yun-Ok Kang[b], Seong-Ho Choi[b]

[a]Korea Atomic Energy Research Institute
[b]Hannam University
shjung3@kaeri.re.kr

Radioisotope hybrid nanoparticles (NPs) such as Mn-56@SiO_2, Sm-153@SiO_2, and Dy-165@SiO_2 were synthesized by neutron irradiation of the Mn-55@SiO_2, Sm-150@SiO_2, and Dy-163@SiO_2 NPs using HANARO research reactor, respectively.

The Mn-55@SiO_2, Sm-150@SiO_2, and Dy-163@SiO_2 NPs were synthesized by calcinations of the hybrid NPs, which is prepared by sol-gel reaction of tetraethyl silicate in the presence of the complex precursors, in air flow at 500 ℃ for 8 h.

Mn-55, Sm-150, and Dy-163 for radiotracers were selected because these elements can be easily gamma-activated from neutrons (activation limits: 1 picogram (Dy), 1-10 picogram (Mn), 10-100 picogram (Sm)).

The successful synthesis of the radioisotope hybrid NPs were confirmed via Transmission Electron Microscopy (TEM), Energy Dispersive X-ray Spectrometer (EDS), Scanning Electron Microscopy (SEM), and Gamma spectroscopy analysis, respectively. The synthesized the radioisotope hybrid NPs could be used as radiotracers in science, environmental, engineering, and industrial fields.

PAR-V04, (Id: 250)

PREPARATION OF ENRICHED NICKEL- 63 FOR NUCLEAR β-VOLTAIC BATTERIES

Alexander Kostylev[a], Igor Ryzhov[a], Sergey Filimonov[b], Peter Gavrilov[c], Vera Mazgunova[a], Igor Merkulov[c], Yuri Fedorov[a], Dmitry Druz[c], Kirill Bocharov[b], Sergey Ziryanov[b], Alexander Lumpov[a]

[a]Khlopin Radium Institute JSC
[b]Electrochemical Plant JSC
[c]Mining and Chemical Complex FSUE
alexander.kostylev@gmail.com

Modern technology in the field of microsystem technology allows producing subminiature and reliable devices for engineering and medicine. Energy for these devices should be also supplied from miniature and reliable power sources with a long service life. Atomic batteries (AB) on the β-voltaic effect (the analog of the photovoltaic effect) most fully meet these requirements. Among possible β- emitting radionuclides nickel- 63 has most optimal characteristics. It is characterized by rather long half-life (100 years), soft β- radiation (17 keV), high specific power (~ 100 mkW/Ci) and chemical resistance.

The efficiency of the energy conversion of β-radiation depends on both the construction features of the atomic battery and the degree of nickel -63 enrichment. The current technology of nickel -63 production are based on irradiation highly enriched nickel - 62 in super high neutron flux ($1x10^{15}$ n/cm^{2}s). The degree of enrichment really attained by this technology is about 20 %. However, theoretical calculations and experimental studies show that for the AB production it is desirable to use nickel- 63 with enrichment no less than 80 %. This will allow nearly tenfold increase in the AB efficiency (from 0.3-1.0 to 20-25 %).

For large-scale production of highly enriched nickel -63 (more than 80 %) we developed a procedure, which is based on irradiation of nickel -62 with mid-level enrichment in industrial nuclear reactors with "conventional" thermal neutron flux ($5x10^{13}$ – $1x10^{14}$ n/cm^{2}s). In the course of subsequent reprocessing we obtain intermediate product of nickel -63 with enrichment of about 6 %, which is then subjected to the centrifugal separation for preparing Ni-63 with 80 % enrichment.

Secondary product (Nickel -62) remaining after enrichment of Ni- 63 can be reused. As a result, a virtually waste-free closed cycle of production is realized, which allows irradiation of the large volumes of raw materials without violation of the nuclear reactor operation.

This technology allows the large-scale commercial production of nickel- 63 for nuclear batteries with reasonable cost for commercial use.

PAR-V05, (Id: 22)

EVALUATING THE IRRADIATION AND PROCESSING HISTORY OF POTENTIAL RADIOLOGICAL DEVICE MATERIALS

Andrew Hodgson

AWE plc
andy.p.hodgson@awe.co.uk

Cobalt-60 and iridium-192 sources are both generated in nuclear reactors through the irradiation of stable target materials. However, variation in: neutron energy, flux and irradiation time; target material characteristics and purity; the activation cross sections of the desired reactions; decay and daughter progeny in-growth; and any post irradiation processing, can play a key part in determining the isotopic and chemical composition of the material produced. These isotopic ratios, together with those of any activated elemental impurities, therefore have the potential to provide information relating towards not only the material's production date, but also the source's production route, irradiation history and original elemental and isotopic composition.

Preliminary studies evaluating the effects of neutron spectra on radionuclide production using computational modeling have indicated a number of potential signatures. These signatures show significant variability depending on the reactor conditions employed, but need to be validated using materials of known production history prior to further utilisation. Chemical dissolution, separation and purification methods are therefore being developed for both source types to enable the isolation and detection of the isotopes of interest. Details of the techniques being used will be provided, and the various issues that source size, target purity and manufacturing conditions have on signature development and identification will be discussed.

PAR-V06, (Id: 70)

TWO-STAGE POLONIUM EVAPORATION FROM LIQUID LEAD-BISMUTH AT LOW TEMPERATURE

Borja Gonzalez Prieto[a,b], Johan Martens[b], Jun Lim[a], Kris Rosseel[a], An Mariën[a], Alexander Aerts[a], Joris Van den Bosch[a]

[a]*SCK-CEN*
[b]*KU Leuven*
bgonzale@sckcen.be

Understanding polonium evaporation from liquid lead-bismuth eutectic (LBE) is crucial for the safe design of innovative spallation targets and accelerator driven systems in which LBE is used as target material and coolant. Po evaporation from LBE has been investigated by several research groups in the last decade [1-5]. However, these evaporation experiments were carried out at higher temperatures than the operation temperatures of LBE-based nuclear installations. Very recent data at operation temperatures suggested much larger Po vapor pressures than expected from extrapolations of high-temperature data [5]. This increased volatility of course could have significant impact on the safety approach for LBE-based installations. In the present work, we have investigated this peculiar low-temperature polonium evaporation behavior in detail.

We carried out a series of time-dependent evaporation experiments below 500 °C using LBE doped with Po by neutron irradiation. The results revealed that the release of Po from LBE occurred in two stages. A first Po fraction already evaporated after short evaporation times. This fraction of Po was highly volatile, but was also depleted quickly during the first hours of the experiment. A second fraction of polonium dominated evaporation at longer times. The evaporation of this fraction was much more temperature-dependent. We also found that the short-time, highly volatile polonium was located at the sample surface, probably associated with a (Pb,Bi) oxide layer on top of the LBE sample. The bulk of the LBE did not show this volatile Po. Mathematical analysis of the data advanced two important conclusions: (i) the volatile surface polonium represented only a small fraction (10-4) of the total Po in the LBE sample and (ii) the bulk polonium evaporated according to the established high-temperature trend. These results showed that the apparently high Po vapor pressures observed in previous work [5] are caused by a small fraction of polonium in the sample and are a transient phenomenon.

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PAR-V07, (Id: 90)

IONCHROMATOGRAPHIC ISOLATION OF N.C.A. Se-73,75 AND NEW CROSS SECTIONS OF ITS IMPURITY As-74 WITH 40 MEV PROTONS

Tobias Wels, Ingo Spahn, Heinz H. Coenen

Forschungszentrum Jülich
t.wels@fz-juelich.de

Selenium-73 (half-life: 7.1 h; positron energy = 1.3 MeV) is a very promising radionuclide for application in positron-emission-tomography (PET). With its optimal radionuclidic properties it is the only suitable option for PET-tracer analogues of sulfur-compounds and for authentic labelling of organic selenium molecules [1]. It is preferably produced by the nuclear reaction As-75(p,3n)Se-73 in the proton energy range of 40 → 30 MeV [2]. To produce adequate amounts of Se‑73 for radiosyntheses, a suitable target material withstanding high beam‑currents is necessary. For this purpose an alloy of copper and arsenic has proven useful [3].

The currently used dry distillation method [4] for isolation of the n.c.a. radionuclide did not prove reliable enough for routine use. Therefore a new wet-chemical method was developed for its separation from the irradiated target.

Selenium‑75 (half-life: 119.8 d), produced by the (p,n)-reaction on the same target material with 17 MeV protons, was used for the determination of mass distribution coefficients and separation factors, due to its longer half-life and easier production possibility at a smaller cyclotron. Therewith a two-step wet-chemical separation was developed and optimized. First, the bulk material of copper and co-produced radiozinc were separated from radioselenium and the bulk of arsenic by use of the cation-exchange resin DOWEX 50Wx8 and diluted hydrochloric acid as eluent. In a second step the separation of radioselenium from arsenic was attained using the anion-exchange resin DOWEX 1x8 and diluted nitric acid as eluent. With this new separation method up to 94 ± 2 % of radiochemically pure radioselenium was obtained in 2 h without the use of any isotopic carrier.

For a precise evaluation of the produced radioactivity the cross section data of the main nuclear reactions and relevant side reactions are necessary. Up to now, for arsenic-74 which is the major by-product in the production of selenium-73 no cross section data in the proton energy range under consideration were reported. To close the existing gap and strengthen the available data for Se-73,75 production cross sections of the proton induced reactions As‑75(p,pn)As-74, As‑75(p,n)Se-75 and As-75(p,3n)Se-73 were measured in the energy range from 40 to 25 MeV. Based on the experimental results an excitation function for the formation of As-74 could be developed for the first time.

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PAR-V08, (Id: 171)

GENERATION AND ISOLATION OF THE POSITRON EMITTER TITANIUM-45

Sebastian Kuhn, Ingo Spahn, Heinz H. Coenen

Forschungszentrum Jülich
s.kuhn@fz-juelich.de

Objectives: A very promising but so far rather less regarded non-standard PET-nuclide is titanium-45. Its low maximum positron energy in combination with the very weak γ-rays and its relatively long half-life of 184.8 min makes it especially suitable for investigations of slow (patho-)physiological processes. The radionuclide is accessible in high yields via the Sc-45(p,n)Ti-45 reaction and thus expands the scope of labelling possibilities. On the basis of recently specified γ- and positron-intensities of titanium-45 new cross section measurements for this reaction have been performed to further strengthen the data in the lower energy range which is especially relevant for the production of Ti-45. Further, a highly efficient separation of the n.c.a. product from bulk scandium is mandatory for medical application and therefore an improved procedure using the extraction-chromatographic resin DGA-normal was developed.

Methods: For the investigation of the Sc-nat(p,n)Ti-45 reaction pure scandium oxide was sedimented on foils of aluminium. These sediments were covered with thin aluminium foils and irradiated using the stacked-foil technique. Foils of aluminium were also used as energy degraders and copper foils as beam monitors. In total three irradiations of 15 minutes each were carried out at the BC 1710 cyclotron of the institute of the INM-5. The applied beam current was 1 μA of protons with incident energy of 17 MeV.

For production of radiotitanium, milled scandium ingots were irradiated with 12 MeV protons. The needed energy degradation was achieved with aluminium foils, whereas thin copper foils were used for beam monitoring. For the radiochemical separation the irradiated target was dissolved in 4 M HCl. Small amounts of this solution were added to pre-conditioned samples of 100 mg of DGA-normal resin at different concentrations of hydrochloric acid. These samples were shaken thoroughly for at least one hour. Resin and solution were separated and aliquots taken to determine the individual distribution coefficients using γ-ray spectrometry. Thus corresponding separation factors of the system (n.c.a.)Ti / (bulk)Sc were calculated.

Results: The excitation function of the Sc-$^{nat(p,n)}$Ti-45 reaction was revised based on the new radiation intensities showing a cross-section maximum of about 800 mbarn with 10 MeV proton energy. An improved radiochemical isolation of the n.c.a. product from the bulk scandium was successfully elaborated by utilization of the DGA-normal resin, showing a separation factor of more than 2500.

Outlook: The optimized separation procedure developed in this work could be utilized in a semi-automatized HPLC-based isolation of n.c.a. Ti-45, allowing high-yield production of this radionuclide for medical application.

PAR-V09, (Id: 99)

INVESTIGATION OF THE POSSIBILITY OF PRODUCTION AND PURIFICATION OF THE THERAPEUTIC RADIONUCLIDE ^{195m}Pt BY BOMBARDING THE ^{193}Ir TARGET WITH NEUTRONS

Nikolay Aksenov, Sarkis Karamyan, Lydia Sokolova, Gospodin Bozhikov, Alexander Madumarov, Gennadii Starodub

Joint Institute for Nuclear Research
nikolay.aksenov@jinr.ru

The advantage of using the Auger electron emitter ^{195m}Pt ($T_{1/2}$ 4.02 days) in medical radiotherapeutic applications are two-food. First there is high yield of low energy beta/gamma radiation, where each decay leads to more than 30 secondary electrons. Second, there is no radioactive contamination after the decay. Effective ways for optimization of the Pt isomer yield at low impurity content must be investigated.

Here we report investigation of the possibility of production of isomer ^{195m}Pt by double neutron capture by the ^{193}Ir target nucleus with consequent population of ^{195m}Pt through β− decay. This approach allows isolation of carrier-free Pt isotopes from the irradiated target using radiochemical methods. We developed a rapid and efficient method for dissolution of Ir metal based on anodic dissolution in aqueous solutions. In addition we developed a chemical separation procedure for the selective separation of ^{195m}Pt from solution (dissolved Ir target) using extraction chromatography. We performed a test experiment on Ir activation with neutrons at microtron MT-25 (FLNR, Dubna), and provided theoretical estimates for the ^{195m}Pt yield [1]. A future full-scale model experiment at the IBR-2 reactor in Dubna will clarify the practical efficiency of the method.

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PAR-V10, (Id: 269)

GENERATORS OF ALPHA-EMITTING RADIONUCLIDES ^{225}Ac→^{221}Fr→^{213}Bi AND ^{223}Ra→^{219}Rn→^{211}Pb

Stanislav Ermolaev, Aino Skasyrskaya

Institute for Nuclear Research of Russian Academy of Sciences
ermolaev@inr.ru

Generators of alpha-emitting radionuclides are of great interest for targeted therapy of cancer. Among possible generator pairs, ^{225}Ac/^{213}Bi and ^{223}Ra/^{211}Pb are the most promising. In addition to α-particle's properties attractive for nuclear medicine such as short range (50-100 μm) and high linear energy transfer (up to 100 keV/μm) in biological tissue, the mother radionuclides ^{225}Ac and ^{223}Ra have half-lives (9.9 and 11.4 days, respectively) convenient for production, transportation and medical use of the generators. A recently developed method of irradiation of natural thorium with medium-energy protons may provide Ci-amounts of ^{225}Ac and ^{223}Ra monthly [1] and promote large-scale applications.

In a usual generator scheme a mother radionuclide is adsorbed in a small volume at the top of chromatographic resin and a daughter is eluted. This scheme does not work well if used directly because the emitted α- and β-particles destroy the resin by radiation impact and radiolysis. The approach of generators ^{225}Ac → ^{221}Fr (4.9 min) → ^{213}Bi (45.6 min) and ^{223}Ra → ^{219}Rn (4.0 s) → ^{211}Pb (36.1 min) presented in this work consists in obtaining ^{213}Bi and ^{211}Pb via isolation of ultra short-lived intermediates ^{221}Fr and ^{219}Rn.

^{225}Ac was recovered from a proton-irradiated thorium target and contained ~0.2 % ^{227}Ac (21.8 y) [2]. Actinium fraction was then adsorbed on a column filled with extraction-chromatographic Actinide Resin (TrisKem) using bis(2-ethylhexyl) methanediphosphonic acid as an extractant. ^{221}Fr was eluted with HCl or HNO_3 solutions of various (0.016-1 M) concentrations. Having passed the column, the eluate was pumped through a pipe long enough for ^{221}Fr decay into ^{213}Bi. ^{213}Bi was concentrated on a second column also filled with Actinide Resin. The solution after the second column was directed to the first column forming a closed loop. As a result, ^{213}Bi was accumulated in the second column up to secular equilibrium with ^{225}Ac which was maintained till the moment of ^{213}Bi elution. Circulation of eluate provided permanent removal of radiolysis products from the columns. In order to strip off ^{213}Bi the second column was switched from the loop to an elution line and solution of 1 M HCl was passed. The total yield of ~90 % was obtained. The radionuclidic purity of ^{213}Bi solution was not less than 99.5 %.

^{223}Ra was recovered from the same thorium target and contained ~10 % ^{224}Ra (3.7 d). The latter generates a similar decay chain ^{224}Ra → ^{220}Rn (55.6 s) → ^{212}Pb (10.6 h). A solution containing radium fraction was evaporated on a quartz support which was then heated at 800°C in argon flow. ^{219}Rn and ^{220}Rn were sublimed and blown out into a silicone pipe where they decayed. Generated isotopes of lead deposited inside the pipe. The values of argon flow, pipe length and accumulation time may be chosen to regulate the impurity of ^{212}Pb in ^{211}Pb down to 0.1-0.5 %. After heating, ^{211}Pb was stripped off from the pipe walls with small amount of 0.25 M HNO_3 solution. The total yield of 80-85 % ^{211}Pb was obtained. The radionuclidic purity of ^{211}Pb solution was better than 99.9 % (except ^{212}Pb). The presented generator based on gas chemical technique is highly resistant to radiation damage.

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PAR-V11, (Id: 163)

PRODUCTION OF HIGH SPECIFIC ACTIVITY RADIOLANTHANIDES FOR MEDICAL PURPOSES USING THE SZILARD-CHALMERS METHOD

Mikael Nilsson, Leila Safavi-Tehrani, George Miller

University of California Irvine
nilssonm@uci.edu

Radioactive lanthanides have become an important imaging, diagnostic and therapeutic tool in the medical field. For example, the neutron rich samarium isotope of ^{153}Sm has been proven to have desirable characteristics for treatment of bone cancer. However, for medical purposes, the radioactive lanthanide isotope must be produced at high specific activity, i.e. low concentration of inactive carrier, so they are both beneficial for therapy and the concentration of the metal ions does not exceed the maximum sustainable by the human body. The objective of our research is to produce radioactive lanthanides with high specific activity in a small-scale research reactor using the Szilard-Chalmers method. Our preliminary experimental results show a decrease of 34 % in the amount of Lanthanide needed for a typical medical procedure. We propose an innovative experiment setup to instantaneously separate the radioactive recoil product formed during irradiation from the bulk of non-radioactive ions. The instant separation prevents the recoiled radioactive nucleus from reforming its original bonds with the target matrix and chemically separates it from the non-radioactive target matrix, resulting in a carrier free radiolanthanide with increased specific activity. We will present methods for preparation and synthesis of the material used for irradiations and the results of enrichment factors and extraction yields in radioactive lanthanide solutions. We will also investigate degradation by ionizing radiation that occurs during neutron activation to determine the stability of the target material during irradiations. The obtained results will be compared to previously published methods and their corresponding results.

PAR-V12, (Id: 69)

DEVELOPMENT OF NEW SORBENT MATERIALS FOR THE PREPARATION OF ^{99}Mo/^{99m}Tc GENERATORS

Vallín García Cruz, Stéphane Vellieux, B. E. Terpstra, H. Th. Wolterbeek, A. G. Denkova

Delft University of Technology
v.garciacruz@tudelft.nl

99mTc is one of the most often applied radioisotopes in diagnostic imaging. ^{99}mTc is typically supplied to hospitals in the form of a ^{99}Mo/^{99}mTc generator in order to facilitate regular availability. The ^{99}Mo used to produce these generators is a fission product of ^{235}U, and therefore it can only be obtained from just a few nuclear reactors in the world. The goal of this work is to investigate sorbent materials that are efficient enough to adsorb large quantities of Molybdenum to allow the use of ^{99}Mo produced by alternative production routes, such as neutron capture of ^{98}Mo, i.e. ^{98}Mo(n,γ)^{99}Mo, which is possible in large number of nuclear reactors.

We have investigated the adsorption capacity of two different aluminum based materials, namely mesoporous aluminum oxide and aluminum oxide nanopowder, and compared them to the conventionally used in generators, namely acid activated aluminum oxide. The kinetic experiments used to determine the adsorption rate showed that the nanopowder has the fastest adsorption (less than 30 s) followed by the mesoporous material and finally the acid activated aluminum oxide. Adsorption isotherms were conducted at pH 2, revealing adsorption capacity of 249 mg/g (nanopowder), 232 mg/g (mesoporous) and 28 mg/g (acid activated aluminum oxide). The capacities were calculated using the Langmuir extended isotherm model (1). The ^{99m}Tc elution was evaluated using ^{99}Mo produced from the ^{98}Mo(n,γ)^{99}Mo reaction. After the adsorption process the sorbers were rinsed with HCl 0.1 M twice, and once with buffer of pH 7.4 in order to eliminate the non-adsorbed Mo and adjust the pH. Finally 0.9 % NaCl solution was added to the sorbers and they were left to equilibrate. The elution experiments were performed every 24 hours in order to simulate a real generator. The total activity and the activity of the supernatant of ^{99}Mo and ^{99m}Tc were measured in a NaI(Tl) gamma counter to estimate the amount of each radioisotope that it is eluted and respectively retained on the sorber after elution. The elution efficiency of ^{99m}Tc for the acidic activated Al_2O_3 was 52±16 % and 53±17 % for 100 and 200 mgMo/gsorber respectively. The mesoporous Al_2O_3 had a ^{99m}Tc elution efficiency of 75±8 for 100 mgMo/gsorber and a breakthrough of 0.8±0.2 % 99Mo. The 99mTc initial elution efficiency was nearly 100 %, but the breakthrough was also higher, i.e. 13 % for the same material but at higher Mo concentration (200 mgMo/g). Subsequent elution showed 77±10 % 99mTc removal efficiency and the Mo breakthrough was reduced to 3±1. It is concluded that the Al_2O_3 nanopowder and mesoporous materials are good candidates as sorbent materials in 99Mo/99mTc generators using ^{99}Mo having low specific activity, i.e. produced by different production routes than fission.

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PAR-V13, (Id: 195)

CYCLOTRON PRODUCTION OF Tc-99m - RADIONUCLIDIC IMPURITIES PROFILE AND COMPATIBILITY WITH COMMERCIAL KITS

Ondřej Lebeda[a], Jan Ráliš[a], Pavel Hradilek[a], Adam Čepa[a], Tomáš Vrba[b], Alexander Zyuzin[c], Erik van Lier[c]

[a]*Nuclear Physics Institute AS CR, v.v.i., Řež, Czech Republic*
[b]*Faculty of Nuclear Sciences and Physical Engineering, CTU, Prague, Czech Republic*
[c]*Advanced Cyclotron Systems Inc., Richmond, Canada*
lebeda@ujf.cas.cz

Cyclotron production of Tc-99m via Mo-100(p,2n) reaction seems to be viable alternative to Mo-99/Tc-99m generators. It is already known that 1) one cyclotron is able to cover daily consumption of large metropolitan area (up to 1.7 GBq at EOB), 2) target processing and separation of Tc-99m as pertechnetate is more or less solved problem including recycling of Mo-100, 3) enough high enrichment of Mo-100 (> 99.5 %) that reduces formation other Tc radioisotopes to acceptable levels is available, 4) time schedule of the separation and quality control seems to comply with Tc-99m half-life and estimated period of validity, 5) economical aspects of the cyclotron production of Tc-99m do not seem to be as disadvantageous in comparison with reactor-based production of Mo-99/Tc-99m generators as originally thought. Anyhow, there are still several open questions that are thoroughly discussed today. Among them, question of radionuclidic impurities impact on both radiation burden and specific activity of cyclotron-produced Tc-99m plays and important role.

In contrast to generator-produced Tc-99m, cyclotron-produced Tc-99m does not in principle contain any highly radiotoxic and long-lived impurities. However, its production results in formation of technetium radioisotopes, mainly Tc-93 (2.75 h), Tc-94 (4.88 h), Tc-95m (61 d), Tc-95 (20.0 h), Tc-96 (4.28 d) and Tc-97m (91 d). Our recent measurements of their production rates [1] makes possible to predict their relative percentage in the product as function of Mo-100 isotopic composition and irradiation & cooling times. The highest increase of radiation burden is due to Tc-95 and Tc-96. Anyhow, we have estimated total increase of patient radiation burden due to all present Tc radioisotopes in the most widespread Tc-99m-based radiopharmaceuticals based on calculations performed with use of RADAR and ICRP data [2,3]. They clearly showed that radiation burden increase due to co-produced Tc radioisotopes can be in order of a few percents related to administered dose of Tc-99m itself, even for relatively high beam incident energies.

Co-production of long-lived Tc-99g and Tc-98g that is negligible from dosimetry point of view, lowers specific activity of cyclotron-produced Tc-99m. Several authors have expressed misgivings concerning this parameter [4]. We have, therefore, tested many kits for preparing majority of Tc-99m based radiopharmaceuticals for compatibility with Tc-99m prepared by irradiation of Mo-100 with 24MeV protons. We have never noticed any problem with labelling yield or radiochemical purity. It should be noted that slight "carrier-addition" may even improve labelling yield, since substrate is usually present in large surplus (many orders of magnitude) in comparison with chemical amount of pertechnetate. Quality of cyclotron-produced Tc-99m pertechnetate was tested by established Pharmacopoeia methods, if applicable. In a few particular cases, alternative methods were employed. No significant qualitative difference between cyclotron-and generator-produced Tc-99m was observed. Also quality control of reconstituted commercial kits with cyclotron-produced Tc-99m has shown no difference to generator-produced Tc-99m up to now. Such results strongly support viability of cyclotron production of Tc-99m as daily supply to hospitals both in emergency cases or regularly. The work was supported by the Nuclear Physics Institute of the Academy of Sciences of the Czech Republic (RVO 61389005) and by Natural Resources Canada’s Non-reactor-based Isotope Supply Contribution Program (NISP).

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Production and Application of Radionuclides (PAR)

Posters

PAR-P01, (Id: 16)

RADIOLOGICAL DECONTAMINATION OF INDOOR BUILDING SURFACES

Iva Vosahlikova[a], Petr Otahal[a], Mojmir Nemec[b]

[a]*The National Institute for NBC Protection*
[b]*The Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague*
vosahlikova@sujchbo.cz

The paper summarizes the results of radiological decontamination of several different types of indoor building surfaces, which were contaminated by radioactive suspension in two different contamination mixtures. The aim of the study was to develop techniques for application of the prepared contamination mixtures to various surfaces, which were then used for testing of selected decontamination solution.

The experiments were carried out in the Mobile Modular Laboratories, which were designed for decontamination procedures of NBC agents in The National Institute for Nuclear, Chemical and Biological Protection in Kamenná in the Czech Republic (SÚJCHBO, v. v. i.).

The radiological contamination was performed by the radionuclide La-140, which had been prepared by irradiation of isotopically natural lanthanum nitrate in 0.1M nitric acid solution in nuclear reactor LVR-15 in Research Centre Rez. Radiochemical purity of the final La-140 in nitrate solution was higher than 99 %.

The isotopic carrier lanthanum nitrate was added to the solution and then the lanthanum carbonate was precipitated by sodium carbonate or sodium hydrogen carbonate solutions. Using the precipitate, two contamination mixtures were prepared. The first one, lanthanum carbonate suspension in water, was applied onto the testing surface by spraying. The second contamination mixture was prepared of lanthanum carbonate mixed together with montmorillonite (i.e. aluminum pillared clay). In this case, the surface contamination was carried out mechanically using a special mould constructed in SÚJCHBO, v. v. i.

The surface activity of contamination and following decontamination levels were measured by hand held-survey meter Colibri TTC with SABG 15+ alpha/beta/gamma probe made by Canberra Packard. In the decontamination experiments, various interior surfaces were tested to evaluate their suitability for decontamination together with selected decontamination solution. For decontamination tests, materials as plaster board covered with an interior paint (Primalex or Betex) on the surface, glass, floor and wall tiles, plastic materials, anti-slip aluminium sheets and floating floor were used.

The military decontamination solution ODS-5 distributed by Oritest was used for surface decontamination, which was provided by wetted pad three times in one direction and then with the same pad three times in the perpendicular direction. The results show that for the first contamination mixture (the lanthanum carbonate suspension in water) applied, the radiological decontamination efficiency varied in range 81.6 - 99.9 %. For the second mixture, the decontamination efficiency between 67.6 - 99.7 % was achieved.

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PAR-P02, (Id: 26)

PRODUCTION OF ^{99}Mo/^{99m}Tc GENERATOR USING SZILARD-CHALMERS REACTION

Yuichi Hatsukawa, Kazuaki Tsukada, Kazuyuki Hashimoto, Tetsuya Sato, Masato Asai, Atsushi Toyoshima

Japan Atomic Energy Agency
hatsukawa.yuichi@jaea.go.jp

Production of ^{99}Mo/^{99}mTc generator using Szilard-Chalmers reaction Y. Hatsukawa, K. Tsukada, K. Hashimoto,T. Sato, M. Asai, and A. Toyoshima, Japan Atomic Energy Agency, Tokai, Ibaraki, JAPAN We proposed and propel a ^{99}Mo production project via the ^{100}Mo(n,2n)^{99}Mo reaction using fast neutrons from accelerator.(1,2) Only low specific radioactive ^{99}Mo, however, can be obtained in this method. In our project, ^{99m}Tc would be extracted from low specific radioactive molybdenum irradiated target, and then technetium labeled compounds from the purified 99mTc will be synthesized and deliver to the end user. Although labeled technetium compounds would be available, small scale technetium generator is still required in medical facilities. In this paper, feasibility study of production of high specific radioactive ^{9}9Mo using Szilard-Chalmers reaction from molybdenum nanoparticle target with accelerator neutron reactions was carried out.

As neutron irradiation target, molybdenum nanoparticles were prepared by grinding with potassium chloride (KCl) powder, then pressed into a 10mm diameter disk. About 1.2 gram of the Mo/KCl target which contained about 100 mg molybdenum nanoparticles was irradiated with accelerator neutrons for 5 hours. After fast irradiation, the Mo/KCl target was dissolved in pure water, then solution and molybdenum nanoparticles were separated by centrifuge method. The solution contained recoiled ^{99}Mo ion by fast neutron reactions was poured into alumina column. About 7 % of ^{99}Mo produced in the Mo/KCl target was absorbed onto the alumina column. Technetium-99m was obtained by pouring saline solution through the alumina column of immobilized ^{99}Mo.

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PAR-P03, (Id: 34)

SYNTHESIS AND EVALUATION OF FERRAGELS AS PERSPECTIVES SOLID ^{99m}Tc RADIOTRACERS

Ernesto Martínez Baez, Judith Dominguez Catasús, Martha Sahyli Ortega Pijeira

InSTEC
ebaez@instec.cu InSTEC

Radiotracer applications for solid phase studies can be done employing radioactive labeling as an alternative in countries where there aren't nuclear facilities to activate materials. In the present work, supported on silica gel/zeolite nano scaled zero-valent iron (FS/FZ) were synthesized in ethanol medium under atmospheric conditions and labeled with Technetium-99m in order to obtain a solid state radiotracer for further industrial applications. Technetium-99m (〖Tc〗^{99m}) sorption and immobilization on the support material were studied. An experimental design 2¬3 was carried out to evaluate the influence of different Ferrragel synthesis parameters (m(〖FeSO〗$_4$· 〖7H〗$_2$ O(s), (m(sílica))∕(m(〖FeSO〗$_4$· 〖7H〗$_2$ O(s)) and (ν(NaBH$_4$))∕(ν(Fe)) ratios) in the sorption yield (R_(ret %)). It was also investigated the time needed for solid/aqueos phase separation by free sedimentation and centrifugation. Presence of Fe¬0 was proved by powder X-Ray Diffraction (XRD). Furthermore iron-on-silica Ferragel (FS) stability in time and stability of the labeling (〖Tc〗^{99m}) of FS and FZ in water presence were also explored. It was proved the Ferragel capacity for 〖Tc〗^{99m} retention in the solid phase using both supported on materials with (R_(ret %)) of 99 %. Both Ferragels demonstrated to be perspectives as solid radiotracers.

PAR-P04, (Id: 55)

PRODUCTION OF ^{135}La BY PROTON IRRADIATION OF ENRICHED ^{135}Ba AND PURIFICATION BY ION EXCHANGE CHROMATOGRAPHY

Alexander Mansel, Karsten Franke

HZDR - Institute of Resource Ecology and Institute of Radiopharmaceutical Cancer Research - Research Site Leipzig
a.mansel@hzdr.de

The global demand for the rare earth elements has been dramatically enlarged. Therefore, it needs a detailed understanding in ore chemistry and separation methods. To simulate these processes, we will use the radiotracer technique. ^{135}La ($T_{1/2}$ = 19.4 h) was choosen as a typical representative element (radionuclide) for the rare earth elements. The isotope can be produced by the nuclear reaction ^{135}Ba(p,n)^{135}La at a cyclotron. We used our recently installed cyclotron Cyclone® 18/9 (IBA) by irradiation of the isotope enriched ^{135}Ba (94.9 %). The [^{135}Ba]BaCO$_3$ was pressed in an aluminium holder with a diameter of 3 mm and a depth of 300 µm . The target was covered by a 100 µm thick aluminium foil to avoid loss of the material during irradiation. The irradiation was done at a beam of 18 MeV protons and a current of 20 µA for 7 hours. After cooling for 2 hours the [^{135}Ba]BaCO$_3$ was dissolved with 2 ml 0.095 M nitric acid. The separation of the radionuclide ^{135}La and the target material ^{135}Ba was performed by ion exchange chromatography with Ln-Resin-C (TRISKEM). The target solution was eluated on the resin and the resin was washed four times with 2 ml 0.095 M nitric acid to remove the ^{135}Ba. Afterwards, the ^{135}La was stripped by triple washing of the resin with 6 M nitric acid. The combined ^{135}La solutions were evaporated to dryness and the residue was dissolved in 0.1 M nitric acid. The detection of ^{135}La was done by liquid scintillation counting. The target material was recovered by evaporating the ^{135}Ba fractions to dryness, dissolving the residue with water and precipitation of the carbonate by bubbling with carbon dioxide.

PAR-P05, (Id: 71)

THEORETICAL CONSIDERATION OF THE SPECIFIC ACTIVITY OF Tc-99m PRODUCED BY THE MO-100(p,2n)Tc-99m REACTION AT CYCLOTRONS

Bernhard Scholten[a], Syed M. Qaim[a], Sandor Sudar[b], Arjan J. Koning[c], Heinz H. Coenen[a]

[a]*Forschungszentrum Jülich GmbH, Germany*
[b]*Debrecen University, Hungary*
[c]*Nuclear Research and Consultancy Group,The Netherlands*
gmbh.scholten@fz-juelich.de

Even today the generator-produced radionuclide ^{99m}Tc is used for the vast majority of nuclear medical diagnoses. The parent radionuclide ^{99}Mo is generally produced via fission of highly-enriched ^{235}U, however, at a few nuclear reactor sites in the world only. Due to ageing reactors the world supply of fission-produced ^{99}Mo has become somewhat insecure over the last few years. Alternative methods of direct production of ^{99m}Tc using accelerators are therefore presently attracting great attention. The (p,2n) reaction on highly enriched ^{100}Mo appears to be the most promising one. Over the years several cross section measurements thereof have been reported.

However, a critical analysis of the data and the influence of co-produced long-lived Tc-isotopes on the specific activity of ^{99m}Tc need to be critically considerated. From ^{100}Mo the two long-lived radioisotopes ^{99g}Tc and 98Tcare co-produced. ^{99g}Tc is formed directly by the ^{100}Mo(p,2n)^{99g}Tc reaction and indirectly via the decay of 99Mo and ^{99}mTc during irradiation and after EOB. ^{98}Tc is generated by the ^{100}Mo(p,3n) reaction directly.

We calculated excitation functions for the formation of 99Mo and ^{99m}Tc as well as for the long-lived technetium isotopes ^{99g}Tc and ^{98}Tc by the code TALYS for the proton-induced reactions on ^{100}Mo. For the first two nuclides calculations were also performed using the code STAPRE. The direct and indirect production of ^{99}mTc was critically analysed. The integral yields of ^{99}Mo, ^{99m}Tc, ^{99g}Tc and ^{98}Tc were calculated for four chosen irradiation times as a function of proton energy. Therefore the activities of ^{99}Mo and ^{99m}Tc as well as the number of atoms of ^{99}mTc, ^{99g}Tc and ^{98}Tc were deduced for six realistic proton energy ranges.

The dependence of the specific activity of ^{99m}Tc was calculated in relation to energy range, irradiation and cooling time. The specific activity of ^{99}mTc produced directly at a cyclotron was critically compared with that obtained from a fission ^{99}Mo loaded generator. The long-lived isotopes ^{99g}Tc and ^{98}Tc cause no significant radiation and mass dose to the patient but have a strong influence on the specific activity of the cyclotron produced ^{99m}Tc depending on the production conditions. At a suggested 22 MeV incident proton energy, for example, the ratio of long-lived Tc nuclei to ^{99m}Tc nuclei may far exceed 5.0, thereby possibly affecting the kit formulation of radiopharmaceuticals and also exceeding the limits set by radiopharmaceutical regulations, e.g. in Italy. Thus, detailed experimental and theoretical investigations related to the effect of a decreasing specific activity of ^{99m}Tc on the preparation of radiopharmaceuticals appear absolutely necessary.

PAR-P06, (Id: 72)

CROSS SECTION MEASUREMENT OF DEUTERON INDUCED NUCLEAR REACTIONS ON GE UP TO 50 MeV: STUDY OF POSSIBLE PRODUCTION ROUTES FOR $^{74}A_S$ AND $^{77}A_S$ RADIONUCLIDES

Sandor Takacs[a], **Marcell Peter Takacs**[a], **Alex Hermanne**[b]**Ferenc Tarkanyi**[a]

[a]*Institute for Nuclear Research, Hung. Acad. Sci. Bem ter 18/c Debrecen, H4026 Hungary*
[b]*Cyclotron Department, Vrije Universiteit Brussel, Laarbeeklaan 103, Brussels B1090, Belgium*
stakacs@atomki.hu

The radionuclides ^{71}As, ^{72}As and ^{74}As have decay properties that are favorable for use in PET investigations, while the heavier isotopes ^{76}As and 7^{7}As could potentially be used for tumor therapy. Due to their longer half-lives the compounds labeled with these 5 radionuclides can be used for studying of long-term biological phenomena. Studying antibodies, which usually have a long biological half life and do not reach optimal target to background selectivity for several days, could be one of their applications.

The cross sections of nuclear reactions induced by deuteron particles on natural germanium targets were investigated by the activation method using stacked target irradiation and standard high resolution gamma spectrometry. Targets were natural germanium deposits with nominal thickness of about 2 micrometers, vacuum evaporated onto 25 micron thick polyimide (kapton) foils. The stack was composed of 26 kapton-Ge-Ge-kapton sandwich targets interleaved with 26 aluminium and 26 titanium foils (nominal 150 and 11 micrometers thickness respectively). The Al foils served as monitors and at the same time energy degrader in the high energy part of the stack while the Ti foils served as monitors in the low energy part of the stack. The irradiation was done with a 50 MeV deuteron beam of about 50 nA for about 1 hour. Activation cross sections were determined for production of the radionuclides ^{70,71,72,73,74,76}As, ^{69,75,77}Ge and ^{66,67,68,72,73}Ga. The deduced experimental cross sections were compared to the results of theoretical calculations taken from the TENDL-2013 data library based on the TALYS computer code. The experimental data published earlier were collected and critically compared to our new results. Thick target yields were deduced from the experimental cross sections and were compared with literature data. The possible production routes of the most interesting arsenic radionuclides (^{77}As and ^{74}As) are discussed.

PAR-P07, (Id: 81)

GENERATION OF ISOTOPE-ENRICHED ^{152}Sm FROM ^{153}Gd PRODUCTION WASTE

Pavel Butkaliuk, Valery Tarasov, Vladimir Lebedev, Alexandr Kornilov, Iryna Butkaliuk, Rostislav Kuznetsov

JSC "SSC RIAR"
orip@niiar.ru JSC

Samarium-153 is a part of chemicals used for therapy of cancerous growth and inflammatory disease of bone tissue. ^{153}Sm is generated by irradiating ^{152}Sm in either a nuclear reactor or charged-particle accelerator.

A natural mixture of samarium isotopes contains only 26.75 % of ^{152}Sm; when irradiated, the specific activity of the generated ^{153}Sm is not enough to use it for the nuclear medicine purpose. Therefore, the initial material enriched in ^{152}Sm is used to produce ^{153}Sm. Nowadays, the material is enriched by an electromagnetic mass-separation.

JSC SSC RIAR produces ^{153}Gd from europium targets irradiated in the BOR-60 reactor. When irradiating europium in a fast spectrum, a short-lived isomeride ^{152m}Eu generates, of which decay takes place in two directions: generation of ^{152}Gd (72 %) and generation of ^{152}Sm (28 %). The generated ^{152}Sm is practically monoisotopic. Impurities of other samarium isotopes result from reaction ^{153}Sm(n,γ) and threshold reactions with a participation of fast neutrons. When extracting ^{153}Gd from irradiated targets, it is purified from impurities, including samarium, europium and terbium. Thus, highly-enriched stable isotope ^{152}Sm is a side product of the ^{153}Gd production and it can be separated from the production waste. Under this work, an experimental sample of ^{152}Sm was separated from a fraction resulted from the purification of commercial batches of ^{153}Gd. The separation and purification were performed by an extraction chromatography using sorbent DAF/Teflon. The DAF content was 25 %wt. The ^{152}Sm-containing solution was evaporated to dryness. The residual was dissolved in 50ml of 0.1M HNO_3 and the solution was then put through a column 50ml in volume. Samarium, europium and gadolinium were eluted with 0.65M HNO_3 1.2l in volume. The activity of impurity isotopes in the column effluent was measured using gamma-spectrometry; the samarium content was evaluated by an atomic-emission analysis.

As a result, a 99.52 %-enriched experimental sample $^{152}Sm(NO_3)_3.6H_2O$ was generated, of which enrichment exceeds the one of ^{152}Sm in the commercial off-the-shelf chemicals produced by the electromagnetic mass-separation. The content of other samarium isotopes is as follows: ^{147}Sm – 0.01 %, 148Sm - 0.02, ^{149}Sm - 0.19, ^{154}Sm – 0.26 %. The content of radioactive isotopes ^{152}Eu and ^{154}Eu makes up ~560 and 620Bq/g, respectively.

PAR-P08, (Id: 83)

PRODUCTION OF ^{45}Ti BY PROTON IRRADIATION OF ^{45}Sc

Yousef Fazaeli, Mohammadreza Aboudzadeh, Ali Sattari

Agriculture and Medicine Research School
youseffazaeli@gmail.com

Objectives: ^{45}Ti with a half-life of 3.08 h is a positron emitter radioisotope with a positron branching of 85 % and also decays 15 % by electron capture with E (β+max), 1.04 MeV. The high β+ yield, short half-life and a stable daughter make ^{45}Ti a suitable candidate for positron emission tomography (PET) imaging .This properties makes this radionuclide useful in the diagnosis of tumors.

Methods: In this study after considering the excitation functions for ^{45}Sc(p,n)^{45}Ti reaction using TALYS and ALICE/ASH codes and comparison with other experimental data's, ^{45}Ti was produced by dint of pressing method with newly designed and manufactured shuttle and capsule. Essential target thickness and physical yield were calculated.

Results: new method for production and purification of ^{45}Ti was evaluated. The scandium oxide target was irradiated at 20 µA current and 21 MeV proton beam energy for 1h.experimental yield of 403.3 MBq/µAh was reported

Key words: 45Ti, Radiochemical Separation, Pressing Method.

PAR-P09, (Id: 100)

ELECTROCHEMICAL DISSOLUTION OF THE NEUTRON IRRADIATED ^{193}Ir METAL POWDER

Lydia Sokolova, Nikolay Aksenov, Gospodin Bozhikov, Yuri Albin

Joint Institute for Nuclear Research
lidia.sokol9@gmail.com Joint Institute for Nuclear Research

Due to its nuclear characteristics, the Auger electron emitter isomer ^{195m}Pt ($T_{1/2}$ = 4.02 d) is a promising radionuclide for radioimmunotherapy. We performed a test experiment to produce the isomer ^{195m}Pt by double neutron capture by the^{193}Ir target nucleus with consequent population of 195mPt through β− decay, and provided theoretical estimates for the ^{195m}Pt yield [1]. One of the advantages of the proposed approach is the possibility to isolate 195mPt from irradiated Ir target (in the form of metal powder) using radiochemical methods. It is known that iridium is a very hard, refractory, difficult to dissolve transition metal of the platinum group. Currently used methods of dissolving iridium do not meet the requirements for isolation of theragnostic radionuclides. We utilized anodic corrosion using alternating currents and solutions of hydrochloric and nitric acids that are used as electrolytes to study dissolution of Ir metal. We determined optimum conditions for electro dissolution of irradiated ^{193}Ir metal powder. In this work we also described and discussed details of the procedure.

The work was supported by Russian Foundation for Fundamental Research (project code 14-03-00745 A) and JINR grants No. 13-501-01 and 04-5-1076.

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PAR-P10, (Id: 143)

NEW TECHNOLOGY FOR ^{99}Mo ISOTOPE PRODUCTION USING LEU-FOIL TARGET

Sami Alwaer

Libya
samiwaer@yahoo.com

ABSTRACT Tajoura Nuclear Research Center (TNRC), Libya, will implement the technology for ^{99}Mo isotope production using LEU-foil target (This target is made of a LEU metallic uranium foil inserted between two concentric aluminum cylinders), to obtain new revenue streams for the TNR-reactor and desiring to serve the Libyan hospitals by providing the medical radioisotopes. Korean target will be used in this work which will be irradiated for 72 hours in the reactor core at flux equal to 1.0 x 1014 N/Cm^2.S. The target will stay 10 h. in the reactor pool for cooling before disassembling it inside a hot cell located in the reactor building. The LEU-foil will be transferred to chemical hot cell pneumatically. A special set up has been designed for the processing of LEU-foil. The set up consists of the dissolver with controlled pressure, nitric acid will be used for dissolution, cold trap cooled in liquid nitrogen for removing the fission gases, precipitation of Mo-99 by fresh 2 % alpha-benzoin-oxime will be done and purification of the final product by using two chromatographic columns: the first one contains AgC (carbon coated with silver nitrate) and the second one is a combined column with C, HZO-1 (hydro zirconium oxide) and AgC. The final product of Mo-99 solution will be filtered with 0.22 μm filter. The final radioactivity of Mo-99 expected to be >150 Ci and 95 % purity.

PAR-P11, (Id: 204)

A NEW WAY FOR SEPARATION OF ^{99m}Tc FROM CYCLOTRON IRRADIATED ^{100}Mo FOIL

Aleksander Bilewicz, Magdalena Gumiela, Ewa Gniazdowska

Institute of Nuclear Chemistry and Technology
a.bilewicz@ichtj.waw.pl

^{99m}Tc is at present, without any doubt, the most extensively used radiotracer in nuclear medicine imaging [1]. Usually, the operation period of research reactors used for the production of ^{99}Mo is about 40-50 years. Most reactors used in the preparation ^{99}Mo have already reached this age, or will reach in the near future. There is a growing interest in exploring cyclotron production of ^{99m}Tc using ^{100}Mo(p,2n)^{99}mTc reaction, a method first proposed by Beaver and Hupf nearly 40 years ago [2]. There is a real necessity to develop separation technologies suitable for use in novel modes of ^{99m}Tc production. Separation of technetium from irradiated molybdenum may be carried out using either ‘‘wet’’ or ‘‘dry’’ chemical processes. “Wet” separation techniques require dissolving of the metallic target under oxidative conditions and then separation of pertechnetate can be achieved using one of many strategies, e.g. liquid–liquid extraction [3], ion-exchange chromatography [4], aqueous biphasic extraction chromatography using ABEC resin [5] and electrochemistry [6].

The aim of our studies is to investigate the possibility of separating microquantities pertechnetate from macroquantities molybdate anions. These studies have been carried out using a natural molybdenum powder. Molybdenum forms heteropolyacids such as ammonium molybdenum phosphate (AMP) precipitating as a characteristic yellow solid. In the first step metallic molybdenum target is dissolved in 3,5 M HNO_3. Next, triammonium phosphate is added and Mo is precipitated from the solution according to the reaction:

$$(NH4)_3PO_4 *3H_2O + 12MoO_4^{2-} + 24H^+ (NH_4)3P(Mo_3O_{10})_4 + 5H_2O$$

We have optimized four parameters of the process: NH_4NO_3 and $(NH_4)_3PO_4 \bullet 3H_2O$ concentrations, temperature and the time of precipitation. From performed studies it can be concluded that the proposed process is promising and allows fast separation of macroamounts of Mo from the solution without co-precipitation of ^{99m}Tc. After optimization of the precipitation conditions, the lowest concentration of MoO_4^{2-} was only 0.37 mg ml-1. The final solution may be required additional purification by separation of $^{99m}TcO_4^-$ by ABEC resin, extraction by HDEHP or by nano-ZrO_2.

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PAR-P12, (Id: 286)

CYCLOTRON PRODUCTION AND RADIOCHEMICAL ISOLATION OF ^{117m}Sn

Gospodin Bozhikov, Nikolay Aksenov, Sarkis Karamian, Gennadiy Starodub, Sergey Dmitriev

Joint Institute for Nuclear Research
bozhikov@jinr.ru

In the recent years there has been significant interest in the production of certain isomers, especially the ones with potential applications in the field of nuclear medicine. ^{117m}Sn has been considered as an emerging radio therapeutic isotope, which is particularly promising due to its favorable nuclear decay proprieties: $T_{1/2}$ = 13.60d, 100 % IT decay mode and main gamma emission of 159 keV (86 %). There are number of potentially available ways for the production of ^{117m}Sn. In the current study the cyclotron method for ^{117}mSn production by α-particles induced reaction on ^{116}Cd has been investigated. The target consisting of enriched ^{116}Cd (98 %) in oxide form was irradiated at U-200 under the following conditions: beam current 5,5 μA and energy of the accelerated α-particles 35 MeV. The cross section of reaction ^{116}Cd(^{4}He,3n) has been taken in consideration in order to optimize the irradiation conditions. For ^{117m}Sn separation from the target material $La(OH)_3$ and LaF_3 precipitations were used. In order to achieve deep purification and concentration, ion exchange chromatography was applied using a micro column loaded with Dowex 1x8 resin in F- form.

The radiochemical recovery of ^{117m}Sn through the separation procedure was above 90 %, with high specific activity of the final product. This work was partially supported by JINR grants No. 13-501-01 and 04-5-1076 and Federal Grant-in-Aid Program «Human Capital for Science and Education in Innovative Russia» (Governmental Contract No. 8176)

PAR-P13, (Id: 287)

RESEARCH OF RADIUM NEEDLES PROCESSING FOR RECYCLING OF Ra-226

Jan Krmela, Josef Podlaha

ÚJV Řež, a.s.
jan.krmela@ujv.cz ÚJV

This theme is the first step to research and develop novel technologies and procedures for recycling and valorisation of historical radiation sources containing Ra-226. Recycling would include their reprocessing to a form suitable for irradiation in a nuclear reactor, production and separation of Ac-227 from Ra-226 and its use for the construction of Ac-227 /Ra-223 radionuclide generator. Ra-226 would be recycled and reused in next irradiations. Ra-223 would then be used for the preparation of radiolabeled biologically active compounds and verification of their properties in model in vitro and in vivo systems (cell cultures, small laboratory animals, plants).

In the first step, a method for opening and processing the radium needle under adequate radiation protection was proposed. For the handling with Ra-226 a procedure and equipment for its processing was designed. Source of Ra-226 (radium needle) with required documentation was obtained and semi-hot cell for opening radium needle with research of radium needle was prepared. This theme of project TA03010027 is supported by TA CR.

PAR-P14, (Id: 330)

EXTRACTION CHROMATOGRAPHY AND ION EXCHANGE CHROMATOGRAPHY AS A METHOD TO OBTAIN NP TRACER FOLLOWING PROTON ACTIVATION OF URANIUM TARGET AT 60 MeV

Renata Kierepko, Miroslaw Bartyzel, Jerzy-Wojciech Mietelski, Ryszard Misiak

The Henryk Niewodniczanski Institute of Nuclear Physics, Polish Academy of Sciences (IFJ PAN)
renata.kierepko@ifj.edu.pl

Anthropogenic nuclides as: Pu, Am, Np and other actinides are present in the components of terrestrial and marine ecosystems as a result of atmospheric nuclear weapon tests, nuclear accident and releases from nuclear installation. In recent years, radiological situation of Pu and Am in environment become better understood since measurements of these elements were more common. This is not the case of Np (Np-237). One of the most important reason of it is lack of available isotopic spike for chemical recovery of Np fraction from samples. Our goal was to test and develop a methodology of purification Np tracer from wide range of elements. For this purpose, uranium (U-235, U-238) target was activated by proton beam (E = 30 MeV or E = 60 MeV, respectively, Imax<40nA) in cyclotron AIC-144 at the IFJ PAN (Poland). One of the products was Np-234 –gamma decay transuranic element with $T_{1/2} = 4.4$ days. Activated target , which was a mix of activation, fission- and decays- products, including Np-234 was subjected to separation using extraction and ion exchange chromatography. These two methods are ideally suited to purification of Np fraction from another elements, because of their good selectivity and simplicity. The most important parameter which decided about the choice of the methodology was time saving concerning short half life time nuclides appeared in the source. This became the starting point for development of methodology dedicated to purification Np fraction. The results of separation were satisfactory and will be presented during Conference. It is planned to search for Np-235 and Np-236 if any present in the obtained Np fraction using ICPMS.

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PAR-P15, (Id: 366)

MEASUREMENT OF 3γ/2γ ^{89}Zr POSITRON ANNIHILATION RATIOS IN SELECTION OF SCINTILLATION AND SEMICONDUCTOR DETECTORS FOR FUTURE APPLICATION IN ONCOLOGY

Khalid Alzimami[a], **Mohammed Alkhorayef**[a], **Nicholas Spyrou**[b]

[a]*Department of Radiological Sciences, King Saud University, Riyadh 11433, PO Box 10219, Saudi Arabia*
[b]*Department of Physics, University of Surrey, Guildford, GU2 7XH, UK*
kalzimami@ksu.edu.sa

Determining the oxygenation status in tumour hypoxia is a challenge in cancer imaging. There are many ongoing clinical trials using conventional positron emission tomography (PET) scans and PET agents as cellular markers for detection of tumour hypoxia depending on the concept of the basic physics of 2γ annihilation. However, Kacperski and Spyrou (2004) proposed, for the first time, to use 3γ annihilation as a new PET molecular imaging modality, where the positronium and its annihilation, could serve as an oxygen-sensitive marker. The effective yield of 3γ annihilation depends on the rates of formation and quenching. Oxygen is known to be a strong positronium quencher where 2γ annihilation replaces the 3γ process. It is thus possible for hypoxic cells to be characterised by higher 3γ rates than those cells which are well oxygenated.

The peak-to-peak and peak-to-valley methods are applied to estimate the relative yields of 3γ positron annihilation. The only limitation of using the peak-to-peak method is when the positron emitting source has only one peak as in the case of ^{18}F. The Zirconium-89 (^{89}Zr) has recently drawn significant interest to be a promising metallo-radionuclide for use in immuno-PET. the ^{89}Zr radionuclide has a positron yield of 22.7 % as well as gamma-ray energy at 909 keV of relative intensity almost 100 % which is emitted almost simultaneously. Therefore, ^{89}Zr seems to be promising for detecting and measuring oxygenation status in hypoxic tumor by using three gamma positron annihilation based on the peak-to-peak method.

The main objective of this work is to explore the possibility of exploiting 3γ annihilation from ^{89}Zr isotope in PET imaging for measuring the relative oxygenation of tissues in oncology applications. In this experimental study four detectors, semiconductor detecors (HPGe and CZT) and scintillation detectors (NaI(Tl)), $LaBr_3$: Ce^{3+}) will be used. The peak-to-peak method will used with a ^{89}Zr source to determine these yields. Aluminium will be employed as a reference material as its high electron density reduces positronium formation and lifetimes. Teflon will also used in order to enhance the formation of ortho positronium, since quenching is low, leading to increased three photon positron annihilation.

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PAR-P16, (Id: 375)

DEVELOPMENT OF THE PRODUCTION OF IMMOBILIZED CESIUM-CONTAINING CLOSED SOURCES

Richárd Kardos[a], Gergő Bátor[b], Péter Kádár[c], Tamás Pálfi[c], Tibor Kovács[a]

[a]*University of Pannonia, Institute of Radiochemistry and Radioecology*
[b]*Social Organization for Radioecological Cleanlines*
[c]*Institute of Isotope Co., Ltd.*
kardosr@almos.vein.hu

With the rising of the global terrorist threat the improvement of the production technology of closed sources potentially able to be used for dirty bomb production becomes more and more important. The risk of radioactive species getting out into the environment can be decreased by embedding those species into insoluble matrices. In this work we would like to report about our research on Cs-137 sources. Our goal is development the production of immobilized cesium-containing closed sources by recycling used sources.

We would like to apply nano-porous systems (e. g. zeolite, titano silicate, and ceramics) in which selective transport occurs. In these systems the ions are bound selectively, and become difficult to mobilize. We prove these allegations with leaching tests.

Titano silicates are versatile materials, their ion exchange capacity is good, the kinetics of the sorption is fast, they resist big exposure doses and already at 800 0C there are changes in the structure of the titano silicates, glass phase is formed, thus making insoluble the bound materials. Other possible binders is the ceramic, we tested three type of pre-selected ceramics samples (stoneware, red tile, light tile). These ceramic type have a good properties making insoluble the bound materials, too. From the materials were made test samples by adding inactive cesium, and the samples were fired at different temperatures (800, 900, 1000, 1100, 1200 °C). After the firing, leaching tests were performed and the activity concentration of the leached cesium was measured with ICP. The leaching tests were accelerated tests, it was made for four days (six samplings), we used three types of solvent and shaker. The results allow the development of a new effective protocol, which can be applied for the recycling of closed sources, and making them safer.

PAR-P17, (Id: 394)

ACCELERATOR PRODUCTION OF Ac-225 FOR GENERATING Bi-213 FOR TARGETED ALPHA THERAPY

Mohammad Anwar Chaudhri[a], **M. Nasir Chaudhri**[b]

[a]*Inst. of Biophysics,Center of Medical Physics & Technology, Uni. of Erlangen-Nuernberg, Gedrmany*
[b]*Pakistan Council of Scientific & Industrial Research, Lahore*
anwar.chaudhri@gmx.net

The generator system Ac-225 / Bi-213 (half life of 45.6 min) is a suitable method of producing an alpha-emitter for targeted alpha thertapy). However, the production of Ac-225 is difficult and only a limited quantity of this isotope has so far been available for clinical use. Till recently it was exclusively produced by the decay of Th-229, which itself is generated by the decay of U-233 (half life of 159200 years). By making use of our production yield curves we have estimated the production of Ac-225 through (p,2n) and (d, 3n) on Ra-226, and also estimated the unwanted activities being produced simultaneously through (p,n), (d,n) and (d,2n) reactions on Ra-226. It is shown that from a thick Ra - target production yields of 1.1 × 10 10 Bq, 1.85 × 10 10 Bq and 2.04 × 10 10 Bq respectively at proton bombarding energies of 20, 30 and 34 MeV can be obtained at incident proton currents of 100 µA but irradiation time of only one day which is a lot more practical than previously quoted 10 days of irradiation. Similarly production yields of Ac-225 through the (d,3n) reactions on Ra-226 have also been estimated to be 4.2 × 10 9 Bq, 1.1 × 10 10 Bq and 1.4 × 10 10 Bq at deuteron energies of 20, 30 and 34 MeV respectively for irradiation time of 1 day at beam intensities of 100 micro-A. As the production yields data is presented in graphical form, the production of Ac-225, from a moderately thick or even a thin Ra-226 target can also be obtained for any irradiation conditions.

PAR-P18, (Id: 401)

PREPARATIONOF Ra-223 BY NEUTRON IRRADIATION OF Ra-226

Ekaterina Kukleva, Jan Kozempel, Martin Vlk, Petra Mičolová, Vopálka Dušan

Czech Technical University in Prague, Faculty of Nuclear Sciences and Physical Engineering
kate.kukleva@gmail.com

Radium-223 is prospective alpha-emmiting therapeutic radionuclide for targeted radionuclide therapy. Although Ra-223 is formed naturally by the decay of U-235, for practical reasons its preparation involves neutron irradiation of Ra-226. The decay of Ra-227 leads to Ac-227, which decays to Th-227 and Ra-223 subsequently. Ra-226 as a decay product of U-238 is generally available in multigram quantities (mainly historical stock). Main purpose of this study was to experimentally and theoretically evaluate and verify available literature data on productionof Ra-223.

According to dates obtained from gamma spectra, the yield of this irradiation and cross sections were calculated.

Radium-226 sample was flame-sealed in a quartz ampoule and irradiated for 11,7 days in a neutron flow. The yield of Ra-223 and other products were determined several weeks after EOB by evaluation of gamma and alfa spectra. Less than one month after irradiation Ra-223, Pb-212, Bi-212, Tl-208 peaks can be found on gamma spectra. In three – four month the best peaks can be seen are peaks of Pb-214 and Bi-214, which are decay products of Ra-226. Also peaks of Ac-227, Th-227, Ra-223, Pb-211, Th-228 and Ra-224 can be found, but some of them are interfered by Pb-214 and Bi-214 peaks, other of them are very small in compare with Pb-214 and Bi-214.

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PAR-P19, (Id: 442)

APPLICATION OF EXTRACTION CHROMATOGRAPHY TO THE SEPARATION OF Sc AND Zr ISOTOPES FROM TARGET MATERIALS

Carina Dirks, Steffen Happel

Radiochemistry, Department of Chemistry, Philipps-University Marburg
carina.dirks@chemie.uni-marburg.de

Non-standard isotopes such as Sc-44/47 and Zr-89 are increasingly finding interest in radiopharmaceutical applications. Methods for the separation of these elements from typical target materials were developed.

The methods are based on the use of extraction chromatographic resins such as UTEVA and DGA resin. Information on the selectivity of the resins (Dw values of selected elements in HCl and HNO_3 of varying concentration) will be presented as well as results of the method development such as elution studies, chemical recoveries and decontamination factors.

Developed methods are based on the use of vacuum supported separation allowing for fast and selective separation..

Separation Methods, Speciation (SEP)

Verbal presentations

SEP-I01, (Id: 194)

COMPLEXATION AND EXTRACTION OF An(III) AND Ln(III) WITH WATER-SOLUBLE SO_3-Ph-BTBP

Petra Panak[a], Christoph Wagner[a], Udo Müllich[b], Andreas Geist[b]

[a]*University of Heidelberg*
[b]*Institute of Nuclear Waste Disposal, KIT*
petra.panak@kit.edu

The recycling of minor actinides as nuclear fuel is complicated by the presence of curium due to its short term thermal power and neutron dose rate. Thus the development of processes for separating americium from curium are of particular interest. A new system was developed to separate only americium, addressing some of the challenges with the EXAm process such as a narrow pH window. The so called AmSel process uses water soluble SO_3-Ph-BTBP and TODGA's for Am(III), Cm(III), and Ln(III) separation. Am(III) + Cm(III) + Ln(III) distribution ratios as a function of HNO_3 and SO_3-Ph-BTBP concentrations were determined in extraction experiments. At low nitric acid concentrations the separation factor of Am(III) over Eu(III) exceeded 1000 and decreased with increasing acid concentration. The formation of 1:2 An(III)- and Ln(III)-aq-BTBP complexes was proven by time-resolved laser fluorescence spectroscopy (TRLFS) investigations of the aqueous phase after extraction. Furthermore, separation factors of Am(III) and Cm(III) for the aq-BTBP/TODGA system were determined at various experimental condition, varying between 1.5 and 3.2. The extraction studies revealed that stripping Am(III) from a loaded TODGA solvent is not impeded by slow kinetics. Buffers or salting out agents are not required.

For a better understanding of the selectivity of SO_3-Ph-BTBP towards An(III) over Ln(III) the complexation of Cm(III) and Eu(III) with SO_3-Ph-BTBP was studied by time-resolved laser fluorescence spectroscopy (TRLFS). Conditional complex formation constants of the 1:2 An(III) and Ln(III) complexes were determined at pH 3 and in 0.5 mol/L HNO_3. Though the stability constants of the 1:2 An(III) and Ln(III) complexes at 0.5 mol/L HNO_3 were lower than at pH 3 by several orders of magnitude, the difference in the stability constants of two orders of magnitude between Cm(III) and Eu(III) remained constant. These results are in excellent agreement with the selectivity determined in the extraction studies and proves that the selectivity of SO_3-Ph-BTBP towards An(III) over Ln(III) is preserved even at highly acidic conditions. Furthermore, to explain the significant decrease of the stability constants of the 1:2 An(III) and Ln(III)-SO_3-Ph-BTBP complexes at 0.5 M HNO_3, fundamental studies on the impact of different parameters such as ionic strength, nitrate complexation and protonation of the ligand were performed. These studies revealed valuable mechanistic information on complexation reactions including the impact of competing reactions and/or ionic strength effects at various experimental conditions.

SEP-V02, (Id: 49)

STABILITY OF PHENYL TRIFLUOROMETHYL SULFONE AS DILUENT IN A GANEX PROCESS

Jenny Halleröd, Emma Aneheim, Christian Ekberg, Foreman MarkElin Löfström-Engdahl

Chalmers University of Technology
hallerod@chalmers.se

At Chalmers university of technology, the main research focus within the transmutation and separation field has been the development of a GANEX (Group ActiNide EXtraction) process. The main idea with partitioning and transmutation is to separate the transuranic elements and the fission products in used nuclear fuel from each other and then use a fast neutron spectrum to transmute the transuranic elements.

The GANEX process is based on two cycles; in the first cycle the uranium bulk is removed from the fuel dissolution liquor and in the second cycle (the actual GANEX extraction is performed in this step) the transuranic elements and the remaining uranium are extracted together to avoid pure plutonium streams.

A GANEX process that combines the two extractants 6,6'-bis(5,6-dialkyl-[1,2,4-]triazin-3-yl)-2,2'-bipyridine ($CyMe_4$-BTBP) and tri-butyl phosphate (TBP) in cyclohexanone has previously been developed at Chalmers. However, due to the low flash point (44 °C) of cyclohexanone, the high water solubility and its degradation in contact with the acidic aqueous phase it is desirable to replace cyclohexanone with a different diluent. It is, however, not easy to find a proper diluent to the GANEX process based on $CyMe_4$-BTBP and TBP. $CyMe_4$-BTBP is hard to dissolve in aliphatic diluents and the extraction kinetics is slow in diluents such as alcohols and aromatics. In this study, stability experiments have been performed on a phenyl trifluoromethyl sulfone based solvent containing $CyMe_4$-BTBP and TBP.

SEP-V03, (Id: 416)

SEPARATION OF MINOR ACTINOIDS(III) OVER LANTHANOIDS(III) BY BTBP OR BTPhen EXTRACTING COMPOUNDS

Petr Distler, John Jan

CTU in Prague
petr.distler@fjfi.cvut.cz

Different extraction systems for the separation of trivalent minor actinoids over lanthanoids were studied during last years. The $CyMe_4$-BTBP and its derivatives have been demonstrated to be prospective extractants for the solvent extraction of minor actinoids over lanthanoids from high-level liquid waste issuing the reprocessing of irradiated nuclear fuel (the r-SANEX process).

The presentation will be focused on different effects of 1,2,4-triazine extracting compounds and diluents on extraction systems properties. The results of testing the $CyMe_4$-BTBP ligand and its new derivatives (such as Cy_5-S-Me_4-BBP, Cy_5-O-Me_4-BTBP, $MeCyMe_4$-BTBP or t-$BuCyMe_4$-BTBP) for the separation of Americium(III) over Europium(III) from HNO3 solutions and influence of the used diluents (both polar and non-polar) will be discussed. Moreover, complexing properties of several novel hydrophilic ligands, such as $(PhSO_3Na)_2$-BTBP, $(CH_2NMe_3)_2$-BTBP or $(PhSO_3Na)_2$-BTPhen will be described as prospective agents for i-SANEX process.

In addition to the dependences of Americium(III) and Europium(III) distribution ratio values and their mutual separation factor values on HNO_3 concentrations, the results of the thermodynamic and kinetic studies will be presented.

SEP-V04, (Id: 339)

ACTINIDE STRIPPING BY A HYDROPHILIC BTP LIGAND IN AQUEOUS HNO_3 FROM TODGA-CONTAINING ORGANIC PHASE

Łukasz Steczek, Magdalena Rejnis, Jerzy Narbutt

Institute of Nuclear Chemistry and Technology
l.steczek@ichtj.waw.pl

N,N,N′,N′-tetraoctyl-diglycolamide (TODGA) is broadly studied as a non-specific extractant for actinides and lanthanides from HNO_3 solutions of nuclear waste, in particular for group actinide extraction (GANEX process). Geist and his coworkers proposed a novel hydrophilic ligand, 2,6-bis(5,6-di-(sulfophenyl)-1,2,4-triazin-3-yl)pyridine (SO_3-Ph-BTP) for selective stripping of actinides(III) from the loaded organic phase [A. Geist et al., Solvent Extr. Ion Exch., 30, 433 (2012)], and determined (by TRLFS) the stability constants of its consecutive (from 1:1 to 1:3) complexes with Cm(III) and Eu(III) in aqueous solutions [C.M. Ruff et al., Dalton Trans., 41, 14594 (2012)].

In the present work, we studied the distribution of some actinides(III-VI) in the two-phase systems: TODGA (in kerosene) / SO_3-Ph-BTP (0–100 mM in aqueous HNO_3); and determined the apparent stability constants of their complexes in the aqueous phase, based on the distribution ratios of the metal ions. The effect of protonation of the SO_3-Ph-BTP ligand in the acidic solutions was discussed.

This work was financed from the National Centre for Research and Development through the Strategic Program Technologies Supporting Development of Safe Nuclear Power Engineering, task 4: Development of spent nuclear fuel and radioactive waste management techniques and technologies.

SEP-V05, (Id: 275)

VARIOUS FLOWSHEETS OF ACTINIDES RECOVERY WITH DIAMIDES OF HETEROCYCLIC CARBOXYLIC ACIDS

Mikhail Alyapyshev, Vasiliy Babain, Lyudmila Tkachenko

Khlopin Radium Institute
malyapyshev@khlopin.ru

Various neutral ligands are studied as potential ligands for separation of actinides from lanthanides. The most effective extractants for selective recovery of actinides from high level wastes are poly nitrogen compounds. The presence of several “soft” donor atoms in ligand structure allows to reach very high Am/Eu separation factor values. Recently a new class of neutral polydentate compounds – diamides of heterocyclic dicarboxylic acids – was proposed for recovery of f-elements from nitric acid. Ligands belonged to this class possess in their structure both “hard” oxygen and “soft” nitrogen atoms. Such combination of coordination centers provides high extraction ability of ligand toward f-elements and better affinity to actinides than lanthanides.

Diamides of 2,6-pyridine-dicarboxylic acid, diamides 2,2'-dipyridil-6,6'-dicarboxylic acid, diamides of 6,6’’-(2,2’:6’,2’’-terpyridine)dicarboxylic acid, amides of 1,10-phenanthroline-2-carboxylic acid and diamides of 1,10-phenanthroline-2,9-dicarboxylic acid were synthesized and tested for extraction of actinides (III, IV, V, VI) and lanthanides (III) from nitric acid solutions. In our work we studied extraction properties of diamides of 2,6-pyridine-dicarboxylic acid (DPA) and diamides 2,2'-dipyridil-6,6'-dicarboxylic acid (Dyp).

DPA effectively extract actinides (III, IV, VI) and lanthanides (III) from nitric acid solutions. Actinides are extracted better than lanthanides. The Am/Eu separation factor up to 6 for extraction from 1-2 M HNO_3 can be reached. Solutions of DPA in polar fluorinated diluents have very high loading capacity on extracted metals and can be used for recovery of actinides from wasted with high lanthanides content (more than 17 g/L)

Dyp have in their structure two pyridine rings and are more selective extractants than DPA. Americium can be selectively extracted from lanthanides with separation factors more than 10. In the present work two flowsheets for actinides recovery and separation them from lanthanides on the base of DPA and Dyp were developed. Both schemes were tested in laboratory scale using simulate solutions of raffinates with high content of fission products.

SEP-I06, (Id: 276)

ACTINIDE AND LANTHANIDE INTERACTIONS WITH ENGINEERED MESOPOROUS MATERIALS

Heino Nitsche[a], Jennifer Shusterman[b], Stephen Jones[b], Erin May[b], Eva Uribe[b], Anthony Bruchet[b], Tashi Parsons-Moss[b]

[a]*UC Berkeley and Lawrence Berkeley National Laboratory*
[b]*University of California, Berkeley*
hnitsche@berkeley.edu

Ordered mesoporous materials are attractive sorbents due to their extremely high surface areas, large pore volumes, open frameworks, and highly-ordered, tunable structures. Ultimately, they could be used for separating actinide and lanthanide ions from assorted solution matrices, as well as from each other. Furthermore, functionalized mesoporous materials may be useful for a variety of nuclear and non-nuclear applications including the sequestration of radionuclides for proper long-term storage, environmental sequestration of heavy metals, and nuclear waste reprocessing. Processing of nuclear waste via liquid-liquid solvent extraction produces large amount of high-level liquid wastes that in turn hamper their permanent disposal. Replacing the organic radionuclide extractant solutions with functionalized mesoporous materials, that have the extraction ligands chemically bound to the mesoporous surface, will result in a significant volume reduction and reusability of the material. We are synthesizing non-functionalized and functionalized mesoporous silica and carbon materials to study their interaction with aqueous solutions of europium, neptunium, and plutonium over a wide pH range. This presentation will give an overview of the current status of this research field. I will discuss the characterization and effectiveness of the functionalization of mesoporous silica and carbon by a variety of analytical techniques (FTIR-ATR; PZC; SEM; 13C ssNMR and 29Si ssNMR; TEM; XRD; XAS), the uptake of radionuclides as a function of pH, and the kinetics and reversibility of these processes.

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SEP-V07, (Id: 145)

INVESTIGATIONS OF WATER-SOLUBLE SALICYLALDIMINE-BASED LIGANDS FOR THE SEPARATION OF ACTINYL AND NON-ACTINYL CATIONS

Cory Hawkins[a], Christian Bustillos[a], Iain May[b], Roy Copping[b], Mikael Nilsson[a]

[a]*University of California, Irvine*
[b]*Los Alamos National Laboratory*
cahawkin@uci.edu

Current systems for the separation of actinide and lanthanide cations often employ organophosphorus reagents in combination or in sequence with anionic extractants under acidic conditions. Organophosphorous reagents do not often display large selectivity between trivalent actinides and lanthanides, as a consequence of the similar chemical properties of these elements and may require addition of soft donor ligands. Several of the actinides have higher oxidations states (e.g., V and VI) available under conditions in which they exist as linear dioxo cations. Under this configuration the actinides behave significantly different from trivalent lanthanides. The stability of these oxidation states can be a challenge for some transuranic actinides under acidic conditions. Studies suggest, however, that these oxidation states may be stabilized by coordination of ligands to the equatorial plane of the actinyl ion. For example, recent studies indicate that Schiff bases have been able to stabilize U(V). In light of these reports we are investigating ligands for the selective complexation of An(V/VI)-cations. Possible improvements in Ln/An separation factors may afford the design of separation systems under conditions not commonly considered for nuclear fuel and waste effluent processing. In this paper we present results for the extraction of lanthanide(III) and actinyl(VI) cations from aqueous buffered solutions containing the water-soluble Schiff base N,N'-bis(5-sulfo-salicylidene)ethylenediamine ($H_2SalenSO_3$) by bis(2-ethylhexyl)phosphoric acid (HDEHP) in a suitable solvent. The effects of pH, buffer composition, and aqueous complex formation on the partitioning of metal ions are examined in terms of the ability of the aqueous ligand to retain actinyl ions while extracting non-actinyl ions. Spectroscopic and potentiometric titrations of $H_2SalenSO_3$ with UO_2^{2+} and NaOH have yielded valuable data, including conditional formation constants and ligand pKa values. Both spectroscopic data and the crystal structure of the complex with UO_2^{2+} confirm that it has a 1:1 stoichiometry. Notably, visible spectroscopic measurements of solutions of the ligand with Nd(III) indicate that interactions between $H_2SalenSO_3$ and Ln(III) are quite weak. Combined with investigations of the effect of ligand hydrolysis on the formation of metal ion complex(es), the results indicate that optimum conditions for complexation occur at acidities lower than those typically maintained in f-element extraction by HDEHP. Therefore, competitive extraction studies have been carried-out at p[H] values between 5 and 6. Continuous contact experiments for U(VI) extraction by HDEHP in toluene in the presence and absence of $H_2SalenSO_3$ demonstrate that the uranyl ion distribution ratios (D) are less than 2 and holdback factors are substantial ($D_0/D \approx 100$ to 800). Because both distribution ratios and holdback factors for Ln(III) extraction under similar conditions remain in the single digits, it is thought that the extent of aqueous ligand hydrolysis and the low acidity present challenges to maintaining extractable species. Investigations of the factors that lead to poor extraction of Ln(III) ions and the evaluation of similar, but more hydrolytically stable ligands, are ongoing.

SEP-V08, (Id: 278)

SIMULTANEOUS EXTRACTION OF RADIONUCLIDES WITH CROWN ETHERS AND N,N,N’,N’-TETRAALKYL DIGLYCOLAMIDES MIXTURES IN FLUORINATED DILUENTS

Lyudmila Tkachenko, Vasiliy Babain, Mikhail Alyapyshev

Khlopin Radium Institute
tk.mila@mail.ru

Simultaneous recovery of long living radionuclides (cesium, strontium and actinides) from high level liquid waste (HLLW) allows to reduce the total volume of the waste and the costs of waste storage. The UNEX process using solvent based on chlorinated cobalt dicarbollide (CCD), polyethylene glycol and phenyloctyl-N,N-diisobutylcarbamoylmethylene phosphine oxide (CMPO) has been proposed for simultaneous recovery of the radionuclides. The main drawback of UNEX process is complicated synthesis of CCD. So development of new solvents and processes on the base of commercially available extractants is an important task.

N,N,N’,N’-tetraalkyl diglycolamides (DGA), well-known ligands for actinides extraction, can also be used for strontium recovery from nitric acid solutions. At the same time the solutions of crown ethers in fluorinated diluents extract cesium from acidic solutions. Thus the mixture of DGA and crown ether is a promising solvent for simultaneous recovery of long living radionuclides from HLLW.

In radiochemical technology saturated hydrocarbons are traditionally used as diluents for neutral ligands. For instance n-dodecane is traditionally used as a diluent for DGA. The main drawback of such diluent is low loading capacity on extracted metals and as a result tendency of third phase formation at high metal concentrations. The usage of fluorinated diluents such as meta-nitrobenzotrifluoride (F-3) allow to increase the loading capacity of the extractant and prevent third phase formation. It is also known that the most effective diluents for crown ethers are fluorinated alcohols.

The goal of this work was to develop a new solvent on the base of crown ether and DGA for simultaneous extraction of actinides, lanthanides and fission products. The extraction of cesium, strontium, americium and lanthanides with different DGA (N,N,N’,N’-tetrabutyl diglycolamide, N,N,N’,N’-tetrahexil diglycolamide, N,N,N’,N’-tetraoctyl diglycolamide), crown ethers and their mixtures was studied.

The solution of di-benzo-21-crown-7 and N,N,N’,N’-tetraoctyl diglycolamide in fluorinated diluent was chosen as a new solvent. The extraction flowsheet was developed and tested in laboratory scale using simulated solutions with high concentration of lanthanides. Optimum conditions for simultaneous recovery of cesium, strontium and actinides from nitric acid solutions, scrubbing and stripping were found.

SEP-V09, (Id: 213)

RECOVERY OF ACTINIDES AND LANTHANIDES ON SOLID-PHASE EXTRACTANTS FROM NITRIC ACID SOLUTION

Elena Zakharchenko, Galina Myasoedova, Nadezhda Molochnikova, Dmitry Malikov

V.I.Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow, Russia
e-zakharchenko@yandex.ru

Recovery of trivalent actinide and rare earth elements from complicated nitric acid solutions is important and difficult task of radiochemistry. Sorption materials for radionuclide recovery must possess the high sorption efficiency, selectivity of recovery, chemical stability and good kinetic properties. Solid-phase extractants (SPEs) prepared by impregnation of solid supports with ligands are the most appropriate for this purpose. Compounds for impregnation provide formation of complexes with actinides and lanthanides in nitric acid solution and ensure the possibility of their recovery. New types of solid supports for impregnation – high-porous and fine-dispersive polymers and carbon nanomaterials – are very promising for the SPE preparation. These materials ensure strong retention of impregnated ligands, efficiency and stability of SPEs in solutions with high content of nitric acid as well as good kinetic and other properties.

This report is focused on sorption ability and efficiency of application of novel SPEs developed by us for recovery of actinide and lanthanide from nitric acid solution. As solid supports we have used Taunit carbon nanomaterial (NanoTech-Center, Russia) and polystyrene polymers – high crosslinked (Isolute, Sweden) or hyper cross-linked (Macronet, UK). For impregnation the phosphorus and nitrogen containing ligands have been used: diphenyldibutylcarbamoylmethylphosphine oxide, tetraoctyldiglycolamide, tri-n-octylphosphine oxide, di-2-ethylhexylmethylphosphonate; these ligands possess of the high efficiency in nitric acid solution also applied in liquid-liquid extraction processes. Impregnation was carried out by solutions of ligands in organic solvents (dichloroethane) or by ligands in nitric acid solution. Impregnation in nitric acid is more advanced technique because it provides high stability of SPEs and efficiency of their application in solution with high content of nitric acid. Novel SPEs have demonstrated high sorption ability toward actinides and lanthanides (distribution coefficients in 3 mol/L HNO_3 are 10^3-10^4 mL/g, good kinetic properties and high efficiency of recovery in batch or column mode. On the base of experimental data we have developed the regimes of sorption preconcentration of actinide and lanthanide elements from 1-3 mL 3 mol/L HNO_3 and determined conditions of their elution.

The selectivity of actinide and lanthanide recovery is conditioned by properties of impregnated ligand and conditions of experiment. In this report we demonstrate examples of selective recovery of trivalent lanthanides with their separation from uranium and thorium. For this purpose we have used solid-phase extractants obtained by impregnation of various types of ligands. By use of multicomponent model solution, the effect of several elements that can be present in solutions of spent fuel reprocessing in nitric acid was examined.

Reference:
E.A. Zakharchenko, D.A. Malikov, N.P. Molochnikova, G.V. Myasoedova, and Yu.M. Kulyako. Sorption Recovery of U(VI), Pu(IV), and Am(III) from Nitric Acid Solutions with Solid-Phase Extractants Based on Taunit Carbon Nanotubes and Polystyrene Supports. Radiochemistry, 2014, Vol. 56, No. 1, pp. 27–31 Ascnowlegement:

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SEP-V10, (Id: 221)

PYROCHEMICAL EXTRACTION ANALYSIS OF AN IMMISCIBLE MOLTEN LiCl-KCl/Cd SYSTEM

K.R. Kim, J.B, Shim, D.H. Ahn, S. Paek, I.T. Kim

Korea Atomic Energy Research Institute
krkim1@kaeri.re.kr

Immiscible liquid contacting is one the most common and important phenomena in the high temperature pyrochemical systems. Among these processes, an extraction system employing molten LiCl-KCl and liquid Cd metal has been proposed for the pyrochemical recovery of actinides in a waste salt treatment step. Understanding the complex interaction of immiscible fluid dynamics with mass transfer is a fundamental importance in a liquid-liquid extraction process. The use of a liquid cadmium electrode, which is the unique features of the process, provides hydrodynamically a free surface contacting with an immiscible molten-salt electrolyte. This free interface of immiscible liquids gives an interface for mass transfer and is inconstant depending on agitated conditions. A computational method to expect an effective area for the mass transfer in the molten-salt and liquid metal system is particularly interesting and challenging for an agitated operation frequently encountered in the pyrochemical system. Details of the calculation of the velocity fields and free surface profiles which evolve in time are given. Representative simulation results are presented to illustrate the capabilities of this method for the molten LiCl-KCl/Cd system.

In addition, this study also presents a new modeling approach for studying an analysis of a counter current multistage extraction in the immiscible molten streams. An operational analysis of a counter current multistage extraction was carried out by the model equations, composed of species material balance and distribution relationships between molten salt and cadmium phase. The solutions were determined by using the matrix-based numerical method and the parametric investigations were simulated for the effect of the operating variables on the decontamination factor. The decontamination performance and species concentration profiles could be obtained by considering the flow ratio of immiscible liquids and oxidant feed throughout the multistage extraction step in a given actinides concentration condition of the waste stream.

SEP-V11, (Id: 175)

DIRECT DISSOLUTION AND ELECTROCHEMICAL STUDIES OF F-ELEMENTS IN IONIC LIQUID

Janelle Droessler, John Kinyanjui, Beatriz Martinez, David Hatchett, Ken Czerwinski

University of Nevada, Las Vegas
droessl2@unlv.nevada.edu

The unique and tunable properties of the second generation moisture-stable ionic liquids (ILs) have generated interest in their applications to the nuclear fuel cycle. Generally, ILs have low vapor pressure, chemical and radiation stability, good conductivity, and importantly, wide electrochemical windows. This beneficial electrochemical property allows for the ability to reach the negative potentials that are required for the reduction of lanthanides and actinides to metal species. Reduction of actinides and lanthanides to the metal has been largely unavailable in aqueous systems without the aid of mercury electrodes. Ionic liquids could therefore be envisioned as a system into which the used fuel once dissolved could be used to recover the uranium and separate other fission products by applying different potentials. However, the solubility of f-elements in ILs has not been extensively explored. Therefore, a more fundamental understanding of f-element chemistry and electrochemistry in ionic liquids is necessary to evaluate the system.

Exploring methods to enhance and control f-element solubility in ILs is presented. In addition, investigation of the conditions for electrodeposition of uranium from the IL and analysis of the deposited species were conducted. A direct dissolution method which uses the protic form of the anion common to an ionic liquid can provide a pathway for increased solubility of f-elements in ILs. The inclusion of water also enhances the direct dissolution process within the IL. The direct dissolution of lanthanide carbonates and uranium carbonate has been achieved in the IL trimethyl-n-butylammonium bis(trifluoromethanesulfonyl)imide ([Me_3NnBu][TFSI]) using the acid bis(trifluoromethanesulfonyl)amide (HTFSI). In addition to the carbonates, direct dissolution of U_3O_8 was performed. Analysis included UV-Visible and IR spectroscopy to characterize the soluble species and investigate possible complexation with the TFSI ligand. Cyclic voltammetry has been performed at common working electrodes such as Pt, Au, and glassy carbon (GC) to investigate the pathway from the soluble species to reduction. Potential mediated deposition of species from the [Me_3NnBu][TFSI] has been achieved and analysis of the deposits was conducted using scanning electron microscopy (SEM) and energy dispersive x-ray emission spectroscopy (EDX). The results indicate that while deposition from the IL is possible despite residual water, the resulting deposited species tend to be oxides. Further studies on electrochemical parameters and utilizing simple methods to remove water are being investigated in an attempt to promote deposition to the metal from IL solutions.

SEP-I12, (Id: 240)

URANIUM EXTRACTION FROM SEAWATER USING RADIATION-GRAFTED UHMWPE FIBER: FROM LABORATORY TO PILOT SCALE

Guozhong Wu, Jingye Li, Jiangtao Hu, Hongjuan Ma

[a]*Shanghai Institute of Applied Physics, Chinese Academy of Sciences*
wuguozhong@sinap.ac.cn

Owing to the fast economic growing and the concern over greenhouse gases and air pollution, uranium extraction is one important option to meet the nuclear fuel consumption in the future. The uranium reserve is one thousand times that in land; however, the big challenge of feasibility is the extremely low uranium concentration in ocean (ca. 3.3-3.5 ppt). Polyethylene fiber modified by radiation-induced graft polymerization of acrylonitrile and following amidoximation has been recognized to be the most suitable material for uranium extraction from seawater, in terms of durability, extraction capacity and selectivity.

Concerning the feasibility of uranium extraction from seawater, a lot of challenges have to be overcome, e.g. mass production of fiber adsorbents at a reasonable cost, high adsorption capacity and selectivity for uranyl ion in seawater, deployment of adsorbents in ocean, stripping of uranyl from adsorbent and reuse of the fiber adsorbent. About five year ago, we started a project on the uranium extraction from seawater, supported by the Chinese Academy of Sciences.

In this talk, we will present our progress in the development of UHMWPE (ultra-high molecular weight polyethylene) fiber adsorbent and uranium adsorption evaluation in simulated seawater as well as in real seawater. UHMWPE fiber is adopted owing to its high tensile strength and excellent durability in seawater. A facility for production of UHMWPE fiber adsorbent will be established in 2014, with the use of 0.5 MeV accelerator, appropriate under-beam system and grafting polymerization system. We also set up a facility for the evaluation of fiber adsorbent in which 1500 L of simulated seawater is flowed through 12 columns in 24 h. It is our target to do marine test in China coastal area in 2014-2015.

SEP-V13, (Id: 146)

A RAPID METHOD FOR ^{236}U DETERMINATION IN SEAWATER

Jixin Qiao[a], **Peter Steier**[b], **Xiaolin Hou**[a], **Robin Golser**[b]

[a]*Technical University of Denmark*
[b]*University of Vienna*
jiqi@dtu.dk

An automated analytical method implemented in a flow injection (FI) system was developed for rapid determination of ^{236}U in 5-10 L seawater samples. After a quick iron hydroxide co-precipitation, extraction chromatography (UTEVA) was exploited to separate and purify target analytes, whereupon ^{238}U was used as a chemical yield tracer. Accelerator mass spectrometry (AMS) was applied for quantifying the $^{236}U/^{238}U$ ratio and inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the absolute concentration of ^{238}U in the original seawater, thus the level of ^{236}U can be calculated. The co-precipitation behaviour of uranium with iron hydroxide was studied and optimized for the sample pre-treatment as well as for the target preparation prior to AMS measurement, respectively, in order to achieve high chemical yields. The analytical results indicate that the developed method is simple and robust, providing satisfactory chemical yields (70-100 %) and relatively short analytical time (4 h/sample). Based on the developed method, sweater samples collected along the Danish cost were analyzed and the distribution characters of ^{236}U were discussed.

SEP-V14, (Id: 50)

SEPARATION TECHNIQUES FOR DETERMINATION OF ACTINIDES IN VARIOUS SAMPLES

Ljudmila Benedik

Jožef Stefan Institute
ljudmila.benedik@ijs.si

Separation methods for determination of actinides applied at the Jožef Stefan Institute are described. Soil and sediment samples were decomposed by conventional wet dissolution with mixtures of HNO_3, $HClO_4$ and HF acids, microwave dissolution using HNO_3 and HF, and alkaline fusion with Na_2CO_3 and Na_2O_2. while preconcentration of actinides from liquid samples was carried out by precipitation using iron (III) hydroxide and ammonium hydrogen phosphate. The dry residue or precipitate with actinides and added tracers were then dissolved in 2M HNO_2. After adjustment of the plutonium oxidation state to Pu (IV) in 2M HNO_3 with 1.25M $FeCl_2$, 1M $NH_2(OH)HCl$ and 1M $NaNO_3$, the solution was adjusted to 8M using conc. HNO_3 and the actinides selectively separated with a combination of ion exchange and extraction chromatography. This 8M HNO_3 solution was passed through an anion exchange column prepared from Dowex 1X8, 100–200 mesh Cl^- form resin. The 8M HNO_3 effluent was used for analysis of americium and uranium radionuclides. The column was washed with 50 mL of 9M HCl to elute thorium. Pu was then eluted with 50 mL of 9M HCl/0.1M NH_4I solution and neptunium was later stripped with 50 mL of 4M HCl solution. The 8M HNO_3 effluen, containing the uranium and americium fraction was evaporated to dryness. The residue was dissolved in 2M HNO_3 and the solution was transferred to sequential columns of Eichrom UTEVA and TRU preconditioned with 2M HNO_3. The columns were washed with 20 mL of 2M HNO_3. After that, columns were split. The UTEVA column was washed with 20 mL of 5M HCl/0.05M oxalic acid to remove impurities. Uranium was stripped from the UTEVA column with 15 mL of 1M HCl. The TRU column with americium was cleaned up with 5 ml of a mixture of 2M HNO_3/0.1M $NaNO_2$ and americium was stripped from the TRU column with 3 mL of 9M HCl and 20 mL of 4M HCl. The solutions with isolated radionuclides were evaporated to dryness and source preparation for alpha-particle spectrometry carried out by the microcoprecipitation method with neodymium fluoride. The methods were applied to reference materials and various real samples such as soil, sediments and water, all analysed in intercomparison exercises for determination of actinides.

SEP-V15, (Id: 121)

DEVELOPMENT OF A RAPID METHOD TO DETERMINE PLUTONIUM IN FOODSTUFFS

Claudia Landstetter, Viktoria Damberger, Michael Zapletal, Christian Katzlberger

Austrian Agency for Health and Food Safety
claudia.landstetter@chello.at

After the Fukushima accident the development of rapid methods for foodstuff was getting more demanding in Austria. Therefore the Federal Ministry of Health financed a project for the development of a rapid method for the determination of plutonium in foodstuffs. Currently our lab determines plutonium just in environmental samples. This method takes about one week with ashing, dissolution, ion-exchange chromatography, micro-coprecipitation and alpha spectrometry. With a few changes concerning the sample preparation and by using the ICP-MS, a short method was developed in our laboratory to measure at least 10 samples within one day (1 person working for 10 h). The new method uses microwave digestion and a quick ion-exchange chromatography. The stripping solution of plutonium (5 ml 1,2 M HCl + 0,125 ml 30 % H_2O_2) is taken for the ICP-MS determination of Pu-239 without further pre-treatment. Pu-242 can also be measured by ICP-MS. Therefore the Pu-242 is added as tracer to the samples and the chemical recovery can be determined. If the determination of Pu-240 and Pu-238 is required the remaining solution of the ICP-MS measurement can be used to perform the micro-coprecipitation and the alpha spectrometry. With this method the requirements of the Council Regulation (Euratom) No 2218/89 of 18 July 1989 amending Regulation (Euratom) No 3954/87 laying down maximum permitted levels of radioactive contamination of foodstuffs and feedingstuffs following a nuclear accident or any other case of radiological emergency, are fulfilled. In this paper the method and the challenges during the development with high thorium und high uranium concentrations in the samples are described. Tests were conducted using sea sediment reference material, fish reference material and spiked samples.

SEP-V16, (Id: 280)

SORPTION OF STRONTIUM RADIONUCLIDES FROM SEAWATER

Valentin Avramenko, Valentin Sergienko, Dmitry Marinin, Veniamin Zheleznov, Tatiana Sokolnitskaya, Elena Kaplun

Institute of Chemistry FEBRAS, Vladivostok, Russia; Far East Federal University, Vladivostok, Russia
avramenko@ich.dvo.ru

The development of nuclear power industry and nuclear technologies resulted in contamination of biosphere, including seawater areas and World Ocean at large, by various radionuclides. Radionuclide accumulation in seabed deposits and migration comprise a great danger for vital functions of different organisms. Strontium radionuclides belong to the group of toxic elements, which causes the necessity as to control their release into the environment as to improve the methods and approaches of their removal from water streams.

The problem of removal of long-lived highly toxic radionuclides can be solved through application of sorption methods, which are primarily used, due to their simplicity and efficiency, to remove dissolved radionuclides down to the level acceptable for decontaminated water disposal into the environment. The efficiency of radionuclide removal depends on the sorbent selectivity in the presence of different components contained in an aqueous medium.

The strontium sorption by barium-containing sorption-reagent materials has been studied and respective sorption mechanisms have been examined. The strontium sorption was also tested for composite barium-containing sorbents based on carbon fibers used as a matrix in sorbent synthesis. The effect of composite synthesis conditions on their sorption properties was demonstrated.

The comparison of strontium radionuclide sorption from seawater by different types of sorbents was performed. The advantages of the sorption-reagent materials obtained in the present work for strontium radionuclide removal from seawater, as compared to other tested sorbents, have been demonstrated.

SEP-I17, (Id: 341)

PREPARATIONS FOR REDOX STUDIES OF SEABORGIUM WITH SISAK COUPLED TO THE FLOW ELECTROLYTIC COLUMN FEC

Jon Petter Omtvedt[a], Kazuki Koga[b], Yukiko Komori[c], Takumi Koyama[d], Jens V. Kratz[e], Hans V. Lerum[f], Sunao Miyashita[b], Kazuhiro Ooe[d], Yoshinari Oshimi[d], Valeria Pershina[g], Daisuke Sato[d], Tetsuya K. Sato[h], Yudai Shigekawa[c], Atsushi Shinohara[c], Akira Tanaka[d], Atsushi Toyoshima[h], Kazuaki Tsukada[h], Shohei Tsuto[d], Takuya Yokokita[c], Akihiko Yokoyama[i], Yuichiro Nagame[h], Matthias Schädel[h], Masato Asai[h], Mohamed F. Attallah[f], Naoya Goto[d], Nalinava S. Gupta[f], Hiromitsu Haba[j], Minghui Huang[j], Jumpei Kanaya[j], Yusuke Kaneya[h], Yoshitaka Kasamatsu[c], Yoshihiro Kitatsuji[h], Yuta Kitayama[i]

[a]*University of Oslo, Department of Chemistry*
[b]*Hiroshima University*
[c]*Osaka University*
[d]*Niigata University*
[e]*Universität Mainz*
[f]*University of Oslo*
[g]*GSI Helmholtzzentrum für Schwerionenforschung GmbH*
[h]*Japan Atomic Energy Agency*
[i]*Kanazawa University*
[j]*RIKEN*
j.p.omtvedt@kjemi.uio.no

An important motivation for investigating chemical properties of the transactinide elements is whether the Periodic Table keeps its validity as an ordering scheme in the transactinide region, i.e. for element number 104 and onwards. Strong relativistic effects, which increase approximately as a function of Z_2 and are thus most pronounced in the heaviest elements, are expected to make the properties of transactinide elements different from their lighter homologs. Therefore, the heaviest elements provide the best "laboratory" to study the influence of relativistic effects. A close link between experiment and theory is in-dispensable as relativistic effects can only be "detected" by comparing experimental results with those predicted by modern quantum-chemical calculations. However, due to the short half-lives and extremely low synthetisation rates of transactinide elements, the experimental challenges are huge: Experiments are performed under “one-atom-at-a-time” conditions which of course restrict available chemical methods significantly. Finding suitable experimental methods is challenging, but in addition these methods should shed light on relevant and interesting properties which can be related to theoretical calculations.

A property which can be studied both experimentally [1] and theoretically [2] is redox potentials. A Japanese-German-Norwegian collaboration has undertaken to investigate redox potentials of element 106, seaborgium, using the fast liquid-liquid extraction system SISAK [3] coupled to the newly developed flow electrolytic column (FEC) [1]. SISAK consist of a series of purpose built small centrifuges coupled to a liquid scintillation detection system. The complete system operates in a true continuous manner, i.e. it is true “on-line”, which makes it one of the fastest liquid-phase systems available for chemical investigation of transactinide elements. The system was successfully used for studies of element 104, rutherfordium [3]. The main idea is to differentiate between seaborgium in its hexavalent state and lower oxidation states (after “on-line” reduction in the FEC). By selecting suitable ligands which make e.g. hexavalent species positively charged and lower oxidation states (tetravalent or pentavalent) negatively charged (or vica versa), an anion or cation extracting reagent should in principle clearly distinguish between reduced and none-reduced seaborgium. Work has been performed at the JAEA tandem accelerator laboratory in Tokai and at the Oslo Cyclotron Laboratory, University of Oslo, to test and further develop the combined SISAK-FEC system to achieve necessary performance for redox experiments on seaborgium, and to find chemical conditions satisfying, or at least approaching, the above mentioned principle.

This presentation will give an overview of the status and achievement of the collaborative effort described above. Further details on the FEC and redox chemistry can be found in a contribution to this conference by A. Toyoshima et al. In a second contribution by M. F. Attallah et al., details about the selection and testing of suitable liquid-liquid extraction schemes are provided. [1] A. Toyoshima et al., Radiochim. Acta 96, 323-326 (2008). [2] V. Pershina and J. V. Kratz: Inorg. Chem. 40, 776-780 (2001) [3] J. P. Omtvedt et al., Eur. Phys. J. D 45, 91-97 (2007).

SEP-V18, (Id: 141)

ISOLATION OF Ho-163 FROM DY TARGET MATERIAL BY HPLC FOR NEUTRINO MASS MEASUREMENTS

Veronika Mocko[a], **W.A. Taylor**[a], **F.M. Nortier**[a], **J.W. Engle**[a], **T.E. Barnhart**[b], **R.J. Nickles**[b], **M.W. Rabin**[a], **E.R. Birnbaum**[a]

[a]*Los Alamos National Laboratory, Los Alamos, NM, USA*
[b]*Department of Medical Physics, University of Wisconsin, Madison, WI, USA*
vmocko@lanl.gov

The rare-earth isotope Ho-163 is of interest for neutrino mass measurements. The experimental evidence for neutrino and antineutrino oscillations between flavor states is compelling, with extensive implications for astrophysics, nucleosynthesis, the origin of dark matter and cosmology [1]. The goal of our experiment is to investigate the electron neutrino mass by a high precision and high statistics calorimetric measurement of the Ho-163 electron capture spectrum. This microcalorimetric experiment requires production of Ho-163 at high rate with high isotopic and chemical purity. Currently, there are no fully validated methods for production and isolation of Ho-163 at purities and quantities required. Ho-163 was produced by proton-irradiation on the University of Wisconsin 16 MeV cyclotron via the (p,n) and (p,2n) reactions using a dysprosium target as suggested in [2]. Separation of the desired elemental holmium (Ho) from irradiated dysprosium (Dy) was performed by high performance liquid chromatography (HPLC). Initial test separations were performed with an analytical-sized column filled with a cation-exchange resin, AG50W-X8, and alpha-hydroxyisobutyric acid (α-HIBA) eluent with varying concentration and pH. The separation was optimized using on-line UV/VIS detection and post column derivatization with PAR (4-(2-pyridylazo)resorcinol). Next, scale up from the analytical column to semi-preparative HPLC column was performed to accommodate the large 55 mg Dy target mass. The Ho fraction was collected and a 2-step process was employed to remove the chelating agent α-HIBA from the final product. Preliminary data from ICP-MS analysis of the purified holmium fraction indicated that the one step HPLC purification process resulted in 99.9997 % removal of Dy.

Successfully isolated Ho-163 is being encapsulated in an absorber for the first microcalorimetric measurement. Detailed information on Ho-163 production, isolation and characterization will be presented.

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SEP-V19, (Id: 62)

CHARACTERIZATION OF THE EXTRACTION PROPERTIES OF THE SELECTED EXTRACTION SORBENTS TRU, TEVA, UTEVA AND DIPHONIX

Jiří Janda, Daniel Sas, Alena Tokárová

University of defense
jiri.janda@unob.cz

The possibility of misusing heavy unstable elements, especially transuranic elements, for military or terrorist purposes, their involvement in nuclear accidents or in fuel cycle makes them elements of interest. Among the most important elements belong uranium, plutonium, americium and curium. These radionuclides are both military significant and also important for nuclear safety. The paper describes the extraction characteristics of selected alpha radionuclides by means of extraction chromatography (EXC) of selected resins - TRU, TEVA, UTEVA, DN and DIPHONIX (all Eichrom Industries, USA). The main effort was to investigate the choice of mobile-phase and especially the effect on percentage of extraction. Furthermore the attention was paid to investigate the conditions leading to degradation of extraction sorbents.

Finally the attention was focused to determine the synergic effect of different cations added to mobile-phase. These effect was evaluated for hydrochloric acid-based and nitric acid-based mobile-phase and sixteen different cations. The obtained results were compared with the results presented by Horwitz et al.

SEP-V20, (Id: 47)

DEVELOPMENT OF MUTUAL SEPARATION METHOD OF Zr, Nb, AND Mo WITH EXTRACTION CHROMATOGRAPHY USING TEVA RESIN

Asako Shimada[a], **Kuniaki Takahashi**[b]

[a]Nuclear Cycle Backend Directrate, Japan Atomic Energy Agency
[b]Japan Atomic Energy Agency
shimada.asako@jaea.go.jp

The reactors at Fukushima Daiichi Nuclear Power Station were damaged severely because of the accident. Cooling water is leaking from the reactor vessels and groundwater is flooding into the basement of reactor and turbine buildings. Consequently, contaminated water is accumulating. The accumulated water processing facility was installed to decontaminate the radionuclides and to desalinate. As a result, secondary waste such as spent zeolite and sludge are generated. In order to evaluate the radioactivity inventory in the waste, water was sampled from inflow and outflow of the apparatus. Zirconium-93 and ^{93}Mo are candidates of the important nuclides because of their toxicity, half-lives, and relatively large effect on the safety assessment. It is considered reasonable to measure ^{93}Zr using inductively coupled plasma mass spectrometry after separation of interfering elements, ^{93}Nb, ^{92}MoH^{+}, etc., and to measure 93Mo using X-ray spectrometry after separation of ^{93m}Nb emitting same energy X-ray.

In the present study, mutual separation of Zr, Nb, and Mo using extraction chromatographic resin impregnated quaternary amine-based liquid anion exchanger, TEVA resin, was investigated for the analysis of ^{93}Zr and ^{93}Mo in the contaminated water. First, distribution coefficients (Kd values) for partitioning of Zr, Nb, and Mo onto the resin from HF, mixture of HF and HNO_3, and mixture of HF and HCl solutions have been determined. In the HF media, the Kd values of Zr, Nb and Mo were gradually decreased with an increase of HF concentration in 0.01−4 M, ca. 3000 to 13 for Zr, ca. 2700 to 220 for Nb, and ca.1600 to 17 for Mo, and approximately constant in 4−8 M, ca. 220 for Nb, ca. 10 for Zr and Mo. The Kd values suppose that these metal ions are extracted on the TEVA resin from diluted HF solution (0.01-2 M HF), whereas Zr and Mo are eluted by >4 M HF but Nb is not eluted by HF solution. In the 0.1 M HF and various concentrations of HNO_3 media, the Kd values of Zr, Nb, and Mo were rapidly decreased in 0.01−1 M HNO_3, and they are under 1 when the HNO_3 concentration is more than 1 M. This supposes that extracted Zr, Nb, and Mo are recovered by 1 M HNO_3 solution. In the 0.5 M HF and various concentrations of HCl media, Kd values of Zr was rapidly decreased with an increase of HCl concentration. Whereas, Kd values of Mo and Nb are once decreased with an increase of HCl concentration in 0.01−1 M and then increased with an increase of HCl concentration in 1−7 M. The Kd values of Nb and Mo are more than 100 and Kd value of Zr is less than 1 at the 0.5 M HF−7 M HCl. This supposes that Zr is separated from Nb and Mo.

Based on the obtained Kd values, chromatographic separation scheme was designed and mutual separation of Zr, Nb, and Mo was successfully carried out. In the future, the influence of interfering nuclides will be studied to apply the separation method to the contaminated water.

SEP-V21, (Id: 23)

PALLADIUM EXTRACTION BY MALONAMIDES

Remi Poirot[a], Damien Bourgrois[b], Daniel Meyer[a]

[a]*CEA*
[b]*CNRS*
remi.poirot@cea.fr

Recycling of valuable metals appears as solution of growing interest for a sustainable supply strategy nowadays. Palladium (Pd), along with other platinum group metals (PGM) and rare earth elements (REEs), represents one of the crucial issues in recovery processes. Malonamides are neutral amphiphilic molecules which have proved their potency for the extraction of f-elements and the recovery of minor actinides. Also, these compounds were demonstrated to be suitable extractants for the recovery of Pd(II) from hydrochloric media. Nitric media were thoroughly studied in frame of nuclear fuel treatment towards lanthanide-actinide separation. However, valuation of nitric effluents containing REEs and PGM is rarely envisioned.

Within this framework, our purpose is to study liquid/liquid (L/L) extraction towards Pd recovery in nitric media, and especially to focus on the molecular level and understand the key physicochemical parameters necessary for an effective separation.

Various experimental parameters such as equilibration time, pH, extractant and nitrate concentrations were investigated in detail. Similarities and differences between palladium and lanthanides were evidenced: Pd, present at +II oxidation state, and lanthanides, each at +III oxidation state, can be both efficiently extracted but in different conditions. A judicious choice of solvent and aqueous phase composition prevents formation of a Pd-rich solid third phase.

Mechanistic studies involved complete analysis of the organic phases, including chemical speciation at the molecular level (coordination chemistry with NMR, IR, XRD and XPS), and supramolecular ordering characterization (with SAXS, DLS and NMR). Pd(II) complexes were identified and characterized. Emphasis was set on the study of the apparent discrepancy between molecular complexes (1:1 Pd:malonamide) and macroscopic behavior (slope 2 for malonamide). Keywords: palladium, lanthanides, L/L extraction, speciation, malonamides.

SEP-V22, (Id: 353)

A NEW WAY FOR IMPROVING EFFICIENCY OF CECE-PROCESS BASED HYDROGEN ISOTOPE SEPARATION PLANT

Vladimir Tkachenko, Yuri Sakharovsky

Mendeleev University of Chemical Technology of Russia
vl.a.tkachenko@yandex.ru

Development of nuclear energetics requires closure of nuclear fuel cycle (NFC). Since existing technologies cannot provide full extraction of tritium from irradiated nuclear fuel (INF) some aqueous media of INF reprocessing will be contaminated with tritium. Recycling this water will cause tritium accumulation in INF reprocessing system. Hence there is need to remove tritium from aqueous streams to avoid accumulation.

Different methods can be used for hydrogen isotope separation. One of the most effective methods is Combined Electrolysis and Catalytic Exchange process (CECE-process). The main advantages of this method are high separation factor and no need to use any additional reactants. The main disadvantages of this method are high energy consumption for electrolysis of water, hydrogen explosion hazard and lack of data on mass transfer in columns with diameter larger than 100 mm.

The main obstacle for using CECE-process is high operation costs. This paper describes one of ways to reduce operation costs through decreasing energy consumption per unit of detritiated water. One of the basic parameters of separation process in counter-current column is Θ, the ratio of the extraction factor Γ to maximum achievable extraction factor Γm. Value of Γm is defined by thermodynamical properties of separation system and Γ is set by plant designer. Increasing Θ leads to enhancing of efficiency of column (in case of constant flow rate), but maximum value of Θ equal to unity can be achieved in column of infinite height.

The method proposed assumes increasing not Γ, but Γm by lowering temperature of column at single or multiple theoretical separation stages. Lowering temperature will cause increase of separation factor and hence Γm at this stages. Extraction factor following stages is lower than on the first one so there is no need to lower temperature at the rest of column height. The main disadvantage of this method is increase of column height due to lowering mass transfer efficiency at low temperature. However, it should be mentioned that growth of capital cost of column could be compensated by lower operation costs (up to 10-15 %) for phase reversal. In addition, there is some uncertainty in determination of separation process parameters in transition temperature zones.

In the paper estimation of effect of improving efficiency of separation column that could be achieved and results of some experiments showing realizability of this method are presented.

SEP-V23, (Id: 82)

A COMPARATIVE STUDY TO DETERMINE ^{63}Ni IN LOW AND INTERMEDIATE LEVEL NUCLEAR WASTES

Celine Gautier, Christele Colin, Cecile Garcia, Florence Goutelard

CEA
celine.gautier@cea.fr

The LASE (Operator Support Analyses Laboratory) develops and implements radiochemical methods devoted to the characterization of Long-Lived Radionuclides in Low and Intermediate Level Nuclear Wastes. ^{63}Ni is generally one of the radionuclides which impose the classification of the radioactive wastes. This radionuclide is produced by neutron activation of stable nickel which is a major component of construction materials used in nuclear industry. As a pure beta emitter, ^{63}Ni must be isolated from the matrices and the interfering radionuclides through chemical separations prior to any measurement [1]. Due to its half-life (98.7 years), the French National Radioactive Waste Management Agency (ANDRA) requests its monitoring in waste packages from an activity threshold of 1 Bq/g [2]. Consequently, a rapid and selective radiochemical procedure is needed to measure ^{63}Ni in nuclear wastes.

The reference radiochemical method which has been used for a long time in the laboratory is standardized [3]. It is based on the extraction of a Ni-dimethylglyoxime (Ni-DMG_2) complex with chloroform followed by a back-extraction with diluted HCl. The aim of this work is to determine an alternative protocol that eliminates chloroform which is restricted through REACH regulation. An alternative method can be the precipitation of Ni-DMG_2 complex followed by its dissolution in HNO_3 [3]. Another procedure consist in implementing extraction chromatography where Ni precipitates on Ni® resin impregnated with DMG and is then eluted in HNO_3 [4,5].

The presentation will first focus on the optimization of the radiochemical procedures by performing speciation calculations with Chess® software. The second part of the work will be addressed to the application of the three separation methods to various types of radioactive wastes (polymers, ion exchange resins, effluents and steels). For all procedures, ^{63}Ni is analyzed by liquid scintillation counting (LSC) whereas the separation yield is determined from stable Ni measured by ICP-AES. The results will be compared in terms of accuracy, separation yields, analysis time and waste production.

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SEP-V24, (Id: 384)

DEVELOPMENT TESTING OF THE MEMBRANE INSTALLATION DESIGNED FOR PURIFICATION OF LIQUID LOW-LEVEL WASTE FROM THE RADIOCHEMICAL PLANT

Pavel Bobrov, Pavel Bobrov

FSUE Mayak PA
bopavalex@mail.rubopavalex@mail.ru

Development testing of the membrane installation designed to purify low-level solutions of the radiochemical plant was carried out. The purification technology of liquid radioactive wastes (LRW) includes the stages of selective sorption, ultrafiltration and two-phase reverse osmosis.

LRW salt content is caused by hardness salts and sodium nitrate. LRW activity is due to radionuclides of cesium, strontium, cobalt, plutonium, americium, etc. In addition, the wastes contain oxalates, sulfates, phosphates and surface-active substances. The objective of the tests performed was to purify radioactive drain solutions for them to meet the established regulatory requirements and to specify technical parameters of the purification process.

The two operating modes of the treatment installation were tested: the maximum purification mode (selective sorption + ultrafiltration + two-phase reverse osmosis) and the more economical operating mode (selective sorption + ultrafiltration + one-phase reverse osmosis).

It was demonstrated during the tests that the use of the combined process of selective sorption and ultrafiltration ensures 99 % purification of the solutions from ^{137}Cs. The content of the selective agent of 2-3 mg/l is enough to achieve the above-stated values. In the course of the installation testing in the economical operating mode the volumetric activity in the treated water varied from 5 to 6 Bq/l for alpha-emitting nuclides, and from 20 to 30 Bq/l – for beta-emitting nuclides. In compliance with the regulatory documents in effect in the Russian Federation the treated water with such volumetric activity may be used for technical purposes without any restrictions.

The use of the installation in the maximum purification mode (two-phase reverse osmosis) allows decreasing approximately by an order of magnitude the volumetric activity of the water treated at the first phase of the reverse osmosis. The volumetric activity of alpha-emitting nuclides in the final purified water was reduced to the level less than 0.5 Bq/L, while the volumetric activity of beta-emitting nuclides achieved 4.0 Bq/l. More than 16,000 m^3 of liquid low-level wastes (LLW) were treated during the development testing.

The obtained results demonstrated that the proposed combination of membrane and sorption methods enables efficient purification of liquid LLW. The treated water may be used in the water circulation network of the Mayak PA or discharged into the open hydrographic system without any restrictions.

SEP-V25, (Id: 210)

1,10-PHENANTROLINE COMPLEX OF IRON(II) NITRATE: THE CHALLENGING SALT FOR THE TECHNETIUM PRECIPITATION FROM NITRIC ACID SOLUTIONS

Tatiana Boytsova, Andrey Murzin, Vasiliy Babain, Aleksander Lumpov

OAO" V.G.Khlopin Radium Institute"
tboytsova@khlopin.ru

Tc-99 is a long-lived radioactive isotope; its main source is a spent nuclear fuel (SNF). Thus, it is necessary to localize Tc either into the glass or in the other solid matrix with a slight leaching or into the matrixes fitted for transmutation to prevent technetium escape into the environment. Due to the widely used hydrometallurgy flowsheet of the SNF reprocessing, Tc occurs as pertechnetate (TcO_4^-) ion in the nitric acid solutions.

The possibility of pertechnetate precipitation with organic complexes of Fe(II) was studied earlier. Among these compounds, o-phenantroline complex of iron(II) (Ferroine nitrate) provided most complete precipitation of pertechnetate ion.[1] The effect of the precipitant amount and the temperature of the initial and the precipitant solutions on the technetium precipitation from 1 M nitric acid solutions was studied.[2] The conditions providing maximal precipitation of Tc (up to 93±5 %) were determined. The main goal of this work was to study the mechanism of the precipitate formation under the conditions providing maximal technetium recovery from the solutions with the aim to obtain stable metal-technetium matrix.

The precipitation of TcO_4^- with Ferroine sulfate from the sulfuric acid solutions (with increasing H2SO4 concentration up to 3 M) was studied. Under these conditions the degree of Tc precipitation was 97±3 %. On changing sulfate to nitrate media the degree of technetium precipitation decreased to 93±5 %. The oxidation of Fe (II) to Fe (III) in the nitric acid solutions and its negative effect on Tc precipitation was demonstrated.

Absorption (UV-vis) spectra of Tc in the course of its precipitation with Ferroine nitrate in 1 M nitric acid solutions were registered. It was found that no TcO_4^- reduction in the presence of iron(II) in nitric acid media was observed. To confirm the composition of the precipitates formed under the conditions providing maximal recovery of Tc (up to 93±5 %), their IR spectra were recorded. The IR band at 1384 cm^{-1} belonging to coordinated nitrate ion and the IR band at 900 cm^{-1} of TcO_4^- ion were clearly observed. The IR bands at 300-600 cm^{-1} of crystal water were also detected. We proposed the following possible formula of the precipitating compound $Fe(phen)_3(TcO_4)_x(NO_3)_y{\bullet}nH_2O$, where x and y changed from 0 to 2 and x+y = 2. Based on the precipitate with the highest degree of technetium precipitation of 93±5 %, which contained maximal amount of Tc and minimal amount of nitrate-ion, the metal-technetium matrix was prepared.

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SEP-V26, (Id: 120)

EXTRACTION CHROMATOGRAPHIC SEPARATION WITH ICP-MS DETECTION FOR THE DETERMINATION OF SELENIUM-79 IN SOLUTIONS

Viktória Sántáné Gerse, Éva Kovács-Széles

Hungarian Academy of Sciences Centre for Energy Research
gerse.viktoria@energia.mta.hu

Radioactive waste produced by nuclear facilities usually contains significant amount of long-lived alpha- and beta emitters (e.g. ^{99}Tc, ^{93}Mo, ^{93}Zr, ^{41}Ca, ^{126}Sb, ^{107}Pd and ^{79}Se). Characterization of radioactive waste is usually carried out only by gamma-spectrometry because of its easy application for determination of full activity level of the waste. It is the main required parameter of the waste for its categorization (low-, intermediate or high level radioactivity). Using gamma-spectrometry determination of long-lived alpha and beta emitters is not possible; however it would be important and useful for management of nuclear waste sites and for characterization, classification and final disposal of the waste. At the same time the international surveys shows that the radioactive wastes contain usually low level waste (1^{-10} Bq/g) in 40 % therefore their analysis could be highly important.

In this work selenium-79 (^{79}Se) was chosen as a key component of low-level radioactive wastes. Due to several technical challenges of the determination of this nuclide introduction and use of novel chemical and instrumental analytical methods are needed. ^{79}Se is a beta emitter radionuclide originated from ^{235}U fission. It is one of the long-lived radionuclides ($t½ \approx 10^5$ years) of interest in nuclear waste disposal. It has potential migration ability from the repository to the environment therefore it would have significant effect in the environmental pollution. Only few papers deal with the measurement of this radionuclide in low and intermediate level wastes despite of its significant presence. Measurement of ^{79}Se using classical radiometric techniques is difficult because of its low activity.

In this work ICP-MS technique was used for determination of ^{79}Se due to its high sensitivity. This technique requires only small amount of the sample (mg) compared to radio-analytical methods which need sometimes kg-s from the samples. The aim of this work was to develop a radiochemical method for sample preparation before ICP-MS measurement. A new extraction chromatographic separation resin with selectivity for Se is under development.

SEP-V27, (Id: 359)

COMPLEXATION OF A NOVEL MULTIDENTATE CHELATING AGENT “$N_2S_2O_2/N_4O_2$” WITH PO(IV)

Julie Champion[a], Ali Younes[a], David Deniaud[b], Sebastien Gouin[b], Gilles MOntavon[d], Cyrille Alliot[c], Bandoleme Marcel Mokilid[f], Nicolas Galland[b], Eric Renault[b], Remi Maurice[a]

[a] *Laboratoire SUBATECH*
[b] *Ceisam*
[c] *ARRONAX/INSERM*
[d] *ARRONAX/Subatech*
julie.champion@subatech.in2p3.fr

Polonium is a highly radiotoxic element, whose main hazard comes from ingestion or inhalation. One of polonium’s isotopes, polonium-210 (Po-210) exists naturally from the uranium-238 decay. 20 % of the annual effective dose of Po-210 comes from inhalation of uranium and thorium radionuclides and 60 % from ingestion. To illustrate the radiotoxicity of Po-210, one may note that 1 µg of Po-210 emits as many alpha particles as 446 kg of uranium-238. Although Pierre and Marie Curie discovered the polonium (Po) element more than a century ago, physico-chemical properties of this element and its compounds and in particular complexes are still barely known. This can be explained by two main reasons: first, polonium is very rare in nature, being found in uranium ores at approximately a ration of 100 µg/ton. Thus, an adapted cyclotron or a reactor is necessary to produce some of its isotopes. Second, polonium has thirty five known isotopes, all of which are radioactive. However, a better understanding of polonium’s affinity with organic or inorganic ligands is essential to improve techniques of biological decorporation or environmental remediation. In this context, there is a need in designing specific decorporating agent for polonium, having a high affinity for this element at a given oxidation degree. A novel water soluble multidentate “$N_2S_2O_2/N_4O_2$” ligand complexing agent was designed and synthesized, as a potential new water soluble - selective chelating agent for possible polonium decorporation. This ligand presents a priori ideal characteristics for polonium complexation, i.e. a platform presenting four soft heteroatoms (N/S) and additional two pendant carboxylic groups to complete the octahedral coordination shell suitable for polonium (IV) complexation. Its affinity for polonium was studied at pH = 7.4 using a liquid-liquid extraction methodology. In parallel, theoretical calculations were applied to understand more specifically the nature of the “microscopic” interactions of polonium(IV) with the functional groups of the synthesized ligands.

Production and Application of Radionuclides (PAR)

Posters

SEP-P01, (Id: 17)

LIQUID RADIOACTIVE WASTES TREATMENT WITH FURTHER IMMOBILIZATION OF RADIONUCLIDES INTO MINERAL-SIMILAR SORBENTS

Anna Voronina, Vladimir Semenishchev

Ural Federal University
a.voronina_v@mail.ru

Sorption method of liquid radioactive wastes (LRW) treatment with further immobilization of radionuclides into mineral-similar sorbents is suggested in this work. Described method can be used for decontamination of LRW from long-lived radionuclides ^{137}Cs and ^{90}Sr; it differs from other methods in higher efficiency of separation of radionuclides as well as in combination of stages of radionuclides concentration and immobilization with the aim of their long-term storage or final disposal. The mixed nickel-potassium ferrocyanide based on hydrated titanium dioxide was used as a sorbent. The method of production of this sorbent is developed by Radiochemistry and Applied Ecology chair of Ural federal university. Spent sorbent meets the demands for matrix materials, therefore, it can be disposed/storaged immediately in hermetically sealed container without additional immobilization into cement matrix, that will allow to reduce volume of RW and decrease storage expense.

The possibility of decontamination of wide spectrum of LRW from caesium and strontium radionuclides was experimentally confirmed.The sorbent efficiently extracts radionuclides from neutral aqueous media: the value of distribution coefficient of Cs from tap water is 10(5,6±1,0) mL/g, static exchange capasity of Cs is 270 mg/g; distribution coefficient of Sr is 10(2,9±0,2) mL/g, capasity is not less than 34 mg/g. The sorbent can be efficiently used for extraction of caesium radionuclides from high level acidic (up to 7 M HNO_3), saltiness (up to 10 g/L $NaNO_3$) and alkalescent (up to 0,002 M NaOH) solutions. With solution acidity increasing, distribution coefficient of caesium decreases to $3.7\cdot10^3$ mL/g at 3 mol/L of HNO_3 and remains almost constant at more acidic solutions. Increasing of NaNO3 concentration up to 10 g/L also leads to decreasing of distribution coefficient of caesium; at $NaNO_3$ concentration up to 300 g/L Kd value remains almost constant on the order of 102,75 mL/g. It is not recommended to use the sorbent alkalescent solutions with NaOH concentration more than 0.01 mol/L in view of partitional destruction of the sorbent.

It was shown that the sorbent can be efficiently used for decontamination of Cs-contaminated waters containing surfactants and EDTA. There is no any influence of surfactants on sorption of caesium at concentrations up to 10 g/L. The affect of EDTA on caesium sorption is determined. It is shown, that at initial concentrations of caesium up to 1 mg/L there is no influence of EDTA concentration (up to 0.01 mol/L of EDTA) on sorption of caesium. Distribution coefficient of caesium at 10^{-3} mg/L of Cs is slightly lower than at 1 mg/L of Cs; the Kd values are respectively 10(4.1±0.2) и 10(4.7±0.2) mL/g. Distribution coefficient of caesium decreases at EDTA concentrations higher than 0.01 mol/L. When initial concentration of caesium is 10^{-3} mg/L, distribution coefficient of caesium doesn't depend on EDTA concentration at whole studied concentration range and its value is 102 mL/g.

Leaching rates of caesium and strontium from saturated samples of the sorbent were determined. When distilled water was used as a leachant, leaching rates were $3.7\cdot10^{-10}$ to $8.2\cdot10^{-12}$ g/(cm$^{2\cdot}$day) for caesium and от $1{,}8\cdot10^{-10}$ to $1{,}2\cdot10^{-12}$ g/(cm$^2\cdot$day) for strontium; for tap water as a leachant leaching rates were $1{,}4\cdot10^{-11}$ to$1{,}5\cdot10^{-12}$ g/(cm$^2\cdot$day) for strontium. Thus, it was experimentally confirmed that the sorbent can be successfully used as a matrix material for immobilization of radionuclides.

SEP-P02, (Id: 43)

INNOVATION IN METROLOGY: FAST AUTOMATED RADIOCHEMICAL SEPARATION FOR STRONTIUM 89 AND 90

Céline Augeray, Magalie Mouton, Lucie Tarlette, Kévin Galliez, Jeanne Loyen, Corinne Fayolle, Marc Gleizes

IRSN
celine.augeray@irsn.fr

Measuring radioactivity in food and for radiological monitoring of the environment around Nuclear Facilities or mining sites purposes requires a quantification of the radioactive isotopes (especially beta emitters) present in the different compartments (liquids or solids).

Strontium 89 and 90 [1], both pure beta emitters are radioactive isotopes of interest. Because of their toxicity and the similarity of their chemical and physical behavior with calcium, these elements may be found through the food chain. After the Fukushima accident, the necessity of a rapid quantification of radioactive isotopes such as strontium 89 and 90 appeared.

The new technique developed deals with the determination of the activity concentration of strontium 89 and 90 in water. It includes two steps: the chemical separation by ionic chromatography and the measurement of the activity concentration of strontium 89 and 90 by Cerenkov Effect. In this poster, this chemical separation by ionic chromatography is explained.

An automated separation has been developed and allows isolating strontium isotopes, including the radioactive ones: strontium 89 and 90. The separation can be done within one hour. It was achieved through the adaptation of existing analytical chemistry equipments with on-line couplings [2]. The protocol of separation is based on the use of ions exchange columns of Ionic chromatography, not as a separation and measurement technique of the cation but only as a separation technique. At the release time of the ion to be quantified, a fraction collector allows its recovery. The test portion collected is then analyzed with appropriate measurement techniques (radioactive measurement with a liquid scintillation counter (LSC) or mass spectrometry) to determine the activity concentrations of strontium 89 and 90.

The results presented at the 17th Radiochemical Conference are linked to the development of the chemical separation of strontium by ionic chromatography. Studied parameters such as the collection time, the test sample volume, the resin capacity will be discussed. This optimized protocol was then tested with standard solutions and proficiency test samples.

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SEP-P03, (Id: 44)

THE SYSTEM CA® (ANALYTICAL KIT “АНФЕЖ®”) FOR DETERMINATION OF LOW LEVELS OF RADIOCESIUM CONTAMINATION IN LIQUID MEDIA.

Remez Victor[a], Evgeny Polyakov[b], Igor Voinov[a], Vadim Tsyvyan[a]

[a]*Ecsorb, the Compamy*
[b]*Institute of Solid State Chemistry, UB RAS*
sorb@bk.ru Ecsorb

The recently developed apparatus named System CA® (Kit “Анфеж®”) and the procedure of its effective application for the concentration and determinination of low levels of radiocesium contamination in liquid media is discussed. The liquid media which can be analyzed by the System CA® include sea water, fresh water, drinking water, wine, milk, juice, human urine etc. The apparatus is designated to rapidly estimate radiocesium contamination of individuals by immediate determination of radionuclides in urine samples. Unlike the known analogs, this analytical Kit is cheap and simple in application. The main element of the system is a plastic chromatographic column which contains 10 to 100 g of granulated ferric cyanoferrate. This chemical is absolutely safe and harmless to human health and is widely recommended as an antidote in the case of radiocesium or thallium poisoning. It is shown experimentally that for quantitative determination of background levels of radiocesium in humans, the volume of the sample should be 900 to 1000 ml of urine and the chromatographic pretreatment may take 3 - 5 min.

Our research showed that this analytical Kit can be also used for high-speed concentration of radiocesium from large volumes of water solutions (to 1000 l of sea water) during a short period of time (to 30 min). According to the experimental testing, the analytical Kit allows quick transfer of the saturated sorbent from the chromatographic column to a well-type scintillation detector. The shelf life of the Kit is 5 years.

SEP-P04, (Id: 54)

EXTRACTION AND SEPARATION OF CESIUM AND STRONTIUM BY CROWN ETHERS IN ORGANIC SOLVENTS

Nadezhda Tsarenko[a], **Aleksandra Strel'nikova**[a], **Aleksey Anan'ev**[a], **Aslan Tsivadze**[b]

[a]*JSC «Scientific-research institute of chemical technology»*
[b]*Frumkin Institute of Physical Chemistry and Electrochemistry,Russian Academy of Sciences*
nadatsar@gmail.com

Extraction and separation of cesium and strontium is an important issue in radiochemistry, how to solve problems relative to the treatment of liquid radioactive waste (LRW), and for analytical purposes. The best extractants suggested for solving this problem are solutions of crown ethers in organic solvents. This paper presents the results of researches on the extraction of cesium and strontium by various substituted crown ethers from nitric acid solutions, and also from neutral solutions in the presence of activating additives. The following macrocycles: dibenzo-18-crown-6 (DB18C6), dibenzo-21-crown-7 (DB21C7), dibenzo-24-crown-8 (DB24C8), 4,4'(5')-di-tert-butyldibenzo-18-crown-6 (DTBDB18K6), dicyclohexyl-18-crown-6 (DCH18C6) and 4,4 '(5')-di-tert-butyldicyclohexyl-18-crown-6 (DTBDCH18K6) were examined. Polar solvents: 1,2-dichloroethane (DCE), nitrobenzene (NB), chloroform (CL), 1,1,7-trihydrododecafluorheptanol (FH) were selected for researches.

The effect of the crown ether structure, the solvent nature and the acid concentration was determined in the extraction of cesium and strontium from nitric acid solution containing 100 mg/L Cs and Sr and 0.1 - 5 mol/L of HNO3 into 0.1 mol/L crown ethers in organic solvents. It has been established that all investigated dibenzocrown ethers considerably extract cesium and don't extract strontium. At the same time dicyclohexylderivatives are the effective extractants for strontium and don't extract cesium. The dependence of the distribution coefficients of metals (DCs and DSr) on the concentration of nitric acid has an extreme character with the maximum at 1 - 3 mol/L HNO_3 depending on the solvent nature. The difference in the extraction ability of dibenzo- and dicyclohexylderivatives of crown ethers may be used for the separation of radionuclides of cesium and strontium from nitrate media.

Also, the processes of extraction of cesium and strontium by 0.01 M solutions of macrocyclic polyethers in organic solvents from neutral nitrate, chloride and sulfate aqueous solutions in the presence of activating additives were studied in this work. Under these conditions, DCs and DSr in the absence of activating additives are close to zero for all examined crown ethers. The introduction of various metal salts as activators into the extraction system doesn't change this situation. Only in the presence of lithium bis(trifluoromethylsulfonyl)imide $(CF_3SO_2)_2NLi$ both dibenzo and dicyclohexylcrowns extract cesium from the aqueous in to the organic phase with noticeable DCs. Under these conditions strontium is extracted insignificantly only by dicyclohexylderivatives. Our studies have shown that the application of the proposed $(CF_3SO_2)_2NLi$ activator allows to solve the task of the efficient separation of cesium and strontium by extraction with dibenzocrown ethers from neutral solutions. These systems can be used for developing analytical techniques and solving problems in radiochemistry.

SEP-P05, (Id: 101)

ANALYTICAL PROCEDURE FOR THE DETERMINATION OF NON-GAMMA-EMITTING RADIONUCLIDES IN RADIOACTIVE WASTE

Veronika Drábová, Dušan Galanda, Silvia Dulanská, Jozef Kuruc, Ján Bilohuščin

Department of Nuclear Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Slovakia
drabova@fns.uniba.sk

A variety of aqueous radioactive wastes are generated during the operation of reactors and other nuclear fuel cycle facilities. The evaporation of low level effluents is a common operation that gives rise to such wastes in a form of evaporator's concentrates. Concentrated aqueous wastes from a number of sources have variety of chemical/radiochemical composition. Such solutions contain high concentration (10 ÷ 500) g·L^{-1} of dissolved salts. The radionuclides present in these wastes, also known as wet solid wastes, included fission products, activation products and actinides. Due to their composition and activity, they are adjusted to the form suitable for long-term storage in appropriate repositories.

The extraction chromatography is a good alternative for separation of radionuclides from these radioactive wastes.

The purpose of this study was to develop suitable and advanced analytical separation procedure of ^{237}Np, ^{239,240}Pu, ^{238}Pu and ^{241}Am for their determination in evaporator's concentrate which results from waste management operations at commercial Nuclear Power Plant.

The extraction chromatography with commercial available resin AnaLig®Pu0$_2$ was a method used for the separation of ^{237}Np, ^{239,240}Pu, ^{238}Pu and ^{241}Am from simulated evaporator's concentrate samples and actual evaporator's concentrate from Mochovce NPP, Slovakia. Currently, there are two units in operation at Mochovce NPP. The other two units are under construction. The reactors are of the Russian WWER-440 design. The predicted overall production of concentrates from four reactors at Mochovce NPP is 600 m^3 per year. The evaporator's concentrate which is represented by fluids of dark brown colour belongs to the most difficult sample of analysis. Samples of WWER-type units contain a high content of boric acid with concentration of borates up to 100 g•L^{-1}. Borates tend to precipitate from solution when there are changes of pH. Solubility of boric acid and borates generally increase with increasing temperature. At pH > 10, boric acid is in the meta borate form [B(OH)$_4$]- with solubility of (14 ÷ 34) wt % from 0 to 50 °C. The specific activity lies in the range between (3.7 ÷ 7.4) x 107 Bq·L^{-1}. For this reason, treatment of the sample is very important. The pH of samples of model and actual solution of evaporator's concentrate was adjusted to ~ 13 by adding of NaOH because of higher solubility of borate solution.

There was a method developed on the model samples of 5 mL volume and hence applied on actual solution of evaporator's concentrate of the same volume as well as conditions of separation were optimised. Samples were spiked with ^{237}Np, ^{241}Am and ^{239}Pu to determine the radiochemical yields of separation procedure. After evaporation, sample was dissolved in 4 M HNO_3. AnaLig®Pu02 resin can only extract tetravalent actinides, oxidation states of monitored radionuclides were adjusted by adding of 0.5 g $NaNO_2$ and sample was transferred to a column. The success of the separation process depends on choice of suitable elution agent. Americium was eluted with 8 M HNO_3, plutonium with 0.5 M NH_4I in 7 M HCl and neptunium with 9 M HCl with addition of $TiCl_3$. ORTEC 576A α-spectrometer equipped with ULTRATM ion implanted silicon detectors (600 mm^2 active area) was used for counting the alpha radioactivity. The spectra were processed by using the Alpha-vision TM 32-bit emulation software from the EG&G ORTEC company. This method reduces analysis time, cost, labour, organic solvent consumption and disposal and provides high radiochemical yields.

Key words: radioactive wastes, extraction chromatography, americium, plutonium, neptunium, tracer techniques, alpha spectroscopy

SEP-P06, (Id: 125)

PREPARATION AND CHARACTERIZATION OF ADSORBENT BASED ON CARBON FOR PERTECHNETATE ADSORPTION.

Pavol Rajec[a], Michal Galamboš[a], Martin Daňo[a], Oľga Rosskopfová[a], Mária Čaplovičová[a], Pavol Hudec[b], Michal Horňáček[b], Ivan Novák[c], Ivan Berek[c], Ĺubomír Čaplovič[d]

[a]*Faculty of Natural Science, Comeniues University, Bratislava*
[b]*Faculty of Chemical and Food Technology STU, Bratislava*
[c]*Polymer Institute, Slovak Academy of Science, Bratislava*
[d]*Faculty of Materials Science and Technology, Trnava*
rajec@fns.uniba.sk

Activated carbon can potentially be used as an adsorbent for removing Tc from aqueous solutions. We have prepared and tested five carbon materials for their capabilities for sorption of pertechnetate (TcO_4^-). A carbon materials were prepared by soaking of fibrous cellulose with different solutions containing inorganic materials suitable for creation of micropores and after drying, material was carbonized at 500-800 °C. Prepared carbon materials were characterized by BET, acid-base titration, XRD and TEM methods.

Sorption of TcO_4^- on carbon sorbents is fast. For some sorbents even 1 minute is enough to reach more than 99 % sorption. Sorption of TcO_4^- is pH dependant. Maximum Kd was in acidic pH (pH 2-3) and reach about 7×104. Kd were decreasing with increasing pH. In sample B sorption of TcO_4^- was high even at pH 8 (Kd 5x103).

SEP-P07, (Id: 130)

METHODS FOR DISSOLUTION OF [^{226}Ra]BaSO$_4$

Jan Kozempel, Martin Vlk, Markéta Floriánová, Barbora Drtinová

FJFI CVUT
jan.kozempel@fjfi.cvut.cz

Groving interest in the research of radium chemistry, its use as target material in nuclear reaction studies and preparation of calibration sources leads to a higher demand for ^{226}Ra in readily available soluble form. Aged radium needle sources containing very insoluble radiobarite may serve as source material of ^{226}Ra and its decay products (e.g. ^{210}Pb). We descibe here several methods for [^{226}Ra]BaSO$_4$ dissolution including microwave assisted reaction and compare their efficiency in model experiments.

SEP-P08, (Id: 149)

EFFECT OF ENVIRONMENTAL CONDITIONS ON THE SORPTION BEHAVIOR OF RADIOCOBALT(II) ONTO PERMUTITE STUDIED BY BATCH EXPERIMENTS

Yaolin Zhao[a], Xianghai Zhao[a], Yong Luo[a], Chaohui He[a], Pengfei Zong[b], Kai Zhang[a], Jeremiah Monari Kebwaro[a], Kui Li[a], Baofeng Fu[a]

[a]*School of Nuclear Science and Technology, Xi'an Jiaotong University, Xi'an 710049, P.R.China*
[b]*Reactor Operation and Application Division,Nuclear Power Institute of China, Chengdu 610005, P.R.China*
zhaoyaolin@mail.xjtu.edu.cn

Discharge of aqueous radioactive waste from nuclear industry has become a major concern all over the world due to its potential to pollute portable water sources. Radiocobalt is one of the most problematic radionuclides in the effluent from nuclear industry because of its high gamma decay energy. A number of methods have been developed to remove these radionuclides from the discharge of nuclear industry. Among these methods, adsorption is one of the cost-effective approaches used to treat the radioactive waste. In this work, the stable cobalt was chosen as adsorbate to simulate the radiocobalt in the adsorption process. The radiocobalt has similar chemical characteristics as stable cobalt. Permutite, a man made zeolite, was employed an adsorbent to remove Co(II) from synthetic solution. The adsorption of Co(II) onto permutite was studied as a function of contact time, solution pH, ionic strength and solid content by using batch technique. Permutite was selected because it contains little impurities and has almost the same particle size as natural zeolites, furthermore it has better cation exchange capacity compared with natural zeolites. The results revealed that the adsorption behavour of Co(II) was significantly dependent on the solution PH and ionic strength under ambient conditions. The adsorption efficiency grew as the solution pH increased at pH<8.0, and dropped slightly as the solution pH increased at pH>9.5. The adsorption of Co(II) achieved the equilibrium quickly, and the kinetic sorption was fitted well by a pseudo-second-order rate equation. The main mechanism of Co(II) adsorption on permutite at low pH values was ion exchange and/or outer-sphere surface complexation, while at high pH values was inner-sphere surface complexation. The adsorption isotherms were simulated by the Langmuir model at three different temperatures of 298.15, 318.15 and 338.15 K. The thermodynamic data which were calculated from the temperature dependent adsorption isotherms suggested that adsorption behavior of Co(II) on permutite was spontaneous and endothermic process. From the experimental results, permutite can be a cost-effective adsorbent for disposal of the effluent of nuclear industry.We thank the finical supports by the National Natural Science Foundation of China (Grant No. 11275147).

Key words: Adsorption, Co(II), Permutite, Kinetic, Thermodynamic data

SEP-P09, (Id: 151)

A RAPID SEPARATION METHOD FOR Pu AND Sr-90 IN SEAWATER SAMPLES FOR EMERGENCY PREPAREDNESS

Hyuncheol Kim, Geun Ho Chung, Mi Jang, Mun Ja Kang, Geun Sik Choi

Korea Atomic Enegery Research Institute
hckim3@kaeri.re.k

Artificial radionuclides are released into the environment as a result of nuclear facility accidents and nuclear weapon testing. Among them, strontium, plutonium and cesium are the most frequently monitored in environmental studies. After Fukushima accident, changes of Cs-134/137 concentrations in seawater adjacent to Fukushima are well documented. However, radiostrontium or plutonium concentrations are poorly reported. It is reason that the chemical separation is necessary to determine strontium and plutonium, being beta/alpha emitters, while preconcentration of seawater for gamma emitters is relatively easy. Sequential separation method of Sr and Pu in seawater is studied to prepare for emergency.

In general, 50~100L of seawater was needed to determine environmental level of strontium or plutonium in seawater. Casauberta (2013) reported that Sr-90 concentrations were increased by 80 times rather than background levels in Pacific oceans (1.2 Bq/m^3) after the accident. At the emergency, 10L of seawater is enough to estimate the impact of the accident. We developed the rapid separation method of Sr and Pu in 1L of seawater and applied it for 10L of seawater. Co-precipitation and extraction chromatography (TEVA, Sr-resin) were used for preconcentration and chemical purification of target radionuclides. And precipitates were dissolved in 8M HNO_3, and passed through TEVA resin and Sr-resin, in order. TEVA resin does not hold Sr in the 8M HNO_3 medium, while Pu shows maximum uptake. A modular automated radionuclide separator (MARS) developed by our laboratory was applied for purification of Pu and Sr-90. Automated approaches show high potential applicability in emergency preparedness in terms of reducing labor, costs, worker exposure and high throughput. For 1L of seawater, yield of Sr and Pu is 90 % and 82 %, respectively and the separation time is less than 3 hrs. The separation of Pu and Sr-90 in 10L of seawater was finished within 10 hrs and yield of Sr and Pu was 60 % and 55.2 %, respectively.

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SEP-P10, (Id: 157)

THERMODYNAMICS AND SEPARATION FACTOR OF URANIUM FROM LANTHANUM ON GALLIUM-INDIUM EUTECTIC ALLOY

Valeri Smolenski[a], **Alena Novoselova**[a], **Alexander Osipenko**[b], **Michael Kormilitsyn**[b], **Yana Luk'yanova**[b]

[a]*Institute of High-Temperature Electrochemistry UD RAS*
[b]*State Scientific Centre -Research Institute of Atomic Reactors*
smolenski@etel.ru Institute

Actinides recycling by separation and transmutation are considered worldwide as one of the most promising strategies for more efficient use of the nuclear fuel as well as for nuclear waste minimization, thus contributing to make nuclear energy sustainable. With this purpose, two major fuel reprocessing technologies have been explored so far to separate the actinides from the fission products arising from nuclear energy production: hydrometallurgical and pyrometallurgical processes.

Fast neutron reactors allow more efficient use of uranium resources. In addition this type of reactors is capable of burning long lived actinides (including those accumulated in thermal reactors spent fuel) thus reducing radioactivity of nuclear wastes. Application of fast reactors results in considerable increase of fuel burn up and, if the reactor is operated as breeder, reproduces fissile materials. At present non-aqueous pyrochemical methods employing molten salts and liquid metals are developed for reprocessing spent nuclear fuels (SNF) of fast reactors. Inorganic melts have very high radiation stability and can be employed for organizing a short closed fuel cycle. Fissile elements and fission products dissolved in a salt melt can be separated employing selective extraction by liquid metals. Detailed information on the properties and behavior of all elements present in SNF in fused salts and liquid metals is required to design a feasible separation process and these include rare earth elements representing an important group of fission products.

Behaviour of lanthanum has so far been studied only in binary systems, Nd-Ga and Nd-In and the behaviour of uranium – only in binary systems, U-Ga [4] and U-In. There is no information on thermodynamic properties of lanthanum and on separation factor of uranium from lanthanum on metallic Ga-In alloys. In the present study the base thermodynamic properties of lanthanum and the separation factor of uranium from lanthanum was determined in Ga-In eutectic alloy.

For calculation of thermodynamic properties of lanthanum and the separation factor of uranium from lanthanum the galvanic cells (1) and (2) were used:

Mo(s) (La}| 3LiCl-2KCl, La(III)|| 3LiCl-2KCl | C(s), Cl_2(g) (1)
La (alloy) | 3LiCl-2KCl, La(III)|| 3LiCl-2KCl | C(s), Cl_2(g) (2)
Variation of the apparent standard redox potential of the couple La(III)/La as a function of the temperature is:
$E^*La(III)/La = -(3.731 \pm 0.004) + (8.3 \pm 0.6)\cdot 10^{-4}T \pm 0.003$ V (3)
Variation of the apparent standard redox potential of the alloy Me(Ga-In) as a function of the temperature were fitted to the following equation using Software Origin Pro version 7.5.
$E^{**}La(III)/La(Ga\text{-}In) = -(2.906 \pm 0.003) + (5.72 \pm 0.06)\cdot 10^{-4}T \pm 0.002$ V (4)
$E^{**}U(III)/U(Ga\text{-}In) = -(2.508 \pm 0.006) + (3.82 \pm 0.11)\cdot 10^{-4}T \pm 0.003$ V (5)
The activity coefficient of the lanthanum in liquid gallium – indium alloy was determined by equation (6):
$\log\gamma La(Ga\text{-}In) = 3F/2.303RT\cdot(E^*La(III)/La - E^{**}La(III)/La(Ga\text{-}In))$ (6)
$\log\gamma La(Ga\text{-}In) = 3.91 - 12496/T \pm 0.08$ (7)
The expression for calculation of the separation factor (θ) of the metals M1 (uranium) and M2 (lanthanum) on gallium-indium eutectic alloy can be written as: $\ln\Theta = [(n-m)FE + mFE^{**}2 - nFE^{**}1]/RT$ (8)
Using the temperature dependences of the apparent standard potentials of lanthanum (4) and uranium (5) in alloys, the following expression for separation factor of uranium and neodymium was obtained:

$\ln\Theta = -6.61 + 13859/T \pm 0.02$ (9)

SEP-P11, (Id: 170)

SORPTION OF U(VI) BY SUBMICRON ZNS PARTICLES FROM AQUEOUS SOLUTION.

Anna Rubailo[a], Alla Krasnopyorova[b], Konstantin Belikov[c]

annarubailo91@gmail.com

Uranium is one of the most dangerous radionuclides which makes a major contribution to the total alpha-activity of liquid nuclear wastes.

The most promising method for the extraction of radionuclides, including uranium from aqueous media is solid phase extraction. In the last time, different inorganic sorbents (including natural zeolites) having certain advantages over synthetic organic ion exchangers are widely used for the liquid nuclear wastes treatment.

Inorganic sorption materials have a high chemical and radiation stability and exhibit high selectivity for certain radionuclides which strongly depends on the pH of aqueous media. Among the inorganic sorbents considerable attention paid to the development of fine sorption materials, which open new possibilities for creating highly efficient process units. A feature of such materials is a large ratio between surface area and volume, which can significantly increase their adsorption capacity. Promising compounds that can be used to produce such materials are fine powders of divalent metal sulfides. It is well known that functional properties of sorbents are largely determined by the size and shape of the particles as well as surface morphology.

The goal of this work was to obtain fine powders of ZnS and to study their sorption properties towards U(VI) at different pH of aqueous medium.

One of the possible ways of using zinc sulfide particles for analytical purposes is the creation on their basis of sorption-scintillator materials for the determination of low concentrations of alpha radionuclides in natural waters. Sphalerite ZnS with the size of particles of 100-200 nm was obtained using the method of chemical deposition from thiourea solutions. Obtained powders were characterized by XRF, SEM and IR techniques. Sorptive properties of ZnS towards U(VI) at pH 2-9 were studied in batch experiments at 25 ºC using the method of limited volume.The time required to establish sorption equilibrium between the solution and the sorbent was determined from the kinetic curves.It was found that sorption equilibrium in the studied system at pH 7 is established during 60-90 min. The concentration of U(VI) in solutions after sorption was determined by a luminescent method.Luminescence spectra and excitation of uranyl ions were recorded using spectrofluorimeters Avantes(Netherlands). Recovery rate of U(VI) in the range of pH 2-9 was 95-99 %. Relative measurement error at a confidence level 0.95 didn't exceed 1 %.

The observed sorption's features of uranyl ions by fine zinc sulfide enable to assume that for this kind of the sorbent may be different types of sorption processes. Structure sulfide sorbents based primarily on close packing of atoms, which are almost always eliminates the formation of voids in the structure of the appropriate sorbents,than for them are less characteristic sorption acts related to the exchange and non-exchange absorption of ions in the structural voids.

High recovery rate of uranyl-ions obtained for ZnS fine powders makes possible their use for water decontamination purposes as well as for analytical concentration followed by determination of uranium radioactivity by alpha spectrometry.

SEP-P12, (Id: 186)

SEPARATION OF TC RADIOISOTOPES FROM PROTON IRRADIATED RU TARGETS BY THERMOCHROMATOGRAPHY –PRELIMINARY RESULTS

Ryszard Misiak, Bogdan WĄs, Mirosław Bartyzel

The Henryk Niewodniczanski Institute of Nuclear Physics Polish Academy of Sciences, Cracow, Poland
ryszard.misiak@ifj.edu.pl

Among neutron deficient Tc isotopes, ^{95m}Tc is a useful radiotracer due to a relatively long half-life ($T_{1/2}$ = 61 d), and high abundance of its gamma-rays. It can be used for studying of a behavior of ^{99}Tc in the environment and waste disposal, as well as in the development of new radiopharmaceuticals of ^{94}m, ^{99m}Tc. Radioisotope ^{95m}Tc can be obtained by a bombardment of Mo-enriched and Nb targets with protons or alpha particles[1].

In the present work ^{95m}Tc was obtained by proton irradiation of natRu targets. Ru or $RuCl_3$ powder with a natural isotopic composition was irradiated. The irradiation condition was 20 nA as proton of energy 60 MeV for 2-3 h at the Cracow AIC-144 cyclotron.

At first stage an investigation of volatilization of Tc, Rh and Ru as oxides by heating the target material – $RuCl_3$ powder in an O_2 stream was carried out. At second stage, the investigation with Ru powder as target material was done in the same experimental conditions as for studies of $RuCl_3$ as target. The similar thermochromatograms were obtained for carrier-free Rh and macroscopic amount of Ru. One oxide of Rh was detected.

Thermochromatogram of macroscopic amounts of Ru oxides showed wide peak in temperature range from 1340K to 300K. This peak corresponds to the oxides: RuO_2 and RuO_3[2-4]. Two peaks of carrier-free Tc have been observed at 620 K and 320 K for $RuCl_3$ target and one peak at 850 K with right-sided tail for Ru target. Thermochromatograms characteristics of Tc i Ru indicate a continuous migration of Ru and Tc oxides into lower temperature[2-4]. In the case of $RuCl_3$ target, the additional formation of volatile Tc and Ru oxychlorides can not be excluded. Taking into account obtained results for isolation Tc from $RuCl_3$ target, high-temperature part of temperature gradient was extended. Tc carrier-free radionuclides were trapped in scrubber with 6 Mol/l HCl. In these experimental conditions about 1 % of total amount of Ru was catched in scrubber, too.

The performed studies made it possible to obtain the following conditions for the separation Tc process: mass of $RuCl_3$ target about 35 mg, starting temperature 1373 K, exposure time 100 minutes, O_2 flow rate 60 cm^3/min. In all experiments one peak of Rh was detected, probably as RhO_2, at this same adsorption temperature independently of gradient temperature, exposure time and irradiated target material Ru or $RuCl_3$ powder. The stable position of Rh peak during experiment indicates the possibility of separation Rh from target material. Further investigation is planned.

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SEP-P13, (Id: 190)

A STUDY ON ARSENIC SPECIATION IN KOREAN MARINE SAMPLES USING ION CHROMATOGRAPHY-INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

Lee Joung Hae[a], Min Hyung-Sik[a], Oh Hae Joon[b], Nam Sang-Ho[b]

[a]*Korea Research Institute of Standards and Science*
[b]*2Mokpo National University*

ecljh@kriss.re.kr

As the toxicity of certain element depends very heavily on their physico-chemical form, it is important to be able to monitor levels of the individual species. Arsenic occurs everywhere in the environment in various forms, including trivalent and pentavalent states, inorganic and organic compounds. In general, pentavalent arsenic is considerably less toxic than trivalent arsenic; inorganic arsenic is more toxic than methylated and other organo-arsenicals. Arsenic speciation in food and dietary supplements is essential in order to provide a meaningful assessment of exposure due to differences in toxicities of the chemical forms.

In this study, ion chromatography has been coupled with mass spectrometry to quantitatively determine arsenic species in Korean marine samples We made use of Inductively Coupled Plasma-Mass spectrometry as a sensitive elemental detector in combination with a selective separation technique such as ion chromatography provides information on the chemical form of arsenic compound in some samples.

The standard seven arsenic species of Arsenite (As^{3+}), Arsenate(As^{5+}), AsC (arsenocholine), DMA (dimethylarsinic acid), MMA (methylarsonic acid), AsB (arsenobetaine) and TMAO (trimethylarsine oxide) were separated with chromatographic methods, then the arsenic species were selectively detected by ICP-MS. Various extraction procedures were also investigated using reference materials to evaluate the extraction efficiency of the different arsenic species in Korean marine samples

SEP-P14, (Id: 198)

SOLVENT EXTRACTION OF PLUTONIUM FROM ENVIRONMENTAL SAMPLES

Alena Tokárová, Daniel Sas, Jiří Janda, Oldřich Navrátil

University of defense
alena.tokarova@unob.cz

The solvent extraction was described for determination of the plutonium presented in the environmental samples. Tri-n-octylphosphine oxide (TOPO) and di-2-ethylhexyl phosphoric acid (HDEHP) were used as the significant reagent of extractants of the plutonium. The extraction properties of TOPO and HDEHP for tetravalent plutonium in 5 mol.L^{-1} HNO_3 into toluene were investigated. The optimal concentration of TOPO for extraction of plutonium was determined (1.10^{-2} mol.l^{-1} and higher). These solutions are easily measurable by liquid scintillation method without any further adjustment procedures. The dependences of equilibrium ratios of the plutonium on analytical concentration of chelating agents and pH were studied. The structure of the complex in the organic phase was determined as $Pu(NO_3)_4$.2TOPO and the value of extraction constant was calculated. Trivalent lanthanides and actinides, important fission products as cesium, zirconium, strontium and also thorium, uranium with concentration up to 1.10^{-4} mol l^{-1} and iron with concentration up to 5.10^{-3} mol l^{-1} do not interfere. The goal of this work was to develop selective solvent extraction method for the separation of plutonium.

SEP-P15, (Id: 203)

LONG TERM IMMOBILIZATION OF Cs-137 BY TRANSFORMATION OF TITANIUM FERROCYANIDE TO LITHIUM TITANATE

Aleksander Bilewicz, Bartoś Barbara, Seweryn Krajewski, Magdalena Gumiela

Institute of Nuclear Chemistry and Technology
a.bilewicz@ichtj.waw.pl

Radioactive waste contains a variety of radionuclides and arises in a variety of physical and chemical forms. In Poland, the amount of activity and waste volume of liquid wastes are relatively small, mostly from operation of research reactor. Despite of the low level radioactivity involved, there are many significant hazards that could arise as a result of inadequate management. Treatment of liquid wastes is needed to produce a waste product suitable for long term storage and disposal. Our idea of immobilization of the ^{137}Cs radionuclide in the matrix of TiO_2 is based on the initial sorption of ^{137}Cs on titanium ferrocyanide (TCF) and then converting TCF to the TiO_{2aq} by hydroxide solution and calcination of the product to ceramic.

We showed that the TCF is a very effective sorbent for ^{137}Cs. In the column experiments we did not observed any breakthrough of the column after passing 10000 bed volumes of the saline solution spiked with ^{137}Cs . After adsorption of the ^{137}Cs on TCF hydroxide solutions were passed through a column and degree of transformation of TCF to TiO_2 and leakage from the column was examined. Hydroxides used were as follows : LiOH , NaOH , KOH , and $(CH_3)_4NOH$.

The obtained results indicate that all hydroxides studied convert, in 100 percent, the black TCF to the white TiO_{2aq}. However, when using NaOH and KOH competing influence of the cations K^+ and Na^+ causes leakage of ^{137}Cs from formed TiO_2 aq. Much better results have been obtained using tetraalkylammonium hydroxide and particularly lithium hydroxide. Competitions from bigger tetraalkylammonium cations and hydrated Li^+ on sorption of small hydrated Cs^+ cation is negligible. Collected samples of the titanium oxide with adsorbed ^{137}Cs were next calcined at 900 °C and the leaching of radionuclides has been studied.

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SEP-P16, (Id: 218)

RAPID DETERMINATION OF RADIOSTRONTIUM IN MILK USING AUTOMATED RADIONUCLIDES SEPARATOR AND LIQUID SCINTILLATION COUNTER

Kun Ho Chung, Hyuncheol Kim, Jong Myoung Lim, Young-Yong Ji, Geun-Sik Choi, Mun Ja Kang

Korea Atomic Energy Research Institute, Environmental Radioactivity Assessment Team
chungkh@kaeri.re.kr

Milk is one of the special important matrices to be rapidly assessed its radioactive contamination in emergency situations such as a nuclear plant accident. Because of its chemical and biological similarities to calcium in milk, radiostrontium can be incorporated into human organism, preferentially in bone tissue, by milk ingestion. Development of rapid analytical methods for radiostrontium in milk is essential for emergency situations. Both ^{89}Sr and ^{90}Sr, produced by the fission reaction of nuclear fuel in a nuclear reactor, are beta emitters which require radiochemical separation for radiometric analysis. The conventional methods for the determination of radiostrontium in milk using time consuming sample preparations and manual chemical separations are usually too slow to take measures for emergency situations.

A modular automated radionuclide separator for $^{89/90}$Sr (MARS Sr-90) has been developed for the rapid and reproducible isolation of radiostrontium. MARS Sr-90, designed and built in our laboratory, was successfully applied to the isolation of radiostrontium in milk samples. MARS Sr-90 consists of four parts; a control module, a pump module, a valve module and a column module. Control software developed on the LabView platform is a virtual instrument to control MARS Sr-90 by means of manipulating the most important input parameters through the graphical user interface on the computer screen. The automated radiochemical procedures for separation and purification of $^{89/90}$Sr in milk are developed. MARS Sr-90 uses cation exchange resin for pre-concentration of $^{89/90}$Sr from a milk matrix and Sr-Spec resin for purification of $^{89/90}$Sr from interfering radioactive nuclides. By using MARS Sr-90 with rapid flow rates, sample preparation time is minimized. The activities of purified $^{89/90}$Sr are simultaneously determined by the measurement of the Cherenkov radiation of ^{89}Sr and liquid scintillation radiation of ^{90}Sr using 1220 Quantulus liquid scintillation counter. The developed automated radiochemical procedures provide a rapid, safe and reproducible separation of $^{89/90}$Sr from milk samples. Compared to conventional $^{89/90}$Sr separation methods carried out manually, MARS Sr-90 is faster, less labor intensive and expected to be widely used as a powerful and convenient tool for the chemical separation and purification of $^{89/90}$Sr found in various foodstuffs for an emergency situation.

SEP-P17, (Id: 229)

SEPARATION AND PRECONCENTRATION OF TRACE AMOUNTS OF Sr-90 AND Tc-99 FROM PRIMARY COOLANT WATER USING COMMERCIALLY AVAILABLE SORBENTS AND ION-EXCHANGERS.

Ewelina Chajduk, Marta Pyszynska, Anna Bojanowska-Czajka, Halina Polkowska-Motrenko

Institute Of Nuclear Chemistry And Technology
e.chajduk@ichtj.waw.pl

Among the fission products of U-235 are: Sr-90 and Tc-99. Information on their content in primary coolant water is very important because it indicates the state of the fuel rods in NPP. Different analytical methods could be used for the determination of Tc-99 and Sr-90, however each method requires separation and/or preconcentration of determined radionulide. The problems are also related to large volume of samples, what is the case of coolant water. This study outlines some batch and column studies for selective separation of strontium and rhenium (as an analogue of technetium) using commercially available sorbents and ion-exchangers. Preliminary results suggest, that it is possible to separate strontium and technetium from boric acid (main components of primary coolant water and from other beta-emitters.

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SEP-P18, (Id: 273)

A USE OF IRON(III) HYDROXO COMPLEXES FOR REMOVAL OF RADIONUCLIDES FROM SOLUTION IN THE PRESENCE OF COMPLEXING ANIONS

Valiantsina Torapava, Nadzeya Varonik, Artsiom Radkevich

Joint Institute for Power and Nuclear Research - Sosny, National Academy of Science of Belarus
valen.toropova@mail.ru

Operation of nuclear power plants and other nuclear industry require solution of the following issues: decontamination of the main equipment and working area, treatment of low radioactive waste (LRW). These problems are closely related to each other, i.e. ineffective treatment of LRW generates large amounts of radioactive waste with complex chemical composition. Behaviour of radionuclides in such processes as sorption, ion-exchange, ultrafiltration, etc., which are used for removal of radionuclides from solution, is largely determined by their speciation in solution.

Speciation of iron (III), cobalt (II) and manganese (II) in aqueous solution was studied. A pH range of existence for mononuclear and soluble polynuclear hydroxo complexes, as well as colloidal particles in the media of weak and strong complex anions was found. It was shown that the presence of complex anions (oxalate, phosphate, iodate, EDTA etc.) affects the hydrolysis and precipitation of metal ions in aqueous solution. The presence of complex anions in aqueous solution shifts the beginning of the radionuclides (^{60}Co, ^{54}Mn, ^{109}Cd, ^{65}Zn) coprecipitation with iron (III) to higher pH values. The higher the concentration of the complex anion in solution, the higher pH is needed for coprecipitation of the radionuclides. A treatment technology of aqueous solutions with complex chemical composition, containing different radionuclides (^{60}Co, ^{54}Mn, ^{109}Cd, ^{137}Cs, ^{110m}Ag, etc.) as well as used deactivation solutions and acidic filtrates from separation columns, was developed. It was shown that by coprecipitation with iron (III) and ultrafiltration at certain conditions total decontamination of the solutions from ^{60}Co, ^{54}Mn, ^{109}Cd, ^{137}Cs, ^{110m}Ag radionuclides is reached. Therewith, decontamination factor of 1.103 using one stage and of 5.106 using three stages purification for ^{109}Cd were obtained.

The results of speciation studies show that iron (III) can be precipitated in the presence of organic complex agents, in a form of iron (III) hydroxide, and the radionuclides can be coprecipitated with it. Therefore, coprecipitation can be used as a possible way for decontamination of the radioactive solutions for removal of radionuclides.

SEP-P19, (Id: 284)

ADDITION OF ALUMINUM SALTS TO WATER FOR REDUCING Co-60 IN ACTIVATED CORROSION PRODUCT DEPOSITS ON PRIMARY SYSTEM SURFACES OF NUCLEAR REACTOR PLANTS

Leonid Moskvin, Anatoly Efimov, Timofey Epimakhov, Oleg Pykhteev

moskvinln@yandex.ru

Radiation situation in occupied areas of nuclear reactor plants is much determined by the activity of loose corrosion product deposits (crud) in the primary system. Co-60 present in crud is the major contributor to personnel exposure because it has a long half-life period and emits hard γ-radiation. Experimental studies have been performed to analyze the possibility of reducing Co-60 in crud on the primary system surfaces. Mechanisms of hydrolysis polymer product formation in mixed nitrate solutions of Fe(III) + Al(III) + Co(II) have been investigated. This hydrolysis process models hydrolysis of corrosion products in the primary coolant water where aluminum salts are added. Analyses have been carried out with gel permeation chromatography and radioisotope and elemental analysis methods. The analysis results show that almost all Co(II) ions which entered hydrolysis polymer products during their initial formation are substituted by aluminum ions as the polymer products age. Since these polymers are precursors to occurrence of loose corrosion product deposits on the primary system surfaces and these deposits include Co-60 as the most important source of radiation exposure, the analysis data attributes improved radiation situation in the occupied areas to addition of aluminum salts to the primary coolant water and demonstrates the usefulness of this addition.

SEP-P20, (Id: 299)

TECHNETIUM AND RHENIUM SULFIDE NANODISPERSION SIZE SPECIATION BY SAXS, NANOSIZER AND ULTRAMICROCENTRIFUGATION.

Alexey Safonov[a,b], Konstantin German[a,b], Varvara Tregubova[a,b], Stepan Kalmykov[d], Evgeniy Abhalimov[a], Yana Obruchnikova[a,b,c], Marina Glazkova[b], Andrey Shiryaev[a], Victor Ilin[a,b]

[a] *Frumkin Institute of Physical Chemistry and Electrochemistry RAS, Moscow, Russia*
[b]*Moscow Medical InstituteREAVIZ, Moscow Russia*
[c]*Mendeleev Russian Chemical Technology University, Moscow Russia*
[d] *Lomonosov Moscow State University, Moscow, Russi*
alexeysafonof@gmail.com

Technetium and rhenium heptasulfides were among the first synthesized compounds of these elements as considered the convenient route for Tc and Re separation from aqueous solutions. Although in the first works its composition was established as M_2S_7 (M = Tc, Re) it was rather surprising in view of Tc and Re redox potentials being in contradiction with those of S^{2-}. No reasonable thermodynamic data is available on the solubility of these compounds mostly due to the variety of chemical nature ascribed to these compounds and difficulties in its nano- and micoro- size speciation/attribution. Only the formation kinetics and colloidal particle size speciation studies [1-3] provided with some reliable information on Tc concentration dependences. Structure unit fragment Tc_3S_{13} for technetium sulfide acc. to EXAFS studies [4] contained trinuclear Tc(IV) cluster with 3-S atom inside it and the planar vacancies filled with multiple disulfide ligands, thus explaining the excesses of S in this compound. In the growing process of Tc-S colloid system, the size of colloid particles was shown to increases by deposition of Tc sulfide on the particle surface, not by coagulation of the particles [3]. Recently mixed oxo-sulfide species of Tc were characterized [5].

Here we continue microcentrifuge size speciation in course of the reaction of Tc(VII) and Re(VII) with sulfide and follow it with size speciation of generated particles in the solution by SAXS at specialized small angle diffractometer SAXSess (Anton Paar (Austia), CuK (1.54 A), transmission analises after collimation correction mode, sealed glass capillaries, registration with ImagingPlate). Based on Log(I) = f(s2) plots, $s = 4\pi\sin(\Theta)/\lambda)$ for the aged samples two types of species were observed in Re sulfide colloidal solution by SAXS. Small particles were monodisperse and quite isotropic with Rg = 0.31 – 0.45 nm. Large particles were disc shaped with 40 nm in diameter and 5 nm height. Both methods supported induction period and kinetic dependent on the $[Na_2S]$ in the solution and the order of mixing the reagents. Based on the similarity of chemical behavior we suggest similarity in composition of technetium and rhenium species obtaind in the identical conditions. The stability of M_3S_{10} (M = Tc, Re) in the resulting solution was dependent of the S^{2-} concentration in it. When higher than 0.06M Na_2S, further grouth of Tc and Re sulfide particles occurred for ≥ 150 h similar to observations made in [3]. For $[Na_2S] \leq 0.04$ M, the M_3S_{10} was reoxidized by present air to Tc(VII) within 175-200 hours thus being resolubilized. The determination of the free Tc and Re species concentration with separation of ionic or nanocolloidal particles with 5 kD "Sartorius" ultramicrocentrifuge tubes gave evidence on the M_3S_{10} nanosulfide formation similar to that observed in [4]. The equation for the Tc sulfide solubility based on these figures was evaluated.

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SEP-P21, (Id: 301)

EFFECT OF THERMAL TREATMENT ON CHEMICAL STABILITY OF RESORCINOL-FORMALDEHYDE RESINS AND THEIR Cs-137 UPTAKE PROPERTIES

Andrey Egorin, Valentin Avramenko, Dmitry Marinin, Mikhail Tutov

Institute of Chemistry FEBRAS, Vladivostok, Russia; Far East Federal University, Vladivostok, Russia
egorin@ich.dvo.ru

Here we present the results of study of interrelations between thermal solidification and selective sorption properties of resorcinol-formaldehyde resins of resol type in highly mineralized alkaline media. Using thermal analysis we have observed a series of exo- and endothermal effects, determined the maximum temperature of thermal treatment, and revealed features of resin solidification in Na- and K-forms.

Investigations of Cs-137 sorption under static conditions have shown that resorcinol-formaldehyde resins heated at 100-130 °C have low chemical stability in 0.1M NaOH solutions, which has a negative impact on Cs uptake. The increase of temperature during thermal treatment stage results in the increased chemical stability and the selectivity of cesium sorption in highly mineralized alkaline media. We believe that this process is related to the decomposition of methylol groups of resitols under elevated temperature and to the formation of new reaction centers, which finally leads to formation of resitols with highly cross-linked polymer network. Such structure determines high selectivity of the resin to cesium and its stability in alkalines.

SEP-P22, (Id: 332)

IODINE ADSORPTION ON MODIFIED NICKEL OXIDE

Lórant Szatmáry[a], Vojtěch Brynych[a], Lenka Procházková[b], Václav Čuba[b]

[a]*ÚJV Řež, a.s.*
[b]*FJFI,ČVUT*
sza@ujv.cz

One the most inportant fission products, considered in radiaoctive waste disposal, is is radioiodine (^{131}I). The most notable iodine radioisotopes are ^{131}I and ^{129}I, with half-life 8 days and 15.7 million years respectively. They have potential radiological effect on the human body and the environment due to of their large nuclear yield, volatility and especially accumulation in thyroid tissues. Therefore it is necessary to control their release from nuclear power plants and potentially from disposed radioactive waste.

The efficient adsorption unit for the atmosphere cleanup system is needed to capture the iodine isotopes. Activated carbon as adsorbent is widely utilised for this purpose. However, activated carbon has poor iodine retention at higher temperatures which are necessary during waste treatment. Another disadvantage of activated carbon is ignition change in presence of nitrogen oxides. Therefore, the development of new thermally stable adsorbents is envisaged.

In presented work, nanomaterials, based on pure nickel oxide, mixed nickel zinc oxide, or nickel oxide doped with silver were developed and tested as potential adsorbents for efficient iodine removal. Simple metal oxides exhibit sufficient radiation and thermal stability. Further improvement of sorption properties may be gained by the functionalisation of nanofiber materials with nickel oxide.

Tested powders were produced by photoinduced precipitation of solid precursors from aqueous solutions containing soluble nickel salts, followed by low temperature calcination.

The sorption properties of nanomaterials were tested by the method based on Standard Test Method for Nuclear-Grade Activated Carbon (ASTM D3803). In comparison with commercially available nickel oxide, newly developed materials show significantly higher sorption capacity.

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COMBINED, SEQUENTIAL PROCEDURE FOR RADIOCHEMICAL ANALYSES OF ^{63}Ni, ^{99}Tc, Pu, Th, Am, U AND ^{90}Sr IN ENVIRONMENTAL SAMPLES

Krzysztof Kleszcz, Jerzy-Wojciech Mietelski, Edyta Łokas, Ewa Tomankiewicz

The Henryk Niewodniczanski Institute of Nuclear Physics, Polish Academy of Sciences (IFJ PAN)
krzysztof.kleszcz@ifj.edu.pl

Environmental samples are sometimes quite unique – the mass of sample collected frequently on remote locations is limited due to need of transportation by hands. The advantage of analyses of as much as possible radionuclides is obvious. The information obtained from ratios between different nuclides are enlarging our knowledge a lot. Moreover, the efforts devoted for dissolution of sample sometimes are large. All this supports concept of developing a single, sequential radiochemical procedure, which applied to a single environmental sample, after single mineralization can give information on many radionuclides. In our laboratory from many years a sequential procedure for radiochemical analyses was developed. Recently sub-procedures for ^{63}Ni and ^{99}Tc were included into existing large sequential procedure for Pu, Th, U, ^{90}Sr radiochemical analyses in environmental (soil, sediment, peat etc.) samples [1]. Soaked with ammonia sample (~10g) is ashed in 400 °C sample (about 10 g). Then tracers are added and wet complete digestion is applied using HF, HNO_3, HCl and H_3BO_3. Sample is converted to 1 M HNO_3 and then it is neutralized up to $pH = 6$ using ammonia. Precipitation contains all actinides and 90Sr whereas Tc and Ni stay in solution. Actinides are then separated using Dowex-1 and TEVA resins and ^{90}Sr using Sr-Resin. ^{63}Ni is separated using DMG and ^{99}Tc using TEVA.

Procedure was positively tested using reference materials spiked with ^{95m}Tc (obtained with AIC-144 cyclotron by us) and $NiCl_2$ as tracers only for radiochemical yield tracing due to lack of RM with certified values for ^{99}Tc and ^{63}Ni) .

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LIQUID-LIQUID EXTRACTION OF TECHNETIUM(VII) WITH TODGA

Magdalena Rejnis, Jerzy Narbutt

Institute of Nuclear Chemistry and Technology
m.rejnis@ichtj.waw.pl

N,N,N′,N′-tetraoctyl-diglycolamide (TODGA) is broadly studied as a non-specific extractant for actinides and lanthanides from HNO_3 solutions of nuclear waste, in particular for group actinide extraction (GANEX process). Unfortunately, some fission products including technetium (in the form of pertechnetate anion, $^{99}TcO_4^-$) are also efficiently extracted from HNO_3 solutions to the TODGA-containing organic phase, accompanying the actinides and lanthanides.

The present work was focused on modelling the process of technetium extraction to organic solutions of TODGA. The TcO_4^- anion is evidently extracted to the organic phase as the ion pair, together with a lipophilic cation – the protonated TODGA molecule. We investigated the effects of acidity, of anions that compete with TcO_4^- for the lipophilic cation, and of diluent on the efficiency of extraction of technetium(VII). The effect of other metals present in the extraction system was also studied.

This work was financed from the National Centre for Research and Development through the Strategic Program Technologies Supporting Development of Safe Nuclear Power Engineering, task 4: Development of spent nuclear fuel and radioactive waste management techniques and technologies.

SEP-P25, (Id: 349)

ANALYSIS OF THE FACTORS THAT MAY LEAD TO MISINTERPRETATION OF U(VI) COMPLEXES TIME-RESOLVED LASER-INDUCED FLUORESCENCE SPECTROSCOPY DATA

Evgeny Shirshin, Vladimir Petrov, Victor Fadeev, Gleb Budylin, Stepan Kalmykov, Daria Enina

M.V. Lomonosov Moscow State University
eshirshin@gmail.com

The aqueous chemistry of Uranium(VI) determines its migration in geosphere under oxic conditions and the efficiency of some technological processes like in situ leach uranium mining, thus being extensively studied in geochemistry. Time-resolved laser-induced fluorescence spectroscopy (TRLIFS) is a powerful method that allows one to determine U(VI) speciation both in aqueous solutions and at mineral-water interfaces. TRLIFS makes use of the sensitivity of U(VI) complexes photophysical parameters (excited state lifetimes and positions of maxima in fluorescence emission spectra) sensitivity to its coordination. Because of high sensitivity and selectivity, this method is extensively used in investigation of various systems containing U(VI), including equilibrium constants determination and monitoring U(VI) speciation in drainage waters.

At the same time, the values of excited state lifetimes of, e.g. uranyl fluoride and sulfate complexes, obtained by different groups differ significantly. Moreover, even the question about the number of components required for fluorescence decay curves fitting is not clear: some researchers consider discreet lifetimes for different complexes, while others postulate a continuous dependency of lifetime on ligand concentration and interpret their data under the assumption of fast ligand exchange.

Here, we'll present the extensive study of the reasons that may lead to the discrepancy of photophysical parameters obtained for the same complexes. First, recently, we have demonstrated that the effect of excited states annihilation may influence the shape of fluorescence decay curves at high excitation intensities, thus leading misinterpretation of fluorescence decay rates. Second, different algorithms of fluorescence decay curves processing (the use of fixed lifetimes, global analysis etc.) may provide different values of complexes amplitudes and, consequently, equilibrium constants. Third, we'll demonstrate the influence of ionic strength of the solution on U(VI) complexes photophysical parameters and stoichiometry by the example of uranyl sulfate complexes.

SEP-P26, (Id: 351)

THE FORMATION OF STRUCTURE IN THE EXTRACTION AT VIBRATION IN AN INTERFACIAL LAYER

Nikolay Kizim, Elena Golubina

nphk@mail.ru

Formation of cruds at the extraction of metals is the negative phenomenon as reduces the rate of extraction, worsens disintegration of the emulsions, and leads to loss extragent and an extractive element. In practice to prevent the formation of structure in an interfacial layer in system aliphatic alcohols add to aliphatic alcohols, for example, octanol - 1.

However there are additional losses extragent, threat of environment increases. The results of researches on influence of the mechanical vibrations on an interface on process of the formation of structure in an organic phase at extraction rare-earth elements by solutions di-(2-ethylhexyl)phosphoric acid are considered. Vibration influence on interfacial layers was carried out by means of the vibrator which represented a high-frequency electrodynamic head with rigidly fixed core, by a coming to an end vibrating element in the form of the triangular prism turned to an interface by top. The vibrator connected to the generator of low-frequency signals.

The effective viscosity and limiting pressure of shift of organic phase exposed to vibration is constant during first ~15 min. At short time (~5 min), the main contribution in system behavior is provided by spontaneous surface convection. At longer time intervals (50–60 min) when spontaneous surface convection is absent, it is the vibrations that disintegrate the resulting structure. The supply of additional energy into interfacial layers of extraction system changes the hydrodynamic situation not only in interface region but also in the adjacent domains of contacting phases. The relative motion of particles increases when exposed to mechanical action. Since resulting particles have different weight and move with different velocity, their shift leads to is integration of aggregates in temporary structure. Thus, mechanical vibrations disintegrate the structure at the weakest coagulation contacts.

However, the viscosity and a limiting pressure of shift of organic phase sharply increases with time. The nascent temporary structure is heterogeneous, therefore the supply of additional energy leads to its disintegration and particles of smaller size prevail in the system. The interaction of reproduced particles results in the formation of a stronger structure.

Thus, the local supply of mechanical energy in an interface layer possible to suppress process of the formation of structure during the initial moments of time.

SEP-P27, (Id: 362)

ADSORPTION OF SELECTED FISSION PRODUCTS ON TITANATE NANOTUBES

Barbara Filipowicz, Seweryn Krajewski, Aleksander Bilewicz

Institute of Nuclear Chemistry and Technology, Warsaw, Poland
b.filipowicz@ichtj.waw.pl

Inorganic ion exchangers are widely used in the treatment of reactor coolant and aqueous nuclear wastes due to their high selectivity, radiation resistance, thermal and chemical stability. Among other inorganic sorbents, hydrous titanium dioxide was proposed as the prospective sorbent for the efficient separation of fission products such as ^{137}Cs and ^{90}Sr. Recently, new forms of nanometer-sized titanate with unique ion exchange properties were obtained. The physicochemical properties of nanostructured titanates are enhanced and the relation between properties and applications is extended.

The aim of our work was studies of ion exchange properties of titanate nanotubes in relation to ^{137}Cs and ^{85}Sr. In the present work we synthesized titanate in nanotube form using hydrothermal procedure. Anatase was heated at the temperature of 140 °C in the 10 M NaOH solution for 24 h. The size and shape were characterized by SEM and TEM methods. The specific surface area was measured by BET technique and the pore size distribution by BJH method. The sorption kinetics studies on titanate nanotubes of ^{137}Cs and ^{85}Sr in form of chlorides were measured in 0.1 M $NaNO_3$ solution. Additionally, the effect of sodium and potassium nitrate concentration and pH on ^{137}Cs and ^{85}Sr sorption were examined.

The structure of nanotubes was confirmed by XRD, SEM and TEM methods. The particles diameter was greater than 5 nm and length greater than 100 nm. The measured specific surface area was ca. 300 $m^2 \cdot g^{-1}$ and pore size distribution was equal 0.50 $m^3 \cdot g^{-1}$. Due to high porous structure ion exchange kinetics were relatively slow for Cs^+ and Sr^{2+}, but 60 % of equilibrium was reached within 1 h. The increasing concentration of Na^+ favoured ^{137}Cs sorption than ^{85}Sr. As expected, K^+ cations influence on sorption was greater. An increase in Kd value with increasing pH was observed for ^{85}Sr, while in the case of ^{137}Cs the highest sorption was reached at pH 7-9, and at pH higher than 9 the Kd decreased.

The results suggest possible applications of titanate nanostructures as inorganic sorbents for the efficient separation of fission products from different liquid wastes, however further studies are necessary. The work has been carried out within the strategic research project entitled "Technologies for the development of safe nuclear energy", phase 7, research task nr 4 (SP/J/4/143 321/11).

SEP-P28, (Id: 368)

RAPID RADIOCHEMICAL ANALYSIS USING MEMBRANE-ADSORPTION METHOD

Vitaly Epimakhov, Leonid Moskvin

evn@niti.ru Nikolaevich

A rapid chromatographic method of radiochemical analysis based on adsorption of radionuclides onto selective pellet sorbents is successfully used for rapidly determining gamma-emitting radionuclides in water [1]. The paper presents a membrane-adsorption method for rapid determination of a- and β-emitting radionuclides. Like the above analysis for gamma-emitters, the proposed method separates individual radionuclides or radionuclide groups from water samples and produces radiation emitters for measuring activity of extracted radionuclides. The difference is in that sorbent pellets which have large self-absorption of a- and β radiation are replaced by planar sorbent geometries with minimum self-absorption. Porous membranes modified by addition of sorbents with selective adsorbing ability are offered as planar alternatives to pellets. To remove radionuclides on suspended matter from NPP water, the analysis scheme with selective adsorption membranes additionally includes microfiltration membranes as “mechanical” filters. A cellulose acetate membrane with pore size of 0.45 μm is used for mechanical filtration by analogy with separation of suspended and “conditionally dissolved” forms of heavy metals from natural water samples. Three types of modified adsorption membranes are suggested for use in radiochemical analyses for nuclear applications. These membranes differ in type of modifier: 1) membranes impregnated with elementary silver, 2) membranes impregnated with potassium ferrocyanide or cobalt ferrocyanide, and 3) membranes impregnated with manganese hydroxide. A cellulose acetate membrane with pore size of (0.65 – 0.75) μm is preferably used as solid substrate for all three membrane types. The first type membranes are suited for selective separation of radioiodines and Po-^{210}. The total activity of radioiodines is determined by measurement of β-radiation and Po-^{210} activity is determined by measurement of a-radiation. The second type membranes selectively remove radiocesium from water flows where salt concentration can reach the level of seawater salt concentration. The total radiocesium activity is determined by measurement of β-radiation. The third type membranes adsorb Pu, Am, and Cm from the coolant water and the activity of these radionuclides is determined by measuring the spectrum of a-radiation from the adsorption membrane.

SEP-P29, (Id: 369)

AUTOMATED PLANT FOR REMOVING RADIONUCLIDES FROM LIQUID RADIOACTIVE WASTE BY REVERSE OSMOSIS

Vitaly Epimakhov, Vitaly Smirnov, Sergey Prokhorkin, Vladimir Tkachenko, Mikhail Oleinik

evn@niti.ru

Liquid radioactive waste (LRW) can contain large amounts of emulsified petroleum products and suspended corrosion particles on which radionuclides concentrate. The optimal approach to removal of radionuclides in different physicochemical forms is using adsorption methods together with baromembrane methods such as microfiltration, ultrafiltration, and reverse osmosis. Alexandrov NITI has developed an automated reverse osmosis plant system with remote monitoring and control features including cleaning of reverse osmosis elements. The plant comprises a microfilter, reverse osmosis filter (ROF), unit for cleaning the reverse osmosis elements, low-pressure pump, high-pressure pump, chemical analysis unit, control unit and power control unit. The plant has a filtration capacity of 500 l/h, operating power of 5 kW max, operating pressure of 5 MPa max (at ROF) and removes at least 95 % of dissolved salts from LRW with a salt concentration of 10 g/l max and activity up to 10 kBq/l and produces concentrated solutions of up to 50 g/l salt content. The cleaning unit is designed to prepare maximum 150 liters of washing solutions heated to 35°C and clean the reverse osmosis filter. The reverse osmosis elements are cleaned every day using the final water of the plant system and every month using chemical solutions prepared from the final water. The most efficient washing solution is 1.5 % solution of citric acid with pH = 4-5. The plant performance is monitored by measuring the solution conductance with the chemical analysis unit and the treatment process is automatically controlled by the control unit equipment. The control and monitoring process does not require presence of the operator in the plant equipment location area. The plant operation is controlled remotely from the operator workstation in another room where the dose rate is below 0.6 μSv/h. Experiments demonstrated that the general demineralization efficiency of the plant was about 75. The system removed almost all petroleum, surfactants, and corrosion products. Alkali metals were removed by ion exchange (pH is reduced). At the same time, the efficiency of radionuclide removal was higher than the general demineralization efficiency. The reverse osmosis efficiency for removal of radionuclides was almost 1000 and even reached the value of 10000 for Sr-90. The chemical cleaning removed fouling consisting of 85 % calcium, about 5 % magnesium, about 5 % iron, and about 1.5 % aluminum species. The specific activity of the washing solutions was 1·106 Bq/l max with Sr-90 being the main source.

SEP-P30, (Id: 377)

POLYACRYLONITRILE BASED COMPOSITE MATERIALS WITH EXTRACTION AGENTS CONTAINING CHEMICALLY BONDED CMPO GROUPS FOR SEPARATION OF ACTINOIDS

Jan Kameník[a], Jan Kameník[b], Ferdinand Šebesta[b], Jan John[b], Volker Böhmer[c], Valentyn Rudzevich[c], Bohumír Grüner[d]

[a]*Nuclear Physics Institute, Academy of Sciences of the Czech Republic*
[b]*Department of Nuclear Chemistry, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague, Czech Republic*
[c]*Abtailung Lehramt Chemie, Fachbereich Chemie, Pharmazie und Geowissenschaften, Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, D-55099 Mainz, Germany*
[d]*Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68 Řež, Czech Republic*
kamenik@ujf.cas.cz

Several extraction agents with functional group of diphenyl-carbamoylmethylphosphine oxide were synthetized and tested in the frame of EUROPART project for actinoids partitioning from nitric acid solutions. Functional groups were chemically bonded with a platform of tert-butylcalix[4]arene, O-pentylcalix[4]arene, and cobalt bis(dicarbollide) cluster ion to enhance extraction properties. The extraction agents were used for preparation of composite materials with polyacrylonitrile (PAN) as a binding polymer to study behavior of these composites in column chromatography. They were compared with CMPO-PAN composite material prepared with neat octyl(phenyl)-N,N'-diisobutylcarbamoylmethylphosphine oxide compound (CMPO). Uptake kinetics was studied with europium as an analog of americium. Weight distribution coefficients (Dg) of europium, americium, plutonium, uranium, and neptunium were determined in nitric acid solutions (0.01 - 5 mol/L) in the presence of sodium nitrate (0.1 mol/L). Europium extraction isotherms from 3M HNO_3 solution were used for capacity determination.

SEP-P31, (Id: 382)

STUDY OF EUROPIUM AND AMERICIUM UPTAKE ON SOLID EXTRACTANT WITH CMPO AND POLYACRYLONITRILE FROM DILUTED NITRIC ACID SOLUTIONS

Jan Kameník, Ferdinand Šebesta

Department of Nuclear Chemistry, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague,
115 19 Prague 1, Czech Republic
kamenik@ujf.cas.cz

Octyl(phenyl)-N,N'-diisobutylcarbamoylmethylphosphine oxide (CMPO) extraction agent and polyacrylonitrile (PAN) as binding polymer were used for production of CMPO-PAN solid extractant. The material was previously studied for application in column chromatography for actinoids separation [1]. High uptake of americium and europium on CMPO-PAN solid extractant was observed in diluted nitric acid solutions (0.001-0.1 mol/L) contrary to minimal uptake by CMPO itself. A set of experiments was performed for explanation of this effect that cannot be solely explained by adsorption on PAN support. Materials prepared by modification of the original procedure were tested and compared. Influence of CMPO content in the composite and total nitrate ion concentration in the solution on the uptake were determined for several acidities. Selected materials were subjected to FT-IR analysis to study interaction of the support polymer and CMPO agent. Europium extraction isotherms were measured in the solution of 0.01M HNO_3 for capacity determination. It was found that addition of sodium nitrate (0.1 mol/L) increases maximum europium capacity by more than an order of magnitude to the value that was determined in 3M HNO_3. The observations indicated that europium and americium uptake mechanism on CMPO-PAN is different in solutions with diluted and more concentrated nitric acid and is influenced by total nitrate concentration.

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* Present address: Nuclear Physics Institute, Academy of Sciences of the Czech Republic, 250 68 Řež, Czech Republic

SEP-P32, (Id: 404)

SEPARATION OF CURIUM FROM AMERICIUM USING COMPOSITE SORBENTS AND COMPLEXING AGENT SOLUTIONS

Kamila Šťastná, Jan John, Ferdinand Šebesta, Martin Vlk

Department of Nuclear Chemistry, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague
kamila.stastna@fjfi.cvut.cz

Two liquid liquid extraction processes intended as a part of the Partitioning and Transmutation strategy have been used as a basis for development of chromatographic systems for separation of curium from americium. The liquid organic phase of the EXAm process was replaced by DMDOHEMA-PAN composite sorbent and TEDGA in nitric acid solution was employed as an aqueous-phase complexing agent. The liquid organic phase of the AmSel process was replaced by TODGA-PAN composite sorbent and sulfonated BTBP derivative in nitric acid solution was employed as an aqueous-phase complexing agent. The influence of aqueous phase complexing agent and nitric acid concentrations on weight distribution coefficients and separation factor as well as the kinetics of the actinide uptake were determined in batch experiments with trace amounts of Am-241 and Cm-244 radionuclides. The efficiency of Cm separation from Am was evaluated in column experiments.

SEP-P33, (Id: 410)

INVESTIGATION OF URANIUM SORPTION ON MATERIALS PREPARED FROM TETRA-N-BUTYLORTHOTITANATE USING LSC AND TRLFS

Jakub Raindl, Irena Špendlíková, Mojmír Němec, Alena Zavadilová

KJCH - FJFI - ČVUT
j.raindl@centrum.cz

Separation of uranium from natural and waste water is a problem, which has been studied for a long time. For such purpose, many organic and inorganic sorption materials have been proposed and titanium dioxide have shown quite promising results. The first aim of this study was to test and characterize sorption materials based on TiO_2 prepared from tetra-n-butylorthotitanate (TBOT) in order to optimize their preparation. The second aim was to implement direct hydrolysis of TBOT in the solutions containing uranium as a method for uranium separation.

Sorption capacities of six prepared materials were deduced from their sorption isotherms with fixed uranium concentrations (10 mmol L^{-1}) and variable values of V/m (50 – 400 mL g^{-1}). In the direct hydrolysis experiments, the uranium solutions of 20 and 0.05 mmol L^{-1} were used. After proper multistage separation, uranium in the samples was measured using liquid scintillation counting and time-resolved laser-induced fluorescence spectrometry which together covered the concentration range of uranium in the samples from tens nmol L^{-1} to hundredths of mol L^{-1}. For three of the six studied materials, the uranium sorption was studied in more details.

In the following experiments, the option of direct hydrolysis of TBOT in the sample was tested. This fast way of uranium separation, which could be suitable for in situ separations, was investigated at various conditions. The results were then compared with the classic sorption method of contacting uranium solutions with pre-prepared, solid absorbers based on TiO_2 at similar conditions. It was found that the method of direct hydrolysis in the sample is more efficient separation step than the classic sorption, but it fairly depends on the conditions of the procedure itself.

SEP-P34, (Id: 415)

EFFECT OF MOBILE PHASE SALINITY ON THE Ac-227/Ra-223 GENERATOR.

Jan Kozempel, Lucie Kománková, Ferdinand Šebesta, Martin Vlk, Ekaterina Kukleva, Petra Mičolová

FJFI CVUT
jan.kozempel@fjfi.cvut.cz

Radium-223 is the first approved alpha emitting radionuclide for use in radionuclide therapy [1]. Radium follows the Calcium metabolism and thus is self targeted to bones. Several generator systems were described in the past [2]. In this study we have focused on a generator system described by Guseva et al. [3], based on a Dowex-1 resin and a mixed methanol/ nitric acid mobile phase. The effect of NaCl addition into a mobile phase on Ac-227/Th-227/Ra-223 generator was studied. The aim of this study was to increase the efficiency of Ra-223 elution and improvement of the Ra-223 elution peak shape. Possible Th-227 breakthrough was also evaluated. Acknowledgement This work was supported by the Ministry of Education Youth and Sports of the Czech republic, grant No.: LK21310.

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SEP-P35, (Id: 417)

KINETIC AND THERMODYNAMIC MODELING APPROACHES OF SELENIUM BY MAN-MADE AND NATURAL GEOLOGICAL BARRIERS FOR NUCLEAR WASTE MANAGEMENT

Sema Erenturk[a], Sevilay Haciyakupoglu[a], Esra Orucoglu[b], Ruveyda Kubra Ileri[a]

[a]*Istanbul Technical University, Energy Institute*
[b]*Istanbul Technical University, Faculty of Mines*
erenturk@itu.edu.tr

Some components of nuclear wastes like ^{79}Se should be taken into consideration due to extremely long half-lives and potential migration ability through the environment. Clay minerals are suggested as a barrier material in radioactive waste management; however they have some deficiencies to retard anionic radioisotopes like selenium due to structural properties. Modification of these minerals may help to improve their retardation ability toward these anionic radioisotopes. There are two predominant reasons for limiting selenium in water: a major limiting factor is the possible damage to plants and crops and selenium can represent reproductive dangers for human.

The study of sorption kinetics is significant as it provides valuable insights into the reaction pathways and into the mechanism of sorption reactions. The reaction can be defined by a sequence of processes that control the rate, diffusion of ions through particle film, diffusion through the particle and chemical reaction with the functional groups. This paper is dedicated to kinetic performance for selenium removal by selenium selective adsorbent. Batch kinetic experiments were performed using a solution containing 250 mg Se/L (pH 4.0) and 40 mg of inorganic pillared bentonite (OPBent) at three different temperatures and at a certain shaking rate. The selenium concentrations of the samples were monitored by taking the samples from the solution at defined times. The samples were analyzed by high resolution gamma spectroscopy system. The kinetic data obtained were evaluated using classical kinetic models and diffusion/reaction models. The transport mechanism of selenium which comprises a diffusion process from aqueous phase to organo-inorgano-bentonite was described by two kinetic models consisting of derived equations: the homogenous particle diffusion model (HPDM) and the shell progressive model (SPM). The effective particle diffusion coefficient Deff values derived from both the HPMD and SPM equations were compared. The mechanism of selenate sorption by OPBent has been postulated from the experimental results.

SEP-P36, (Id: 426)

STUDY OF THE DTPA AND MALONIC ACID SOLUTION FOR THE SELECTIVE AM STRIPPING IN THE CEA EXAM PROCESS

Petr Distler[a], **Irena Spendlikova**[a], **Fabien Burdet**[b], **Manuel Miguirditchian**[b]

[a]*CTU in Prague, Brehova 7, 115 19 Prague 1, Czech Republic*
[b]*CEA Marcoule, Nuclear Energy Division, Radiochemistry & Processes Department, SMCS/LEPS, Bagnols-sur-Cèze, F-30207, France*
petr.distler@fjfi.cvut.cz

In the frame of the development of the French CEA EXAm process (Am selective separation from a PUREX raffinate by solvent extraction), the selective stripping of americium from lanthanides was studied using a solution of DTPA and malonic acid. This step is similar to a reverse-TALSPEAK system developed for Am/Ln separation.

Organic phase containing 0.3 M HDEHP and 0.6 M DMDOHEMA in TPH was first loaded with the aqueous phase containing Am/lanthanides/fission and/or corrosive products. The loaded organic phase was then contacted with the aqueous solution of DTPA and malonic acid at pH around 2.5. The impact of DTPA and malonic acid concentrations, pH dependence, kinetic and thermodynamic studies were studied on americium and lanthanides extraction. In addition, the impact of the nature of the base used to pH adjustment and the stability constants of DTPA with Am(III), Eu(III) and Ce(III) were determined in process conditions.

These results showed that DTPA and malonic acid extraction system can selectively strip Am(III) over lanthanides (Ce(III) and Eu(III)) and other fission products potentially present in organic phase (Fe(III), Y(III)). The results are important for a better understanding of the process chemistry and are used for the modelling and the simulation of this step of the EXAm process.

SEP-P37, (Id: 432)

NANODIAMONDS AS A PROSPECTIVE SORBENT FOR RADIONUCLIDES

Yulia Buchatskaya[a], Anna Yu. Romanchuk[b], Stepan N. Kalmykov[b], Mojmir Němec[a], Jan Kozempel[a]

[a]*Czech Technical University in Prague*
[b]*Lomonosov Moscow State University*
julia.buchatskaya@gmail.com

Detonation nanodiamonds (DND) are potentially promising candidate for sorption applications due to their unique properties: high surface area, highly developed surface, low weight, chemical and radiation resistance. The oxygen-containing groups on the DND surface are responsible for the cation-exchange properties. The sorption capacity of DND is found to be comparable with other carbon nanomaterials as carbon nanotubes and graphene oxide and higher than that of carbon black. The sorption of radionuclides showed to be effected by surface chemistry of DND. It was shown before, that DND can effectively remove U(VI), Am(III), Th(IV), Pu(IV) cations from solutions [1].

In this work the sorption regularities of Th(IV), Ra(II), Ba(II), Ac(III) were studied for different samples of DND: commercially available nanodiamond powder (Sigma-Aldrich) and concentrated suspension, produced at the Special Construction-Technological Bureau "Technolog" of Saint-Petersburg State Institute of Technology (Technical University) (Russia). The radionuclides of interest were chosen with the aim to test nanodiamonds as a prospective sorption material for preparation of ^{227}Ac/^{223}Ra generator.

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SEP-P38, (Id: 443)

CHARACTERIZATION OF A TBP RESIN AND DEVELOPMENT OF METHODS FOR THE SEPARATION OF ACTINIDES AND THE PURIFICATION OF Sn

Carina Dirks[a], Nora Vajda[b], Eva Kovács-Széles[c], Aude Bombard[d], Steffen Happel[c]

[a]*Radiochemistry, Department of Chemistry, Philipps-University Marburg*
[b]*RadAnal Kft*
[c]*Centre for Energy Research, Hungarian Academy of Sciences*
[d]*TrisKem International*
carina.dirks@chemie.uni-marburg.de

TBP is a widely used extractant in liquid–liquid extraction, especially in the extraction of actinides, one of its most prominent examples being the Purex process.

A TBP based extraction chromatographic resin has been characterized with respect to its U capacity and the weight distribution ratios (DW) of U, Th, Pu, Np and numerous other cations in different concentrations of HNO_3 and HCl.

Based on obtained data methods for the separation of Pu from Th and U, and for the purification of Sn, with special focus on decommissioning and radionuclide production, have been developed.

Chemistry of Nuclear Fuel Cycle (NFC)

Verbal presentations

NFC-I01, (Id: 21)

EXPERIENCES OF REPROCESSING PLUTONIUM RICH MIXED CARBIDE FUELS

Natarajan Rajamani

Indira Gandhi Centre for Atomic Energy
rnr@igcar.gov.in

The mixed carbide (70 % Pu, 30 % U) spent fuel from the Fast Breeder Test Reactor (FBTR) at Kalpakkam, India is being reprocessed at the CORAL facility since 2003. Several campaigns with progressively increasing burnups and reducing cooling periods have been carried out in this facility. Presently spent fuels with a burn up of 155 GWd/Te with cooling periods as around two years are being reprocessed. The satisfactory operation of this facility has provided valuable inputs for the design of process, equipment and other systems. Sustained operation of critical process equipment such as chopper, dissolver and solvent extraction equipment enabled in the fine tuning of design for reliable operation and easier maintenance. Design optimization for the future plants DFRP and FRP which are under construction for closing the fuel cycle of FBTR and Prototype Fast Breeder Reactor (PFBR) respectively could be carried based on the operating experience with single pin chopper. The apprehension that mixed carbide fuel would be difficult to dissolve and not give a satisfactory solvent extraction performance, is alleviated by the experience of quantitative dissolution and recovery of plutonium. Typical hull losses have been experimentally found to be less than 0.08 % for plutonium. Though some carbide carbon was found to be there in the dissolver solution, it does not affect the solvent extraction performance. The highly oxidative dissolution conditions required for the dissolution of the spent fuel, call for material of construction other than the conventional stainless steel, as its corrosion rate of under such condition is unacceptably high. Alternate material of construction has been identified and deployed for the CORAL dissolver. Inspection of the dissolver after around three years of operation has revealed satisfactory performance. Though three solvent extraction cycles have been provided in the plant, it has been found that the required decontamination could be achieved with a single cycle. Typical decontamination factors of greater than 10^3 for Ru-106 and 10^4 for Cs-137 have been achieved. The recovery of plutonium and uranium are greater than 99.9 % and 99.8 % respectively. The centrifugal extractors have provided extremely satisfactory performance with progressive improvement in the performance in terms of reduced maintenance requirements with incorporation of design changes during the campaigns.

R&D work has been concurrently taken up based on the performance evaluation of the facility for improving the recovery, decontamination factors, economy and reducing the waste volumes. With the computer code PUSEP(Ver-II) developed by the reprocessing group, IGCAR, an innovative extraction flowsheet is formulated to meet the decontamination requirements of both ^{95}Zr and ^{106}Ru while reprocessing fuels with less than two years cooling period. With this code it has been possible to establish the flow rate controls required for avoiding the third phase formation due to excessive plutonium loading in the solvent phase. Also, it has been found that closer to the stoichiometric requirement of uranous for separation of plutonium from uranium is possible. These findings will substantially reduce the number of solvent extraction cycles and hence the waste volumes. Reduction of solvent waste using vacuum distillation and the removal of dissolved organic by diluent wash using efficient contactors to address the red-oil formation during waste evaporation, are a few R&D activities in progress to improve the plant performance.

Another important offshoot of the operation of the CORAL facility is the development of a variety of hot cell equipment and systems for remote operation and maintenance with least plutonium contamination in the operating area. Based on the satisfactory experience, it is expected that the reprocessing of PFBR spent MOX fuel would not pose a challenging problem as the plutonium content in PFBR is much less (around 25 %).

NFC-V02, (Id: 160)

ELECTROCHEMICAL BEHAVIORS OF EUROPIUM(III)/EUROPIUM(II) IN LiF-NaF-KF MOLTEN SALT

Wei Huang, Lifang Tian, Changfeng She, Feng Jiang, haiyang Zheng, Dewu Long, Qingnuan Li

Shanghai Institute of Applied Physics (SINAP), Chinese Academy of Sciences (CAS)
huangwei@sinap.ac.cn

Electrochemical separation method is an option in reprocessing the nuclear spent fuel from molten salt reactor (MSR). To develop the electrochemical technique in fluoride-based molten salt, the LiF-NaF-KF eutectic (46.5-11.5-42.0 mol %, FLiNaK) was adopted because of its low melting point (727 K) and other attractive physical-chemical properties. Herein, the electrochemical behaviors of Eu, one of the typical fission product elements, were investigated in FLiNaK. Despite the fact that only EuF_3 was added initially, the co-existence of Eu (III) and Eu(II) in FLiNaK was confirmed by electrochemical method and XPS as well. The electrode reaction mechanisms were determined by cyclic voltammetry and square wave voltammetry. The results indicated that the electrode reaction involved a one electron exchange process, corresponding to the reduction and oxidation between Eu(III) and Eu(II). This process exhibited a reversible and diffusion-controlled behavior. The diffusion coefficients of Eu(III) and Eu(II) were measured by the conventional cyclic voltammetry with changing scanning rates and a modified method with additionally changing the area of working electrode. The values obtained by these different techniques matched each other. Furthermore, the temperature dependence of the diffusion coefficients was examined and the activation energy of this diffusion process were subsequently calculated to be (38.9 ± 4.6) kJ mol^{-1} for Eu(III) and (34.7 ± 1.6) kJ mol^{-1} for Eu(II).

NFC-V03, (Id: 162)

DISSOLUTION OF CARBIDE FUEL MATERIALS

Mark Sarsfield, Tamara Griffiths, Katie Bell, Chris Maher

National Nuclear Laboratory
mark.sarsfield@manchester.ac.uk

As part of the strategic research agenda for sustainable nuclear energy in Europe [1], carbide fuel is proposed as a potential candidate fuel for sodium cooled fast reactors and is the fuel of choice for gas cooled fast reactors. Carbide fuels have also been demonstrated to achieve high burn-up (> 155 GWd/t) in the sodium cooled Fast Reactor Fuel Reprocessing technology being pursued at the Indira Gandhi Center for Atomic Research (IGCAR), Kalpakkam. There are a number of issues that need to be addressed in the reprocessing of carbide fuel in order to demonstrate a sustainable closed nuclear fuel cycle.

Carbide fuel can be problematic when applying the traditional PUREX reprocessing technology of solvent extraction from a nitric acid solution. The dissolution of uranium carbide (UC) in hot nitric acid can lead to the formation of soluble organic molecules that can interfere with the extraction of uranium and plutonium reducing their extraction and recovery efficiencies. The organics can also lead to emulsions causing difficulties within industrial processes. Even when the U and Pu have been removed from the soluble organics the remaining liquor contains highly radioactive fission products in the presence of organic material that requires volume reducing before immobilising in a glass matrix. The presence of organics can present a safety issue and needs to be effectively managed.

In this paper we present the dissolution results from first titanium carbide (a potential barrier material in GCFRs) and then from unirradiated uranium carbide fast reactor blanket fuel pellets.

The kinetics of dissolution will be discussed together with comments on the organic materials produced and carbon mass balance.

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NFC-V04, (Id: 200)

DISSOLUTION OF MO-BASED CERMET FUEL: ESI-TOF MS SPECIATION IN NITRIC ACID MEDIUM

Elena Laura Ebert[a], Meijie Cheng[b], Michael Steppert[b], Clemens Walther[b], Giuseppe Modolo[a], Dirk Bosbach[a]

[a]*Forschungszentrum Jülich GmbH IEK-6*
[b]*Leibniz Universität Hannover IRS, Karlsruher Institut für Technologie INE*
e.ebert@fz-juelich.de

The main long term contributors to spent fuel radiotoxicity are plutonium followed by the minor actinides (MA = Np, Am, and Cm). A possibility to reduce the radiotoxic inventory and the footprint of the repository is to separate the most radiotoxic and long-lived elements from spent fuel and to transmute them into nonradioactive elements or elements with a much shorter lifetime. For the transmutation in accelerator-driven systems (ADS) fuels with a high content of Pu and MA are preferred. To increase the burn-up of transuranium elements (TRU) and to reduce the formation of new TRU inert matrix fuels (IMF) [1-3] are favored. These are ceramic substrates or metallic matrices with high thermal conductivity, which are free of uranium and also have small cross sections for reactions with neutrons. The reprocessability of (Pu,MA)-oxide within a metallic ^{92}Mo matrix (CERMET) is under investigation within the EU project ASGARD [4].

Dissolution in nitric acid is the first step in reprocessing. Therefore, detailed knowledge of the speciation of molybdenum in nitric acid medium is crucial on the one hand to understand this dissolution process and on the other hand as a basis for the design of a tailored extraction process. The speciation of molybdenum has been studied intensively in hydrochloric and perchloric acid medium[5,6], but little is known about the speciation in nitric acid medium, especially at high acidities, which are relevant for the dissolution of IMF. The solution species of molybdenum in strongly acidic nitric acid medium need to be extensively characterized and quantified. Therefore, electrospray ionization mass spectrometry, which can probe the stoichiometry and relative abundances of solution species, was applied.

Here, we present new experimental data on the speciation of molybdenum as a function of nitric acid concentration. Isotopically pure ^{98}Mo powder was dissolved in nitric acid and measured with the ALBATROS ESI-TOF [7]. Monomeric, dimeric, trimeric, tetrameric, and pentameric cationic molybdenum species have been detected. Besides the presence of hexavalent Mo species the spectra show that pentavalent Mo species are present in solution in spite of the oxidizing condition in strong nitric acid.

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NFC-V05, (Id: 241)

RADIONUCLIDE DISTRIBUTION IN CORROSION LAYERS OF HISTORIC RADIOACTIVE WASTE OF NPP A1

Boris Andris, Milan Žatkulák

VUJE a.s.
boris.andris@vuje.sk

The radioactive waste management in Slovak Republic complies with the waste acceptance criteria for repository of Slovak Republic. The essential criterion is a declaration of radionuclides disposed in waste packages. The group of 19 limited radionuclides comprises various gamma, beta and alpha radionuclides. The activity of alpha radionuclides is monitored as a total alpha radioactivity, the limit for the total alpha activity per one waste package is 400 $Bq.g^{-1}$ in average, or a local activity and then the local limit is 4000 $Bq.g^{-1}$, which is usually applied for the smallest produced unit of a RAW (200 L drum, 60 L drum, or compacted product after high-pressure compacting).

Legacy radioactive wastes treated during D&D of NPP A1 represent greater amount of conditioned RAW disposed in the repository. Nuclear power plant A1 was shutdown after an INES 4 accident in 1977, when one of fuel assemblies had melted down in a reactor channel. Any kind of deactivation process had not been applied since shutdown of NPP and basically all deactivation and pre-decommissioning works have started in 90', and therefore there were lot of possibilities for corrosion of contaminated materials. This corrosion impacts also more than 300 pieces of casks used for spent fuel assemblies storing. Cladding defections and also deformations caused by incorrect storage conditions caused other cladding defects, which led to massive contamination of spent fuel casks. Outer and inner surface of casks is contaminated mainly by ^{137}Cs, ^{90}Sr and alpha RN (^{241}Am and Pu isotopes). According to the pre-disposal measurements by alpha scanner fragmented casks cannot be disposed without treatment because of exceeding limit for total activity of alpha RN.

The paper describes analyses performed with samples taken from inner surfaces of fragments of spent fuel casks to prove that contamination is only in a corrosion layer and not in core material of casks (carbon steel). This proof would help to enhance waste management of spent fuel casks. Determination of alpha isotopes by alpha PIPS spectrometry and determination of gamma emitting radionuclides by gamma spectrometry is described. Separation of ^{241}Am and Pu isotopes ^{238,239,240}Pu was carried out by means of extraction chromatography with TRU-resin sorbent. The depth distribution of contamination was performed on the assumption that during electrochemical sampling with identical conditions same amount of iron will be taken. After determination of iron concentrations by AAS it was possible to calculate thickness of corrosion and subsequently calculate depth distribution of radionuclides in several layers of corrosion. These data should help to enhance process of managing legacy metallic RAW from NPP A1.

NFC-I06, (Id: 378)

HUMIC COLLOID-ASSOCIATED MIGRATION OF TRIVALENT RADIONUCLIDES IN AN ARGILLACEOUS FORMATION

Christophe Bruggeman[a], Norbert Maes[a], Stéphane Brassinnes[b]

[a]*Environment, Health and Safety Institute (EHS), SCK•CEN, Boeretang 200, B-2400 Mol, Belgium*
[b]*ONDRAF/NIRAS, Kunstlaan 14, 1210 Brussel, Belgium*
cbruggem@sckcen.be

It is generally accepted that natural humic colloids in the argillaceous Boom Clay formation (Belgium) modify the speciation and transport characteristics of several long-lived radionuclides [1]. However, universal formalisms to describe the complex suite of processes and mechanisms in such environment were lacking, resulting in "operationally defined migration parameters" [2] that did not allow significant confidence building with regard to safety assessments.

In this paper we present a comprehensive overview of the latest achievements that have been obtained in the understanding, interpretation and description of trivalent radionuclide retention and migration in the Boom Clay. Using a classical bottom-up approach, a geochemical modelling concept relying on thermodynamic sorption models (TSMs) is presented. With this approach, we have succeeded in describing adsorption of Eu(III) and Am(III) in batch suspensions of increasing complexity, from relatively straightforward mixtures of illite and dissolved organic matter (DOM) [3], to Boom Clay suspensions. The results of these adsorption experiments demonstrate that trivalent radionuclides are strongly bound to the solid phases present in Boom Clay, but that their solid-liquid distribution is heavily influenced by DOM.

Hereafter we discuss results from short-term and long-running (>10 years) column migration experiments with Am(III) on Boom Clay cores. These experiments clearly indicate the existence of a kinetically-controlled colloidal transport pathway that determines the flux of Am(III) through the clay core. A modified kinetic colloid transport model has been developed [4], based partly on the aforementioned adsorption models, that allows for the quantitative description of all experimental data obtained thus far. In this model, it is considered that the radionuclide is predominantly transported as an organic matter complex/colloid that slowly dissociates, and both the colloid as well as the dissolved radionuclide ions are capable of sorbing to the solid phase.

The role of humic colloids as a transport vector is thoroughly discussed and evaluated within the larger framework of geological disposal of radioactive wastes.

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NFC-V07, (Id: 322)

CESIUM UPTAKE BY CA/MG BENTONITE: EVALUATION OF SORPION EXPERIMENTS BY A MULTICOMPONENT TWO-SITE ION-EXCHANGE MODEL

Dušan Vopálka[a], Barbora Drtinová[b], Zdeněk Klika[c], Jenny Gondolli[d]

[a]*Department of Nuclear Chemistry, Czech Technical University in Prague, Czech Republic*
[b]*Czech Technical University in Prague, Czech Republic*
[c]*Department of Analytical Chemistry and Material Testing, VŠB-Technical University Ostrava, Czech Republic*
[d]*Fuel Cycle Chemistry Department, ÚJV Řež, a. s., Czech Republic*
vopalka@fjfi.cvut.cz

Understanding the migration processes in the near-field of the geological disposal of nuclear wastes at the basic level can help to develop models, which may be used in transport codes that can predict the migration of radioactive contaminants in the field scale. Cesium is well adsorbed by clay minerals and many studies concerning adsorption of cesium on different types of clay minerals have been published so far. As in the Czech project of deep underground repository the application of local bentonite is proposed, in this work, cesium adsorption on Czech Ca/Mg bentonite (Rokle deposit, NW Bohemia) has been studied. In our previous study two main differences between Rokle bentonite and worldwide studied Na-bentonites were observed: (1) the great influence of phase ratio m/V on the shape of Cs sorption isotherm in the range of higher Cs concentration, and (2) a substantial content of micas and mica-type clay minerals (about 19 wt. %) that are believed to cause the specific Cs sorption in the lower concentration range due to the presence of the Frayed Edge Sites (FES).

In this work, cesium sorption on Ca/Mg-bentonite of the Czech origin was studied using batch technique for wide ranges of both bentonite-to-water ratio (m/V) and initial concentration of CsCl (10^{-7} – 0.1 mol/l), isotope Cs-137 was used as a tracer. The total cation-exchange capacity of the bentonite was 0.50 equiv/kg. The experiments revealed non-linear character of cesium sorption, substantially influenced by the m/V. The numerical evaluation of batch experiments performed with the use of PHREEQC, in which exchange reactions between added Cs^+ and Mg^{2+}, Ca^{2+}, Na^+ and K^+ ions sorbed initially on the bentonite were taken into account, enabled to determine selectivity coefficients of all mentioned cations, according to the Gaines-Thomas convention. The model describing exchange reactions mentioned was successfully verified on a broader set of experimental data that was previously interpreted by a simple ion-exchange model taking into account the exchange of cesium with an unspecified divalent cation. The shape of equilibrium isotherms indicated for initial concentrations of cesium smaller than 0.001 mol/l the possibility to describe the cesium uptake on Ca/Mg-bentonite by a two site model. Using this assumption, capacity of the second type of sites with higher selectivity to cesium, was calculated as about 0.01 equiv/kg. This specific cesium sorption capacity, which is generally believed to be associated with the frayed edge sites (FES) of illitic materials, was also measured using AgTU method. The values resulting from both the methods were of the same order, differences were discussed. The first results of 1D transport modelling in the PHREEQC environment respecting the developed multicomponent ion-exchange model could help by the interpretation of results of diffusion transport of some cations in the layer of compacted bentonite.

NFC-V08, (Id: 357)

COMPARATIVE STUDY OF CHLORIDE AND IODIDE DIFFUSION IN COMPACTED BENTONITE

Eva Hofmanová, Tomáš Rosendorf, Dušan Vopálka

Department of Nuclear Chemistry, Czech Technical University in Prague
hofmanova.eva@gmail.com

In the many concepts of high level radioactive waste repository (HLWR), compacted bentonite is planned as a buffer/backfill material due to its very low permeability and high sorption capacity. However, anionic species such as as 36Cl-, 129I- are not retarded due to their negligible interaction with engineered and/or natural barriers and may migrate to the biosphere much faster than cationic species. Chloride and iodide are the most stable species under in situ conditions of the deep repository and thus significantly contribute to the potential overall long-term dose. The transport of chloride and iodide in the bentonite barrier can be reduced by anion exclusion effect, which occurs due to the electrostatic repulsion of anions from negatively charged surfaces of clay minerals. Therefore, this work was focused on the fundamental understanding of diffusive behavior of chloride and iodide anions in compacted bentonite. In order to demonstrate the anion exclusion effect, chloride and iodide diffusion experiments were further compared with diffusion experiments performed with neutral species in form of tritiated water. A set of through-diffusion experiments on the compacted bentonite B75 (commercial milled and homogenized bentonite originated from Rokle deposit, Czech Republic) at different dry densities was performed. Chloride and iodide in trace concentration (as 36Cl and 125I; radioanalytical detection) as well as in non-active form in concentration of 0.01 mol/L (ion selective electrode detection) were used. All experiments were performed under ambient condition and at the ionic strength of 0.1 mol/L in order to compare diffusive behavior of these anions.

Apparent and effective diffusion coefficients were evaluated from two types of data sets (break-through curves and concentration profiles), using own computer module EVALDIFF. No significant difference in diffusive behavior of chloride and iodide was observed despite the fact that chloride and iodide differ in the ionic radius and charge density.

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NFC-V09, (Id: 340)

SPECIATION OF TECHNETIUM AFTER SORPTION AND DIFFUSION IN OPALINUS CLAY

Maria Lübke, Tobias Reich, Samer Amayri, Jakob Drebert

Institute of Nuclear Chemistry; Johannes Gutenberg University Mainz (Germany)
luebke@uni-mainz.de

The long-lived radioactive isotope technetium-99 (^{99}Tc, $T_{1/2} = 2.14 \cdot 10^5$ a) is a fission product of ^{235}U and ^{239}Pu and can be released to the environment from nuclear facilities, high-level radioactive waste repositories or as a result from nuclear weapon testing. Its geochemistry is dominated by the very mobile and soluble pertechnetate anion (TcO_4^-) under oxic, and a less mobile and less soluble $TcO_2 \cdot nH_2O$ phase under anoxic conditions [1]. For the storage of high-level nuclear waste, argillaceous rocks are under investigation as potential host rocks for repositories in several European countries. Thus, detailed information about the interaction of Tc with these host rock formations is mandatory for the assessment of the long-term safety of high-level nuclear waste repositories.

For our studies we selected Opalinus Clay (OPA) from Mont Terri, Switzerland, and its corresponding pore water. OPA is mainly composed of clay minerals (66 wt. %), quartz (14 wt. %), calcite (13 wt. %), siderite (3.0 wt. %), pyrite (1.1 wt. %), and organic carbon (0.8 wt. %) [2]. The sorption of 4-13 µM Tc(VII) on OPA powder was studied in batch experiments under aerobic and anaerobic conditions as a function of pH, clay concentration, and amount of dissolved Fe(II). Diffusion experiments were performed with intact OPA bore cores (20x10 mm and 25x11 mm) with diffusion parallel and perpendicular to the bedding. The experiments were performed under aerobic conditions with 7 µM TcO_4^- at neutral pH. Furthermore, different sorption samples on OPA thin sections (contact area 16 mm²) with 3-35 µM Tc(VII) were prepared under anaerobic conditions for spatially resolved, molecular-level investigations to determine the speciation of Tc on the mineral surface.

The batch experiments showed that in the neutral pH range the sorption of Tc on OPA is very low, i.e. ≤ 1 % under aerobic and 8 % under anaerobic conditions. We also found that the sorption is independent of the clay concentration. Addition of dissolved Fe^{2+} increased the uptake of Tc by OPA up to 99 %. The low sorption of Tc on OPA under aerobic conditions agrees well with our results from diffusion experiments, where Tc(VII) migrates quickly through an intact OPA bore core within about one week in case of diffusion parallel to the bedding. For diffusion perpendicular to the bedding, TcO_4^- migrates through the bore core within one month. µ-XRF mappings of the sorption samples showed a homogeneous distribution of Tc on the OPA surface with some local enrichments. In these spots the dominant oxidation state of Tc was found to be tetravalent as determined by Tc K-edge µ-XANES measurements.

Our results indicate that OPA is able to reduce at least part of TcO_4^- to a less mobile and less soluble Tc(IV) species and thus may retard the migration of Tc from the repository to the environment.

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NFC-V10, (Id: 173)

RUPRECHTOV NATURAL ANALOGUE SITE: SUMMARY OF THE REAL SYSTEM BEHAVIOUR

Radek Červinka[a], Václava Havlová[a], Ulrich Noseck[b], Thomas Brasser[b], Juhani Suksi[c], Melissa A. Denecke[d]

[a]*ÚJV Řež, a. s., Czech Republic*
[b]*Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH, Germany*
[c]*University of Helsinki, Finland*
[d]*Karlsruhe Institute of Technology, Institut für Nukleare Entsorgung, Germany*
radek.cervinka@ujv.cz

Deep geological repositories (DGR) for the final disposal of spent nuclear fuel and high-level radioactive waste are primarily based on a multi-barrier concepts, consisting of a host rock as a natural geological barrier and an engineered barrier-system. Detailed investigations of suitable geological analogues may lead to a better understanding of the complex interrelations between transport and sorption of radionuclides in multi-barrier systems under natural conditions and especially on very long-term scales relevant for performance assessment.

The Ruprechtov site (W Bohemia) was chosen as a natural analogue because the geological and geochemical conditions are similar to sedimentary sequences which in many cases cover the potential host rocks for DGR. The site selection supported also natural accumulations of U, which enabled to identify the main mobilisation/immobilisation processes. During the international research, which took place at Ruprechtov site since 1995, multidisciplinary investigations were performed, including detailed hydrogeological, geological, mineralogical and geochemical characterisation. Furthermore, the core part of the investigations were focused on natural U occurrences as analogue for U migration and immobilisation in the DGR post-operational phase.

The Ruprechtov site represents a Tertiary basin with argillized volcano-detritic sediments, underlain by kaolin and granite. U-enrichments mainly occur in distinct layers of limited thickness on top of the kaolin close to the clay-lignite seams (Noseck et al., 2004). The combination of different analytical methods was applied to gain an insight into the behaviour of U in a complex natural system such as wet chemistry (distribution of U(IV) and U(VI), sequential extraction, ^{234}U/^{238}U-activity ratios determination) and various spectroscopic methods (SEM–EDX spectroscopy, synchrotron-based l-EXAFS, EMPA and confocal l-XRF). Noseck et al. (2008) presented the scenario for U enrichment: Microbial activity in the clay/lignite horizon led to the reduction of dissolved sulphate by sulphate-reducing bacteria, thereby leading to the formation of pyrite nodules. Noseck et al. (2008) also identified using determination of ^{234}U/^{238}U activity ratios that the accumulation process has to be at least older than 1 Ma year. In this period, CO_2-rich water likely initiated U release from accessory minerals in the granite by formation of soluble uranyl-carbonate complexes. Uranium was transported into the clay/lignite horizon and accumulated there by reduction of U(VI) to U(IV) by thin As-pyrite layers on pyrite nodules formed by microbial sulphate reduction. Moreover, microbial degradation of organic matter in the clay/lignite horizon probably caused also phosphate release into the groundwater. The increased phosphate concentrations caused the precipitation of U as secondary phosphate minerals (e.g. ningyoite). The key processes involved in U immobilisation in the argillaceous layers have been identified and can be used to reconstruct the geological history at the site. The gained results were summarized in several publications (e.g. Noseck et al., 2008, 2009, 2012).

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NFC-V11, (Id: 37)

NUMERICAL ANALYSIS OF TRANSPORT AND RETARDATION FOR CESIUM IN CRUSHED GRANITE USING MULTI-STAGE ADVECTION-DISPERSION COLUMN EXPERIMENTS

Chuan-Pin Lee[a], Ming-Chee Wu[a], Shih-Chin Tsai[b], Ching-Yuan Liu[c], Tsuey-Lin Tsai[d], Chun-Hua Pan[a], Mon-Shieh Yang[a]

[a]*Department of Earth Sciences, National Cheng Kung University, Tainan, Taiwan*
[b]*Nuclear Science and Technology Development Center, National Tsing Hua University, Hsinchu 30013, Taiwan*
[c]*Department of Chemical and Materials Engineering, National Central University, Taoyuan 32001, Taiwan*
[d]*Chemistry Divisions, Institute of Nuclear Energy Research, Taoyuan 32546, Taiwan*
bennis6723@gmail.com

In order to assess the safety of an underground repository for high-level radioactive waste (HLW), reactive transport models designed to evaluate the fate and transport of radionuclides must be established based on experimental observation using both laboratory and on-site geological analyses. In this study, a systematic analysis of cesium (Cs) through crushed granite (0.297 - 0.840 mm) was constructed where synthetic groundwater (GW) and seawater (SW) were employed as the liquid phase. To build such models, multi-stage advection-dispersion column tests (length: 2 cm; diameter: 5 cm, bulk density:1.45 g/cm^3 , porosity: 0.45) were conducted in order to determine the major transport processes and the calibration/validation of the hypothesized reactive transport models. In addition, a non-reactive radionuclide, HTO, was preferentially used to assess its physical properties in crushed granite. The experimental breakthrough curves (BTCs) for HTO and Cs were both matched with their corresponding numerical breakthrough curves by adjusting reaction and transport parameters such as forward or backward reaction rate constants(Kf or Kb), dispersivity (α), and porosity θ(mobile and immobile zone). From the results of the non-reactive HTO column tests, a mobile/immobile transport model was proposed to capture the major transport processes in our column system. However, the mobile/immobile transport models were not completely simulated to provide numerical BTCs matching the Cs experimental BTCs. The extra diffusion/dispersion effect on the BTCs was due to an unnecessary column connection space volume.

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U(VI) RETENTION BY POTENTIAL HOST ROCKS: COMPARISON OF CLAY AND CRYSTALLINE ROCK

Katja Schmeide[a], Claudia Joseph[b], Vinzenz Brendler[a]

[a]Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology
[b]Glenn T. Seaborg Institute, Physical & Life Sciences Directorate, Lawrence Livermore National Laboratory
k.schmeide@hzdr.de

The long-term disposal of high-level nuclear waste in deep geological formations is discussed worldwide as main strategy for nuclear waste management. This approach requires the use of a multiple barrier system consisting of engineered, geo-engineered, and geological barriers to prevent any release of radionuclides into the geo- and biosphere. Sorption of radionuclides on the host rock of a repository is one important process for retarding their migration. Potential host rocks for nuclear waste repositories that are investigated internationally are salt domes, clay rock, and crystalline rock.

In the present work, the retention behavior of clay and crystalline rock towards U(VI) is compared. For this, sorption of U(VI) onto Opalinus Clay from the Mont Terri rock laboratory (Switzerland) was studied in the presence of Opalinus Clay pore water ($pH = 7.6$; $I = 0.36$ M) [1]. This is compared to U(VI) sorption onto anoxic diorite from Äspö Hard Rock Laboratory (Sweden) that was studied in the presence of Äspö groundwater ($pH = 7.8$; $I = 0.18$ M) [2]. The impact of various parameters, such as solid-to-liquid ratio, initial U(VI) concentration, temperature and atmosphere, on U(VI) sorption was studied. Distribution coefficients, Kd values, determined for the U(VI) sorption onto Opalinus Clay and diorite at 25 °C, amount to 22.2 ± 0.4 L/kg [1] and 3.8 ± 0.6 L/kg [2], respectively. This shows that U(VI) sorption onto Opalinus Clay is stronger than onto diorite, which can be attributed to its larger surface area. TRLFS and ATR FT-IR spectroscopic measurements showed that the U(VI) speciation in Opalinus Clay pore water as well as in diorite groundwater is predominated by the weakly sorbing $Ca_2UO_2(CO_3)_{3(aq)}$ complex. Reduction processes of U play only a subordinate role. The U(VI) sorption increases with increasing temperature.

U(VI) diffusion experiments with intact Opalinus Clay bore cores [3] also showed that Opalinus Clay has a good retardation potential for U(VI) since the molecular diffusion process through Opalinus Clay retards the migration of $Ca_2UO_2(CO_3)_{3(aq)}$. Generally, it can be concluded that U(VI) retention by clay rock is stronger than that by crystalline rock. This supports decisions to use clay rock not only as host rock but also as backfill material. In case of crystalline rock the natural retention capacity for U is insufficient and has to be strengthened by additional geo-technical and technical barriers that preserve their enclosing capabilities over very long time scales.

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NFC-V13, (Id: 243)

RETENTION OF SELENIUM AND CESIUM ON CRYSTALLINE ROCK: THE EFFECT OF REDOX CONDITIONS AND MINERALOGICAL COMPOSITION OF CRYSTALLINE ROCK

Kateřina Videnská, Václava Havlová, Jenny Gondolli

ÚJV Řež, a. s.
via@ujv.cz

Cesium and selenium belong among long-lived fission products, being present in spent nuclear fuel (SNF) and high level waste (HLW) and contributes significantly to the risk associated with the storage of radioactive waste in deep geological repositories. The presented work is focused on study of sorption behaviour of cesium and selenium species, selenite Se(IV) and selenate (VI), on two types of crystalline rock, granitic rock from Melechov Massif (Czech Republic) and diorite Äspö from the underground laboratory Äspö (Sweden). Used rock samples differed one from each other in mineralogical composition, sampling depth and redox conditions during the core drilling and sample preparation. The drill core samples from Melechov massif were obtained and completely prepared (sawed, crushed, sieved, washed) under aerobic conditions. On the other hand, drill core samples from Äspö underground laboratory were drilled and later prepared under anaerobic conditions in argon glove box. The main aim of experiments was to compare sorption behaviour of cesium and selenium on different crystalline rock samples under aerobic and anaerobic conditions and determine the influence of redox conditions during sample preparation on their sorption properties. The other aim of experiments was to identify potential retention mechanisms of selenium on crystalline rocks and to observe correlation between sorbed selenium and iron present in rock samples.

The sorption behaviour of cesium and selenium was studied by static batch method and was described by values of sorption distribution coefficient Kd. The batch sorption experiments were conducted on two fractions of crushed rock material with different grain size and on intact samples (coupons) under aerobic and anaerobic conditions.

Results of batch sorption experiments demonstrated different sorption behaviour of studied elements. Selenate Se(VI) behaved as non-sorbing, conservative tracer without any retention on rock samples; however selenite Se(IV) and cesium showed weak sorption without significant influence of different grain size of rock samples or redox conditions (aerobic/anaerobic). No significant differences between Czech granite and Sweden Äspö diorite were observed concerning Se and Cs sorption. The spectroscopic techniques of surface analysis were used for study of Se forms on the rock surface after the contact with selenite and selenate solution. The Electron Spectroscopy for Chemical Analysis (ESCA) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) were used. These methods can provide information about distribution of selenium on rock surface and information about oxidation state of sorbed selenium. The results of surface analysis of studied samples confirmed the initial assumption that retention mechanism of selenium species can be correlated to the presence of iron-containing minerals in the rock but the change of selenium oxidation state on samples surface was not observed.

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STUDY ON SORPTION AND DIFFUSION OF SR IN CRUSHED AND INTACT BASALT AND GRANITE INVESTIGATED IN COLUMN METHOD

Ming-Chee Wu[a], Chuan-Pin Lee[a], Shih-Chin Tsai[b], Tsuey-Lin Tsai[c], Chun-Hua Pan[a], Lee-Chung Men[c]

[a]*Department of Earth Sciences, National Cheng Kung University, Tainan, Taiwan*
[b]*Nuclear Science and Technology Development Center, National Tsing Hua University, Hsinchu 30013, Taiwan*
[c]*Chemistry Divisions, Institute of Nuclear Energy Research, Taoyuan 32546, Taiwan*
mcwu@mail.ncku.edu.tw

This study investigates sorption and diffusion of Strontium (Sr) in two potential host rocks (granite from Kinmen Island and basalt from Penghu Island) by using batch and through-diffusion methods in order to establish a reliable safety assessment methodology. These methods were applied to crushed and intact rock samples to investigate the actual geological environment. According to solid-phase analysis, including X-ray diffraction, elemental analysis, auto radiography, and polar microscopy, the sorption component primarily contained iron–magnesium (Fe–Mg) minerals in basalt and granite. Moreover, the distribution coefficient (Kd) of Sr in various concentrations (~10−2–10−7 M) obtained from batch tests indicated a higher sorption capacity in basalt than that in granite because of the 10 % Fe–Mg mineral content. The diffusion of Sr both in granite and basalt reach steady state after 100 days and apparent diffusion coefficient (Da) were 3.29×10^{-11} m^2/s (for Sr in crushed granite), 4.17×10^{-12} m^2/s (for Sr in crushed basalt), respectively. However, diffusive result (Da) of Sr in intact rocks was estimated a lower value than those obtained using crushed rocks. According to the diffusive results in crushed and intact rocks, it showed that major retardation of Sr depended on the microporous structure of tested media, such as decreases of constrictivity (δ) and increases of tortuosity(τ). In fact, the solid/liquid (S/L) ratio decreased as is the case when switching from batch to column experiments and the sorption effect on minerals became even more negligible in retardation of radionuclide migration.

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EFFECTS OF CEMENT SUPERPLASTICIZERS ON EU SORPTION ONTO KIVETTY GRANITE

Stellan Holgersson

Chalmers University of Technology
stehol@chalmers.se

Superplasticisers (SP) are cement additives used for the conditioning of the cement for increasing its workability in construction work. In the construction of a deep underground repository for nuclear waste in a geological formation there are a number of applications where the use of cement cannot be avoided. Examples of use can be floor plates, tunnel plugs and grout injections against water intrusion during the construction work. A recent literature review have shown that there is a potential for finding adverse effects of SP on radionuclide sorption onto host rock [1]. In this work a number of parameters that may affect Eu sorption in the presence of SP were investigated:

- Solid phase: one rock type from the Finnish Kivetty site, graphite-free, 0.045-0.2 mm sieved fraction.
- SPs from concrete leaching: two types of concrete, one Ordinary Portland Cement type and one low-alkaline type used for preparing the leaching solutions.
- SPs: 4 types: Sikament EVO26, a polycarboxylate (PC), Glenium51 (also a PC) and Rheobuild1000, a polynaphtalenesulphonate (PNS) and Mighty150 (also a PNS).
- SP concentrations: in experiments with SP additions, 0.1 and 1g/L were used.
- Water phase: the saline Olkiluoto water [2], adjusted to three different pH: 8.5, 9 and 10 Batch sorption experiments were accomplished by preparing batches of 0.5 g of crushed rock in 10 mL synthetic groundwater phase (S:L = 1:20). Samples of the water phase were taken after 1 day, 1 week, 1 month, 3 months and 6 months of contacting time. All experiments were made in a nitrogen-flushed glove box. The final results at 6 months show for the reference case Rd(m^3/kg) = 2.5±0.3, 1.5±0.4 and 1.4±0.8 for pH 8.5, 9 and 10, respectively. The addition of 0.1g/L EVO26 gave Rd(m^3/kg) = 0.13±0.01, 0.048±0.000 and 1.2±0.0, respectively. The addition of 1g/L EVO26 gave Rd(m^3/kg) = 0.18±0.01, 0.12±0.03 and 0.076±0.002, respectively. Thus, a clear effect of EVO26 on Eu sorption onto granite was established and the magnitude of effect seems to be pH dependent. The addition of 0.1g/L Glenium51 gave Rd(m^3/kg) = 1.1±0.1, 0.27±0.01 and 0.18±0.00, respectively. The addition of 1g/L Glenium51 gave Rd(m^3/kg) = 0.14±0.01, 0.045±0.003 and 0.016±0.000, respectively. The effect of Glenium51 was larger than for EVO26 and it is also pH dependent. The addition of 0.1g/L Rheobuild1000 gave Rd(m^3/kg) = 2.2±0.8, 2.4±0.7 and 1.5±1.0, respectively. The addition of 1g/L Rheobuild1000 gave Rd(m^3/kg) = 1.8±0.2, 1.5±0.1 and 0.48±0.01, respectively. Thus, an effect of Rheobuild1000 was seen only for the highest concentration and at pH10. Finally, The addition of 0.1g/L Mighty150 gave Rd(m^3/kg) = 3.1±1.1, 0.60±0.03 and 0.87±0.13, respectively. The addition of 1g/L Mighty150 gave Rd(m^3/kg) = 1.6±0.2, 0.84±0.17 and 0.68±0.14, respectively. The effect of Mighty150 seems to be the same for both concentrations: a reduction of Eu sorption at pH9 and 10. The batch experiments were repeated using leaching solutions of OPC and low-alkaline cement with the SPs added in the cement curing at realistic concentrations. However, no effects on Eu sorption with these low-concentration leaching solutions could be established. Based on these results, normal usage of SPs in cement curing should not have an effect on Eu retention of the surrounding host rock. However, the more elevated concentrations that also were used clearly established that the two PNS types of SP were more inert in respect of potential metal-mobilizing complexation reactions, compared with the two PC types of SP. It may therefore be preferable to use a PNS type of SP in the building of a waste repository from a long-term safety perspective.

NFC-V16, (Id: 161)

SPECIATION OF CARBON-14 IN A CEMENTITIOUS REPOSITORY FOR RADIOACTIVE WASTE: IDENTIFICATION OF ORGANIC COMPOUNDS IN ANOXIC CORROSION EXPERIMENTS WITH IRON POWDERS

Benjamin Cvetković[a], Judith Rothardt[b], Götz Schlotterbeck[c], Dominik Kunz[a], André Büttler[c], Sönke Szidat[d], Erich Wieland[a]

[a]*Paul Scherrer Institut*
[b]*Eawag*
[c]*University of Applied Sciences Northwestern Switzerland*
[d]*University of Bern*
benjamin.cvetkovic@psi.ch

Carbon-14 is an important contributor to the annual dose released from a cement-based repository for low- and intermediate-level radioactive waste (L/ILW) in Switzerland. In current performance assessment it is assumed that ^{14}C mainly contributes to dose in its organic form, such as ^{14}C bearing organic compounds, which are only weakly retarded in the cementitious near field. Compilations of the activity inventories reveal that, in the already existing and future arising of radioactive waste in Switzerland, the ^{14}C inventory in L/ILW is mainly associated with activated steel (~85 %). In nuclear power plants ^{14}C is produced by the activation of nitrogen impurities in stainless steel exposed to thermal neutron fluxes (e.g. in nuclear reactors) according to the reaction ^{14}N(n,p)^{14}C. The chemical speciation of ^{14}C in the cementitious near field upon release from activated steel is only poorly known.

Identification and quantification of the ^{14}C bearing organic compounds formed during the anoxic corrosion of activated steel is a major challenge, firstly due to the low ^{14}C inventory of activated steel, and secondly due to the extremely low corrosion rate of stainless steel in alkaline solution (few nm/year). Thus, conducting a corrosion study with activated steel requires the development of an analytical method with a very low ^{14}C detection limit for the identification and quantification of the ^{14}C bearing organic compounds released during the anoxic steel corrosion, such as compound-specific ^{14}C accelerator mass spectrometry (AMS).

As a first step towards the development of the AMS-based analytical technique, batch-type corrosion experiments with non-activated, carbon-containing iron powders were carried out with the aim of identifying potentially ^{14}C bearing organic compounds. The iron powders were immersed in artificial cement pore water solutions in zero-headspace, gas-tight vials and time-dependent changes in the concentrations of low molecular weight (LMW) dissolved and volatile carbon species were monitored over a period of 35 days. Dissolved and volatile organic compounds were determined in the supernatant solution using high-performance ion exclusion chromatography (HPIEC) coupled to conductivity detection (CD) and mass spectrometry (MS) for the dissolved species and headspace gas chromatography (GC) coupled to mass spectrometry for the volatile compounds. Organic carbon species were identified to be volatile hydrocarbons, like methane, alcohols, aldehydes, and carboxylic acids, with a maximum of up to four carbon atoms. Results from the corrosion experiments with non-activated iron powders will be discussed in detail along with the conceptual approach for the future corrosion study with activated steel.

NFC-V17, (Id: 138)

A SENSITIVITY AND PROBABILITY ANALYSIS OF THE SAFETY OF THE DEEP GEOLOGICAL NUCLEAR WASTE REPOSITORY DEPOSITED IN A CRYSTALLINE ROCK

Aleš Vetešník[a], Jiří Landa[b], Antonín Vokál[c], Dušan Vopálka[d]

[a]Department of Nuclear Chemistry, FNSPE, CTU in Prague, Břehová 7, Prague, Czech Republic
[b]Fuel Cycle Chemistry Department, UJV Rez, a. s., Hlavni 130, Husinec - Rez, Czech Republic
[c]SURAO, Dlážděná 6, Prague, Czech Republic
[d]Department of Nuclear Chemistry, FNSPE, CTU in Prague, Břehová 7, 115 19 Prague, Czech Republic
vetesale@fjfi.cvut.cz

A deep geological waste repository shall be designed so as to ensure the safety for thousands of years. The safety concept of a repository system is substantially affected by a type of a host rock. In a rock salt, the safety concept relies on a very slow migration of radionuclides in an almost free water environment and on a gradual self-sealing of excavations due to creep of the salt. In a clay, the safety relies on a very slow diffusion transport due to a highly impermeable rock and also gradual self-sealing of excavations due to creep of the clay. In a crystalline rock, however, the safety that might be strongly affected by advection through fractures in the host rock relies also on long-term performance of engineered barriers, primarily on corrosion resistant canisters.

The aim of this paper is to present the sensitivity and probability analysis of a model of the Czech safety concept of deep geological repository The repository is, in this model, considered as a connected system of engineered and natural barriers. The fuel matrix consisting of uranium dioxide crystals in which are incorporated minor actinides and fission products forms the first barrier. The nuclear waste is supposed to be enclosed in steel based canisters which are placed in vertical boreholes at depth of ~ 500 m. The space between canisters and host crystalline rock is backfilled with compacted bentonite which forms the last engineered barrier.

After failure of canisters, instant release fraction of radionuclides located mainly between spent fuel cladding and uranium matrix can release immediately. Radionuclides fixed in the uranium dioxide matrix will be released from the matrix congruently with the relative rate of dissolution of the matrix, which is considered to be very low, 1•10 ^{8} a^{-1} approximatelly. Released radionuclides will diffuse through the layer of compacted bentonite and rock (granite) matrix and will reach flowing water in granite rock fractures.

The following processes influencing the migration rate of radionuclides from the repository to the biosphere are taken into account in the tested conceptual model: the water chemistry, the solubility, diffusive and sorption properties of radionuclides, and the water flow rate in the fractures. For the analysis performed, the repository system was simplified into a system of compartments. To account for various types of uncertainty, e.g. incompleteness associated with the reduction of complex heterogeneous system to a compartment model, randomness of rock fractures; the values of some model parameters were considered as uncertain. Parameters uncertainties were modelled via probability density functions which were assigned by expert judgment. The sensitivity analysis was performed using a variance based method which decomposes a total variance of a model output into contributions from each parameter. The calculation of the variance decomposition was based on a Monte Carlo simulation with Sobol' quasi-random sequences. The results of the analysis are presented for a set of critical radionuclides, in particular 14C, 36Cl, 79Se, 129I and ^{210}Po, the latter was assumed as the ending isotope of a simplified 4n+2 decay chain There are identified the main contributors to the variance of model output. The reduction of uncertainties of those parameters would lead to the decrease of spread of model output.

NFC-I18, (Id: 385)

NITRIDE FUEL FABRICATION: TECHNOLOGICAL PROCESSES AND EQUIPMENT

Mykola Odeychuk

NSC KIPT
odeychuk@kipt.kharkov.ua

Uranium and plutonium mononitrides are considered as potential fuel for use in fast breeder reactors and high-temperature gas-cooled reactors. At the present time as a separate nuclear fuel is considered uranium (plutonium) carbonitride. Revision of requirements that apply to fuel of economically competitive nuclear reactors of generation IV, and the desire for the largest possible compatibility of fabrication and reprocessing technologies of nitride fuel with fabrication and reprocessing technologies of oxide fuel makes nitride fuel rather perspective. This is conditioned by a number of significant advantages over other fuels, the most important of which is high density and high thermal conductivity. Nitrides can be produced at the same facilities as the oxides, without substantial modifications, and the initial stage of purex process for reprocessing of irradiated oxide fuel is applicable to nitride fuel. During irradiation in nitride fuel radioactive isotope of carbon ^{14}C is generated, which may complicate the of irradiated fuel elements reprocessing technology and radiation situation. Generation of carbon-14 under irradiation of nitride fuel can be substantially reduced by using of nitrogen which enriched with nitrogen-15 isotope. The main directions in the development of nitride fuel fabrication processes are: nitriding of metallic uranium (plutonium); nitriding of uranium (plutonium) halides; carbothermic reduction of uranium (plutonium) dioxide in the presence of nitrogen and others. Currently these processes are underway when using of main reagent flow – nitrogen. As a new direction in the development of nitride fuel fabrication processes is considered the using of closed volume and catalytic methods for nitriding of uranium (plutonium). Development of this approach allows to realize of economically expedient production of nitride fuel on the basis of Nitrogen-15. In the report is considered in detail technological applications of the specified processes that allows to make up to (1.5-2.0) kg / h of the desired product and yield up to 99 % when the content of carbon and oxygen impurities up to 0.05 wt. % of each. Special attention is given to consideration of technological processes for fabrication of compact products from nitride (carbonitride) uranium (plutonium). Systemized data and equipment review for the technological sites for making of materials and products from nitride (carbonitride) uranium (plutonium) are presented.

NFC-V19, (Id: 253)

NEW FLUORINATED DILUENTS FOR TRIBUTYLPHOSPHATE

Vasiliy Babain[a], Andrey Konnikov[b], Mikhail Logunov[b], Ivan Tananaev[b], Mikhail Alyapyshev[a]

[a]*Khlopin Radium Institute*
[b]*PA "Mayak"*
babain@khlopin.ru

The extraction ability of ligands strongly depends on the type of the diluent. The fluorinated compounds provide an opportunity for variation of diluents structure and polarity. Different types of fluorinated compounds (alcohols, ethers and other fluorinated aromatic compounds) were tested as diluents for bidentate organophosphorus compounds, chlorinated cobalt dicarbollide and crown ethers. It was shown that in some cases using of polar diluents allowed to increase extraction ability of studied ligands. The main goal of the present work was to study the influence of new fluorinated diluents (fluorinated ethers and formals of fluorinated alcohols) on extraction ability of tributylphosphate (TBP) toward nitric acid and metals. It was found that fluorinated ethers and formals of fluorinated alcohols which contained in their structure –CF_2H groups decrease the extraction ability of TBP like in the case of chloroform. Both classes of studied compounds are highly resistant to gamma-radiolysis in the presence of nitric acid.

From the technological point of view fluorinated diluents are very promising as they allow receiving of concentrated uranium solutions.

NFC-V20, (Id: 277)

DYNAMIC TEST OF NEW EXTRACTION SYSTEM – TODGA IN META-NITROBENZOTRIFLUORIDE

Mikhail Logunov[a], Alexander Mashkin[a], Yuriy Voroshilov[a], V.S. Ermolin[a], R.N. Khasanov[a], Vasiliy Babain[b], M.Y. Alyapyshev[b], E.V. Kenf[b]

[a] *PA "Mayak"*
[b] *Khlopin Radium Institute*
cpl@po-mayak

Tetraoctyldiamide of diglycolic acid – (TODGA) is actively studied as promising extractant for actinide separation. Extraction properties of TODGA in various diluents were studied. It was shown, that maximal metal concentration in the organic phase can be achieved when meta-nitrobenzotrifluoride (F-3) was used as a diluents.

Actinide and lanthanide extraction from HLW by 0.2 M TODGA in F-3 was tested in dynamic test. Simulated HLW – PUREX process raffinate with high concentration of lanthanides was used as a feed solution. Extraction mock-up has worked more 110 hours, about 5,5L of feed solution was used, solvent had more two cycles.

High efficiency of actinide (americium, thorium, uranium) and lanthanides extraction (more 99,.9 %) was demonstrated. Zirconium and molybdenum partly remained in raffinate. The distribution of components between the stages of flowsheets was studied on the base of stage sampling. Lanthanide extraction is in the raw: La < Ce < Nd < Gd < Sm < Eu < Y. Extraction of americium is very close to such lanthanides as Nd and Gd. These trends are in good accordance with literature data for TODGA – dodecane solvent.

The loss of TODGA with raffinate is about 10 mg/L.It's noted that Tc has not been full stripped from solvent. TODGA – metanitrobenzotrifluoride is very promising solvent for HLW processing

NFC-V21, (Id: 380)

CO-CONVERSION OF MINOR ACTINIDES IN URANIUM BASED OXIDIC PRECURSORS BY INTERNAL GELATION

Christian Schreinemachers, Andrey Bukaemskiy, Martina Klinkenberg, Stefan Neumeier, Giuseppe Modolo, Dirk Bosbach

Forschungszentrum Jülich GmbH
c.schreinemachers@fz-juelich.de

In the context of advanced nuclear fuel cycles including partitioning and transmutation (P&T), actinide co-conversion processes, such as sol-gel routes, play an important role to close the fuel cycle. During the heterogeneous recycling of minor actinides, oxidic materials containing uranium as main matrix are used as innovative nuclear fuels.

Advanced fuel concepts replace the conventionally used pellets by particles (Sphere-pac or Vipac fuel) [1]. Particle fuels show good swelling behavior and can easily be fabricated. A suitable dustless preparation method is the internal gelation. This wet chemical method is a conversion process which transforms an aqueous colloidal solution sol into a solid gel. The internal gelation method was used for the particle synthesis during this work. Acid deficient uranyl nitrate (ADUN) and neodymium nitrate solutions were used as precursor, while urea acts as complexing agent and hexamethylenetetramine (HMTA) as gelification agent [2]. Pure uranium oxide and uranium / neodymium oxide microspheres with a variable content of Nd (5 % - 40 %) were fabricated in the framework of the EU project ASGARD [3]. Neodymium is used as surrogate for trivalent actinides, such as americium.

Mass- and size- characteristics of the prepared particles were studied. TG/DSC analyses were performed to investigate the thermal behavior. Finally the particles were thermally treated under reducing conditions at 1300 °C and 1600 °C. The products were investigated by the use of SEM/EDX and X-ray powder diffraction (XRD). Lattice parameter calculations were performed using the XRD data.

The particles, treated at 1300 °C showed only one cubic phase, for the whole observed χ(Nd) range. The expected linear behavior according to Vegard's rule was observed for compositions $\chi(\mathrm{Nd}) \leq 27.59$ %. The thermal treatment of the particles with compositions $\chi(\mathrm{Nd}) \geq 33.49$ % was repeated for 5 hours with a higher temperature (1600 °C). The expected linear trend could be confirmed and it could be demonstrated that equilibrium solid solutions of the UO2 / Nd_2O_3 system can be fabricated with the internal gelation synthesizing route.

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NFC-V22, (Id: 390)

CERAMIC WASTE FORMS FOR THE CONDITIONING OF MINOR ACTINIDES

Stefan Neumeier, Andrey Bukaemskiy, Felix Brandt, Sarah Finkeldei, Yulia Arinicheva, Julia Heuser, Giuseppe Modolo, Dirk Bosbach

Forschungszentrum Jülich GmbH
s.neumeier@fz-juelich.de

The disposal of high level radioactive waste is one of the most pressing and demanding challenges. With respect to long-term safety aspects of geological disposal, the minor actinides (MA) such as Am, Cm and Np and long-lived fission products such as ^{35}Cl, ^{135}Cs, ^{79}Se, ^{90}Sr and ^{129}I may be of particular concern due to their long half-lives, their high radiotoxicity and mobility in a repository system, respectively. Ceramic waste forms for the immobilisation of these radionuclides have been investigated extensively in the last decades since they seem to exhibit certain advantages compared to other waste forms (incl. borosilicate glasses and spent fuel) such as high loadings and chemical durability. Currently, most on-going nuclear waste management strategies do not include ceramic waste forms. However, it is still important to study this option, e.g. with respect to specific waste streams and certain constraints regarding deep geological disposal.

In the present communication we report on the research program in Jülich regarding ceramic waste forms for the conditioning of MA. It is based on fundamental science and follows an integral approach that covers the separation of elements or elemental groups with similar chemical properties from a waste stream by liquid/liquid extraction as well as the immobilisation in ceramic materials as hosts. The research focuses on single phase ceramics such as Monazites and Zirconates with Pyrochlore structure and includes:

1.) Development and optimisation of synthesis routes suitable for immobilisation of MA into ceramic waste forms and the handling of radionuclides such as sol-gel route, hydrothermal synthesis and co-precipitation,

2.) structural and microstructural characterisation using state of the art spectroscopic (Raman, TRLFS, EXAFS), diffraction (powder and single crystal XRD) [3] and microscopic (SEM, FIB/TEM) techniques,

3.) determination of thermodynamic data (calorimetry) and reactivity under conditions relevant to geological disposal, in particular with respect to leaching/corrosion in aqueous environments (static & dynamic dissolution experiments on powders and pellets) as well as

4.) studies on radiation damages (irradiation with α-particles and/or heavy ions, and incorporation of short-lived actinides such as ^{238}Pu, ^{241}Am or ^{244}Cm).

Finally, a fundamental understanding of the long-term behaviour on the atomic scale will help to improve the scientific basis for the safety case of deep geological disposal concepts using ceramic materials.

NFC-V23, (Id: 9)

BIOLOGICAL TREATMENT OF RADIOACTIVE WASTES BEFORE CEMENTATION

Olga Gorbunova[a], Alexey Cafonof[b], Varvara Tregubova[b], Svetlana Ostalkevich[a]

[a]*FSUE "RADON"*
[b]*Фрумкин ИФХЭ РАН*
olg-gorbunova@yandex.ru

The possibility of the preliminary microbiological treatment of the oil- and nitrate containing liquid radioactive waste (LRW) before solidification in the cement matrix was studied. It was experimentally proved earlier that the oil- and nitrate-containing cement compounds during long-term storage are characterized with the microbiological degradation due to the reaction of biogenic organic acids and gases with the minerals of the cement matrix.

We propose to biodegrade the LRW components before their solidification, thus reducing the total volume of LRW and preventing the destruction of the inorganic cement matrix during the long term storage.

The biodegradation of the nitrate-containing LRW (denitration) is possible by using the radioresistant microflora which can use oxygen from nitrate for cellular respiration converting it to molecular nitrogen form (denitrification). It can also degrade some organic molecules as electron donors for cellular respiration and as carbon source. Bacteria were cultivated for 3-4 days for reducing nitrate concentration from 3 gram to 10 mg per liter. We used two ways of cultivation: anaerobic bioreator-denitrifier and biofilter system. All method are suitable for nitrate removing from low level liquid radioactive waste.

The biodegradation of the oil-containing LRW is possible by using the radioresistant microflora which oxidize the organic components of the oil to carbon dioxide and water. Simultaneously there is the biosorption of the radionuclides by bacteria and emulsification of oil in cement slurry due to biogenic surface-active substances of glycolipid nature. It was experimentally found that after 7 days of biodegradation of oil-containing liquid radioactive waste the volume of LRW reduces by factors varying from 2 to 10 due to the biodegradation of the organic phase to the non-radioactive gases (CH_4, H_2O, CO_2, N_2), which are derived from the volume of the liquid radioactive waste. The ussage of an aerobic bioreactor with air mixing and bubbling (at fluidized bed) for high oxygen concentration is the most suitable method for this process.

At the same time, the microorganisms due to sorption processes on the cellular structures are able to extract from the LRW up to 80-90 % of alpha-radionuclides, up to 50 % of ^{90}Sr, up to 20 % of ^{137}Cs. The radioactive biomass is subject to dehydration and solidification in the cement matrix.

NFC-V24, (Id: 260)

CERIA CERAMIC: COLD PRESSING AND SINTERING OR SPARK PLASMA SINTERING?

Lyudmila Golovkina[a], Albina Orlova[a], Maksim Boldin[a], Oleg Belkin[a], Alexey Nokhrin[a], Vladimir Chuvil'deev[a], Mikhail Logunov[b], Igor Manakov[b], Alexander Ryakov[b]

[a]*Nizhegorodskiy State University*
[b]*FSUE "PA"Mayak"*
golovkina_lyudmila@mail.ru

In connection with the high rates of development of nuclear power engineering a problem of optimizing the process of nuclear fuel production and improving its performances remains relevant. Currently, the main way to obtain UO_2 fuel pellets is the method of Cold Pressing and Sintering (CPS). The main disadvantages of this method are large sintering duration (up to several hours) and high temperature of sintering. The innovative method of producing ceramics for various purposes (manufacture lasers, catalysts, semiconductors, dielectrics, biomedical materials, etc.) is the method of Spark Plasma Sintering (SPS). In this method, the powder samples placed in a graphical cuvette are heating with high speed by passing pulses of direct current with simultaneous application of hydrostatic pressure. This method is characterized by high rates of process shrinkage. In the present work ceramic from CeO_2 (as analogue of UO_2 and as candidate for the inert matrix fuel, IMF, for the transmutation of actinides) was received by CPS and SPS methods and the results were compared. CeO_2 powder was prepared by decomposition of cerium nitrate $Ce(NO_3)_3{\bullet}6H_2O$ (puriss.). SPS method was carried out on the installation Dr.Sinter Model-625. Optimized conditions of sintering of ceramics: - by CPS method: Tsintering = 1800 °C, P = 108.4 MPa, t sintering = 2 h; - by SPS method: Tsintering = 1062 °C, P = 88.6 MPa, t sintering = 25 min including cooling. Relative density of the ceramics obtained by CPS method constituted 79.9 % of the theoretical, ceramics obtained by SPS method - 95.4 %. As can be seen from the received data, ceramics obtained by SPSmethod, has a higher relative density, the sintering occurs at a lower temperature and pressure and in less time. Shrinkage of the sample begins at a temperature of 840 °C, finishes at 1060 °C, the maximum shrinkage rate (0.02 mm/s) is observed at 940 °C. Time of shrinkage is 3.5 min.

NFC-V25, (Id: 398)

PHOTO- AND RADIATION-INDUCED SYNTHESIS OF NANOCRYSTALLINE UO_2, ThO_2 AND MIXED UO_2–ThO_2 OXIDES

Tereza Pavelková, Václav Čuba, Ferdinand Šebesta

CTU in Prague, Czech Republic
tereza.pavelkova@fjfi.cvut.cz

In recent years, much attention has been drawn to the photo- and radiation-induced synthesis of various materials. In presented work, radiation-induced synthesis of nanocrystalline uranium and/or thorium oxides is investigated. Uranium(IV) oxide is widely used as a fuel in various types of nuclear reactors [T. Abe and K. Asakura: 2.15 Uranium Oxide and MOX Production. In: Comprehensive Nuclear Materials. Amesterdam: Elsevier, 2012, 394-422. ISBN: 978-0-08-056027-4]; thorium(IV) oxide and mixed uranium-thorium oxides are currently tested as a promising alternative [P. R. Hania and F. C. Klaassen: 3.04 Thorium Oxide Fuel. In: Comprehensive Nuclear Materials. Amesterdam: Elsevier, 2012, 88-108. ISBN: 978-0-08-056027-4]. Study of photo-/radiation- induced preparation of these oxides may contribute to the research in the field of nuclear fuel cycle in two ways:

1) Synthesis of oxides; these oxides are under suitable conditions highly pure and nanomentre-sized with narrow distribution of particle size.

2) Removal of radionuclides from solutions originated from irradiated fuel reprocessing. Photo- and radiation-induced synthesis of nanocrystalline uranium and/or thorium oxides is based on formation of amorphous solid precursor in aqueous solutions containing uranium and/or thorium nitrate and ammonium formate under UV radiation (low/medium pressure mercury lamp) or ionizing radiation (accelerated electrons). Subsequent heat treatment under various atmospheres leads to formation of nanocrystalline UO_2, ThO_2 or UO_2–ThO_2 solid solution at minimum temperatures in the interval 300–550 °C. The materials consist of nanoparticles from 3 to 15 nm in diameter and with narrow size distribution. The most advantageous preparative method, consisting in irradiation of uranium and/or thorium nitrates (0.01 mol.dm-3) and ammonium formate (0.1 mol.dm-3) by low pressure mercury lamp, is distinguished by the yields of oxides – 75 % for both UO_2 and UO_2–ThO_2 solid solution, whereas the yield of ThO_2 is 95 %.

Proposed method for uranium and/or thorium oxides synthesis is fast, simple and prepared oxides fulfil the prerequisites for the production of the high-quality nuclear fuel. The preparation of nanocrystalline UO_2, ThO_2 and mixed UO_2–ThO_2 oxides under medium pressure mercury lamp irradiation has been recently published [T. Pavelková, V. Čuba, F. Šebesta: Photo-induced low temperature synthesis of nanocrystalline UO_2, ThO_2 and mixed UO_2–ThO_2 oxides, J. Nucl. Mater. 442, 2013, 29-32. (Letter to the Editor)].

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NFC-V26, (Id: 202)

DEVELOPMENT OF INTEGRATED SOFTWARE FOR MATERIAL BALANCE OF TECHNOLOGICAL PROCESSES CALCULATION, EQUIPMENT OPERATION MODES OPTIMIZATION AND SAFETY OF NUCLEAR FUEL CYCLE RADIOCHEMICAL NODES APPROVAL

Svetlana Tretyakova[a], Ol'ga Shmidt[a], Inga Makeeva[b], Viktor Dubosarskiy[b], Vasiliy Pugachev[b]

[a]*Bochvar Institute (VNIINM)*
[b]*Zababahin Institute (VNIITF)*
djilyn@yandex.com

At this time development of any complex chemical plant (including spent nuclear fuel reprocessing plant) should be accompanied with plant governing model development. Creation of such a model is especially significant while developing innovative plants, many technological processes of which have no industrial-scale solutions and number of processes require R&D work in corresponding areas.

Material balance calculation of all flowsheet and separate nodes is one of the functions of governing model. Purpose of balance calculations is determination of flow rates and properties of products and wastes. Also the results of balance calculations can be used for estimation of realizability and practicability of technological solutions proposed, considering volume and activity of radioactive waste.

By the time “Balance model” of backend nodes of closed nuclear fuel cycle has been developed in the VNIINM. This model represents database consisting of mathematic models of separate radiochemical processes. User interface allows creating of different sequence of operations for any part of SNF reprocessing flowsheet using database and performing balance calculations for all technological flows of the scheme.

The paper describes cooperative works of VNIITF and VNIINM, targeted at creation of software, representing the plant governing model which will allow for closed nuclear fuel simulation, balance calculation, optimization of equipment operation modes using simulated experiment and providing data for assessment of nuclear safety of certain nodes and the whole flowsheet. Within this work integration of the “Balance model” database with creation of appropriate interface and integration of particular models of radiochemical processes and equipment considering physicochemical properties of working media, operation conditions, etc. is underway. Integration is performed in three ways: development of interface for data exchange between external process model, adaptation of existing model for developing software requirements and creation of certain models, according to developing software requirements.

Model developing has the following advantages: maximum flexibility while creating flowsheet and editability of model database. The latter is especially significant for successful creation of model database simultaneously with carrying out R&D works in according directions.

NFC-V27, (Id: 169)

NITRIC ACID ADDUCTS FORMATION DURING CRYSTALLIZATION OF BARIUM AND STRONTIUM NITRATES AND THEIR CO-PRECIPITATION FROM NITRIC ACID MEDIA.

Nadezhda Mishina, Boris Zilberman, Aleksandr Lumpov, Dmitry Ryabkov, Yulia Tuzik

Russian Federation
mishina@khlopin.ru

$Ba(NO_3)_2$ precipitation is one of the limiting factors in HLW evaporation during NPP spent fuel reprocessing. The model was proposed in our previous work [1] for approximation of the $Ba(NO_3)_2$ and $Sr(NO_3)_2$ solubility in HNO_3 solutions using the law of mass action. As a result the two linear areas where identified according to slope of the solubility on total nitrate ion concentra-tion in logarithmic scale and the existence of the adducts, containing 1-2 molecules HNO_3 molecules with $Ba(NO_3)_2$ and 2 ones with $Sr(NO_3)_2$ were suggested. The $Ba(NO_3)_2$ solubility in neutral solutions of $Sr(NO_3)_2$ is higher, while in the presence of ammonium and sodium or RE nitrates the curve shape is also characterized by the minimum, indicating in all the cases on the effect of nitrate complexation. In $Ba(NO_3)_2$ KNO3 system the formation of the slightly soluble double salt $Ba(NO_3)_2{\cdot}2KNO_3$ is observed.

The chemical analysis using ^{137}Cs or $Be(NO_3)_2$ as a reference mark in the case of $Ba(NO_3)_2$ or $Sr(NO_3)_2$, respectively, was carried out to calculate the volume of mother liquor captured by the precipitate. The amount of excess NO_3 - ion was compared with the excess of H^+- ion in relation to metal amount in the precipitate. $Ba(NO_3)_2$ and $Sr(NO_3)_2$ precipitates in the range from 0 to 5 mol/dm^3 HNO_3 contained only small permanent amount of excess, occluded by precipitate. In-creasing of HNO_3 concentration in the liquor > 7 mol/dm^3 HNO_3 led to a sharp increase of acid con-tent in precipitates, indicating on the complex compound formation during crystallization. In the same area co-crystallization of Ba and Sr nitrates took place. IR spectra [2] including differential ones confirm the presence of excess nitric acid and/or wa-ter in wet precipitates of barium and strontium nitrates and in their solid solutions precipitated at the high acidity or obtained by re-crystallization during their mixing in wet form.

X-ray diffraction patterns and chemical analysis [2] of individual and co-crystallized barium and strontium nitrates also indicated on the formation of $(Ba,Sr)(NO_3)_2$ solid solutions of three compositions at 4 mol/dm^3 HNO_3 and more in mother liquor, the composition depending on Sr to Ba ratio in the liquor at significant $Sr(NO_3)_2$ molar excess and typical solubility of the latter. The pattern of double salt $Ba(NO_3)_2{\cdot}2KNO_3$ was indentified as well.

So, the formation of adducts of barium and strontium nitrates with nitric acid was qualitative-ly confirmed by different methods indicating on their metastable nature, resulting in possible dis-placement of nitric acid monohydrate from forming matrix into pores of crystals.

[1] Mishina, N.E., Akhmatov, A.A., Zilberman, B.Ya., et al. Radiochemistry, 2010, vol. 52, Iss. 5, pp 523-529.
[2] Mishina, N.E., Zilberman, B.Ya., Lumpov, A.A., et al. Radiochemistry, 2013, vol. 55, Iss. 2, pp (in printing).

Chemistry of Nuclear Fuel Cycle (NFC)

Posters

NFC-P01, (Id: 0)

USING BASALT CONTAINERS FOR STORAGE OF GLASSED RADIOACTIVE WASTE

Vladimir Kulemin, Vladimir Krapukhin, Sergey Kuluykhin, Elena Krasavina, Viktor Lavrikov

Frumkin's Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences
kulemin@ipc.rssi.ru

The generation of a great amount of radioactive waste of various radionuclide compositions and activity levels call for the development of various methods of waste reprocessing and storage, as well as the production of new equipment and setups. Vitrification is considered to be one of the main directions for high-level waste disposal. Vitrified waste must be placed in containers meeting specific requirements. One of the most promising materials for making the containers is cast stone. The material has high radiation and corrosion resistance, waterproofness, destruction resistance at 400-500 °C, and a good molding ability. Cast stone products display high strength properties and resistance to aggressive media. On the other hand, when a filled container is cooling down, the differences in the thermal expansion coefficients of glass and stone casts (the coefficients may differ by a factor of 3) inevitably lead to the appearance of strain in any parts of the contact between the container material and glass, which may provoke the cracking of both the glass unit and the container material during. Placing a ready glass unit in the container is associated with loading problems, because owing to the difficulties associated with mechanical treatment of the glass unit containing high-level waste, it is virtually impossible to ensure a precise fit of the glass unit shape and the internal space of the container. Therefore, even if all technological manipulations during the packing of vitrified waste are carried out properly, the appearance of voids or strains is inevitable due to the differences in their shapes and thermal expansion coefficients. To remove this drawback, we suggest using mineral wadding between the container walls and the glass unit. The mineral wadding is made of stone melting at 1500 °C. The material has a good insulation ability in a wide temperature range, high mechanical and chemical stabilities, and compression strength. It is inflammable and does not absorb water. However, special samples having good water absorption are produced too.

Ensuring the leak tightness of the containers with vitrified radioactive waste is of great importance during waste preparation for a long-term storage. Using cast stone containers is associated with lack of tightness between the cover and the container. Towards this end, a pilot setup for sealing the containers has been developed.

Thus, the obtained results allow us to conclude that using cast stone containers lined with mineral wadding from the inside have good prospects for storage of vitrified radioactive waste.

NFC-P02, (Id: 2)

DECONTAMINATION OF LOW RADIOACTIVE LIQUID WASTE FROM OILS AND PETROCHEMICALS USING UV RADIATION AT NPPs

Vladimir Kulemin, Sergey Kuluykhin, Vladimir Krapukhin, Viktor Lavrikov

Frumkin's Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences
kulemin@ipc.rssi.ru

Nuclear power plants with WWER and RBMK reactors annually generate 30000 to 100000 m^3 of various liquid radioactive wastes. The increasingly growing amount of liquid radioactive waste of medium (MAW) and low activity (LAW) has made their reprocessing an acute issue. The main task is the separation of the long-lived radionuclides of fission products, the residual amounts of actinides (U, Np, Pu, Am, and Cm), and radioactive corrosion products of the construction steels (^{60}Co, ^{63}Ni, ^{54}Mn, ^{55}Fe, ^{59}Fe, etc.). In addition to the radionuclides, liquid MAW and LAW contain a large amount of various salts (up to 200 g/l), chelating compounds (EDTA, surfactants, etc.), traces of various oils, petroleum, and organic compounds. Their presence complicates both the separation of radionuclides from liquid waste and liquid waste decontamination technologies. The main methods of concentrating liquid LAW at nuclear power plants are distillation and ion exchange. During the evaporation of oil-containing aqueous LAW, part of the petrochemical products get into the condensate. Decontaminating this condensate with ion-exchange resins leads to their oiling and, consequently, decreases their operation resource. This work studies the possibility of using UV radiation for decreasing the content of petrochemical products in liquid LLW. The experiments were carried out on distilled water containing spindle oil in a model solution and real liquid LAW from the Kalinin Nuclear Power Plant. The model solution contained the following compounds (g/dm3): $NaNO_3$ (0.166), Na_2SO_4 (0.074), KNO_3 (1.576 and 1.295), NH_3 (1.0), and spindle oil (17.10^{-3}). The real solutions contained water from the floor drain pan (FDP), the degassed water pump (DWP), and the pure condensate tank (PCT). In addition to petrochemicals, the floor drain water contained ^{134}Cs ($4.18.10^5$ Bq/dm^3), ^{137}Cs ($6.85.10^5$ Bq/dm^3), ^{54}Mn ($23.94.10^2$ Bq/dm^3), ^{131}I ($4.07.10^4$ Bq/dm^3), ^{60}Co ($7.92.10^3$ Bq/dm^3), and ^{24}Na ($12.32.10^3$ Bq/dm^3); Fe (1.2 mg/ dm^3), Na (3 mg/dm^3), and K (0.27 mg/dm^3); H_3BO_3 (2.2 g/dm^3); pH 9-12. The work used mercury lamp placed directly in the solutions, which led to the heating of the irradiated solutions. The obtained data show that UV irradiation allows decreasing the petrochemicals content in the water solutions to a great extent, which will benefit the operation of ion-exchange resins in the liquid LAW decontamination systems.

NFC-P03, (Id: 3)

PURIFICATION OF ISOTOPICALLY ENRICHED ^{92}Mo FROM REPROCESSING OF CERMET Mo-BASED TRANSMUTATION FUEL

Kamil Vavřinec Mareš, Jan John, Ferdinand Šebesta

CTU in Prague
mareskam@fjfi.cvut.cz

The aim of this work is a separation of ^{137}Cs from model solutions of ammonium molybdate, which probably will be issuing from a reprocessing of CerMet Mo-based transmutation fuel for ADS. Comparing the effectiveness of different sorbents were performed based on the Dg values. The best material KNiFC-PAN (inorganic-organic composite ion exchanger based on potassium-nickel hexacyanoferrate active compound and polyacrylonitrile binding matrix) was characterized by kinetic studies and determination of weight distribution coefficients dependence of ceasium on the pH and the concentration of molybdenum and determination of sorption isotherms. The final column experiment confirmed the suitability of KNiFC-PAN for separation caesium from slightly alkaline, concentrated solution of molybdenum.

NFC-P04, (Id: 7)

CEMENTATION OF LIQUID RADIOACTIVE WASTE WITH HIGH CONTENT OF BORATE SALTS

Olga Gorbunova

FSUE "RADON"
olg-gorbunova@yandex.ru

The report reviews the ways of optimization the cementing of boron-containing liquid radioactive waste. The most common way to hardening the low-level liquid radioactive waste (LRW) is the cementing. However, boron-containing liquid radioactive waste with low pH values can not be cemented without alkaline additives, to neutralize the acid forms of the borate compounds. Cement setting without additives, happens only on the 14-56 day, the compounds have low strength, and hence an insufficient reliability of the radionuclides fixation in the cement matrix. The alkaline additives increase the volume of the final cement compound that enhances the financial and operational costs.

The physical and chemical methods of accelerating setting and hardening of cement compounds, containing boron compound aqueous solutions with low pH and determined the main components of the liquid radioactive waste, which prevent the hardening. To control the speed of hardening the cement solution with a boron-containing liquid radioactive waste and removing the components, that prevent hardening of the cement solution, it is proposed an electromagnetic treatment of the liquid radioactive waste in the eddy layer of the ferromagnetic particles.

The results of the infrared spectroscopy show, that the electromagnetic treatment of liquid radioactive waste changes the ionic forms of the borates and raises the pH due to the dissociation of the oxygen and hydrogen bonds in the aqueous solutions of the borate compounds.

It has investigated the various types of the ferromagnetic activators of the eddy layer, including the highly dispersed nano-powders and the magnetic phases of the iron oxides.It has determined the technological parameters of the electromagnetic processing of liquid radioactive waste and the subsequent cementation of this type of liquid radioactive waste. By using the method of scanning electron microscopy it is shown, that the nano-particles of magnetic phases of the ferric oxides are involved in the phase formation of hydro-aluminum-calcium ferrites in the early stages of the hardening and improving the strength of the cement compounds with liquid radioactive waste.

NFC-P05, (Id: 8)

CEMENTATION OF THE SOLID RADIOACTIVE WASTE WITH POLYMER-CEMENT SOLUTIONS USING THE METHOD OF IMPREGNATION

Olga Gorbunova

FSUE "RADON"
olg-gorbunova@yandex.ru

Cementation of the solid radioactive waste (SRW), i.e. the inclusion of solid radioactive waste in the cement matrix without cavities - is one of the main technological processes during the conditioning of the low and intermediate radioactive waste. The main task in the process of mixing the solid radioactive waste with the cement solution is to maximize the radioactive waste filling of the final compound, preserving the required regulated properties.

However, to achieve the desired quality of the final compound is possible only including a maximum finely dispersed solid radioactive waste (e.g., ash) no more than 20-30 % of the weight.

In the FSUE "Radon" was developed and since 2003 has cemented the solid radioactive waste by using an industrialized method of impregnation. The technology is that the polymer-cement solution, having high penetrating properties, is supplied under pressure through a tube to the bottom of the container in which is preliminarily placed solid radioactive waste. The polymer-cement solution is evenly moving upwards through the channels between the particles of solid radioactive waste, fills the voids in the bulk volume of the waste and hardens, forming a cement compound, the amount of which is equal to the original volume.

On the cementing go various kinds of diverse sizes of SRW: large lump fragments of the retiring equipment, bulk material with a size of 1-30 cm, particulate materials such as soil or ash from the incineration of the SRW with particle size of 0.5-150 mm. Justified the technological parameters and the composition of the high penetrating polymer impregnation solution for the solid radioactive waste of different granulometric compositions.

It has experimentally confirmed that when moving the cement solution through a bulk layer of solid radioactive waste, the initial ratio of the liquid and solid phases of the solution changes. As the cement solution is a suspension, the dispersed in water solid particles, in the impregnation process can settle on the cemented material. This process can lead to the depletion of the cement content in the solution in the subsequent layers of the impregnated material, whereby therein will be the slurry with less cement with higher S / C ratio (e.g., the initial solution with S / C = 0.6, at the exit will be depleted liquid solution with S / C = 0.8-1.0), which ultimately leads to a deterioration in the quality of the resulting product.

In addition, the settling cement particles, at the entrance, fill the voids of the impregnated material and prevent the further conducting cementing process, even more depleting the cement penetrating in the subsequent layers of the solution. It has been chosen a polymer, which is a stabilizing and water-retaining component of the cement slurry. It allows reaching a bigger mass transfer of the cement particles in the upper layers of the bulk volume of SRW. The experiments confirm that the polymer increases the permeability of the cement solution in 2-2.5 times, the fluidity in 1.2 times, the stability of the consistency in 1.5-1.7 times, and extends the operating range of the W / C ratio to 0.5-1.1. The report presents the experimental data and scientific justification of the process of cementation the solid radioactive waste by an impregnation method using polymer-cement solutions.

NFC-P07, (Id: 60)

A STUDY OF NITROGEN OXIDES RELASED INTO THE GAS PHASE DURING URANIUM NITRIDE DISSOLUTION IN NITRIC ACID

Yulia Voskresenskaya, Andrey Shadrin, Sergey Kulyukhin, Oleg Ustinov, Aleksey Bessonov

julya.voskresenskaya@gmail.com

In this work, we studied the release of nitrogen oxides (N_2O, NO, and NO_2) during UN dissolution at different concentrations of HNO_3 (3^{-16} mol/l) at a ratio between the solid (S) and liquid (L) phases of 1 : 7.5, as well as at an HNO_3 concentration of 7.2 mol/l. and L : S ratios from 3 to 30. The UN amounts were varied from 50 mg to 500 mg. The experiments were carried out at a temperature of 50–60 °C in the air or argon atmosphere.

The experiments were performed using a specially designed laboratory facility. The compositions of the nitrogen compounds in the gas were determined using IR spectroscopy. The IR spectra were measured in gas cells (working space length 10 cm) using a Specord M 80 spectrophotometer. The amounts of the nitrogen oxides were calculated according to the following bands: = 2236 cm^{-1} (= 0.2244 mol^{-1} l cm^{-1}) for N_2O, = 1792 cm^{-1} (= 0.0107 mol^{-1} l cm^{-1}) for NO, and = 1628 cm^{-1} (= 0.3178 mol^{-1} l cm^{-1}) for NO_2. The measurement accuracy was ±10 %.

The formation of N_2O, NO, and NO_2 was observed in all the cases. In addition, N_2O_4 appeared in the gas phase during UN dissolution at an HNO_3 concentration of more than 9 mol/l.

Major attention was given to the formation of the N_2O nitrous oxide during the interaction of uranium nitride with nitric acid (S : L = 1 : 7.5). Table 1 shows the dependence of the N_2O release on the nitric acid concentration in air and argon. As seen in Table 1, the release of the nitrous oxide linearly rises with an increase in the nitric acid concentration, whereas the atmosphere of the experiment does not influence the formation of N_2O.

Table 1. Release of nitrous oxide during the interaction of uranium nitride with nitric acid (S : L = 1:7.5) at different concentrations of HNO_3

HNO_3 concentration, mol/l	N_2O : UN ratio, mmol	
	argon	air
3	0.4	0.4
5	0.5	0.6
7	0.6	0.6
9	0.7	0.7
12	0.8	0.8
16	0.8	1.0

On the other hand, the dependencies for NO and NO_2 are of a more complex character, which might be due to the possible transformation of NO into NO_2 and NO_2 into N_2O_4. The data on the volume ratio of these oxides is given in Table 2. The N_2O volume ratio does not change with an increase in the nitric acid concentration in the experiments in argon, whereas in air, an increase in the HNO_3 concentration leads to a drastic drop of 20 to 6 % in the N_2O volume ratio. With raising the nitric acid concentration from3 mol/l to 16 mol/l, the NO volume ratio decreases from 83 to 42 % in the experiments in the argon atmosphere. The explicit volume ratio of NO dependence of HNO_3 concentration does not exist in the experiments in air. With raising the nitric acid concentration from 3 to 16 mol/l, the NO_2 volume ratio increases from 7 to 49 % in the experiments in the argon atmosphere. On the other hand, no explicit dependence of the NO_2 volume ratio on the HNO_3 concentration is observed in the experiments in air.

Table 2. Volume ratios of nitrogen oxides released during the interaction between HNO_3 and UN for the different HNO_3 concentrations and atmospheres.

HNO_3 concentration, mol/l	Volume ratio, %.					
	argon			air		
	N_2O	NO	NO_2	N_2O	NO	NO_2

3	10	83	7	20	70	10
5	9	82	9	18	66	16
7	11	66	22	13	75	12
9	13	61	26	7	83	10
12	11	56	34	6	76	17
16	9	42	49	6	71	23

Table 3 shows the dependencies of the N_2O, NO, and NO_2 release on the L : S ratio in the argon and air atmosphere, respectively. As seen in Table 3, no explicit correlation between the volume ratios of the oxides and the L : S ratio is observed, but there is a tendency to an increase in the volume ratios with a decrease in L : S. For NO_2, there is a tendency to an increase in the its volume ratio with a decrease in the L : S ratio in either argon or air.

Table 3. The volume ratios of N_2O, NO and NO_2 in the gas phase during UN dissolution in HNO_3 (7.2 mol/l) as a function of the L : S ratio in argon and air

Argon				Air			
L : S	Volume ratio, %			L : S	Volume ratio, %		
	N_2O	NO	NO_2		N_2O	NO	NO_2
25	8	78	13	30	7	84	8
14	6	83	11	20	9	83	8
8,5	7	78	1				

NFC-P08, (Id: 61)

A STUDY OF NITROUS OXIDE ABSORPTION IN AQUEOUS SOLUTIONS

Yulia Voskresenskaya, Andrey Shadrin, Sergey Kulyukhin, Oleg Ustinov, Aleksey Bessonov

julya.voskresenskaya@gmail.com

Nitrogen oxides (N_2O, NO, and NO_2) going into the gas phase during nitride fuel dissolution in HNO_3 should be captured before emission into the environment. Very many decontamination technologies allowing an efficient trapping of NO and NO_2 have been developed. On the other hand, N_2O is not a salifiable compound that can hardly react with acids and alkali. However, there are literature data on partial absorption of N_2O by various aqueous solutions. The aim of this work was a study and a comparison of N_2O absorption by different aqueous solutions from a gas phase under dynamic conditions. The experiments were carried out on a specially developed laboratory facility with bubblers of different designs. The nitrous oxide was fed from a vessel, mixed with air, and passed through a bubbler at a rate of 0.12-0.22 l/min. The contact time was 0.3-0.6 sec. The gas after bubbler was collected in a measuring cell and was studied using a Specord M 80 spectrophotometer. The table shows the absorption value measurements for the obtained solutions.

Table. Data on N_2O absorption values in the different aqueous solutions at 20-25 °C
(V = 30 ml, h = 60 mm, d = 28 mm, = 1 mm, = 0.12-0.22 l/min).

NN	Aqueous solution	Amount of N_2O, mM		Absorption value of N_2O, %
		initial	final	
1	H_2O	1.52	1.17	22.6
2	cc. HNO_3	1.52	1.41	7.4
3	cc.HNO_3	1.79	1.65	7.8
4	7.2 M HNO_3	1.47	1.46	0.9
5	cc. NH_4OH	1.61	1.46	8.9
6	1.0 M NaOH	1.61	1.43	11.1
7	1.0 M N_2H_4 nH_2O	1.88	1.67	11.2
8	0.5 M $(NH_2)_2CO$	1.70	1.51	11.1
9	0.1 M $KMnO_4$	1.61	1.54	3.9
10	0.1 M $KMnO_4$ + cc. H_2SO_4	2.05	2.05	0
11	0.1 M $KMnO_4$ + cc. HNO_3	1.88	1.80	3.8
12	0.2 M $UO_2(NO_3)_2$	1.56	1.55	0.3
13	0.1 M $K_2Cr_2O_7$	1.79	1.74	2.8
14	0.4 M $K_2Cr_2O_7$ in cc. H_2SO_4	2.05	1.43	30.2

Note: V is the volume of the aqueous solution; h is the height of the solution absorption layer; d is the bubbler diameter; is the bubbler nozzle diameter; is the bubbling rate.

As follows from the table, the maximum N_2O absorption value under the experimental conditions was observed for a saturated solution of $K_2Cr_2O_7$ in concentrated H_2SO_4 (~30 %) and water (~22 %). For concentrated HNO_3 and NH_4OH, 1.0 mol/l NaOH, 1.0 mol/l $N_2H_4 \bullet nH_2O$, and 0.5 mol/l $(NH_2)_2CO$, the N_2O absorption value was in a range of (7.5 - 11.5) %. In the other solutions, the absorption values were fewer than 4 %.

These results will be used for the assessment of the N_2O behavior in different stages of spent nuclear fuel recovery; however, an efficient purification of N_2O should require the development of other methods.

NFC-P09, (Id: 75)

REPROCESSING OF CARBIDE FUELS IN MOLTEN CHLORIDES

Zana Bikbajeva, Clint Sharrad

University of Manchester
zana.bikbajeva@postgrad.manchester.ac.uk

Innovative reprocessing methods of spent nuclear fuel are now under development worldwide in order to deliver reprocessing technology compatible with future reactor technologies and novel GEN-IV fuels, including carbide fuels proposed for gas cooled fast reactor (GFR). The main aim of this study, as a part of the ASGARD project (Advanced fuels for Generation IV reactors: Reprocessing and Dissolution) has been to investigate the feasibility and to explore pyrochemical and electrochemical methods for reprocessing of carbide fuels in molten chloride systems.

The solubility, reactivity and the potential for thermal oxidation of silicone carbides (SiC, α-SiC, β-SiC) and TiC, which are considered as potential cladding materials for carbide fuels were investigated in three different high-temperature molten chloride systems: $CaCl_2$, $CaCl_2$ + $CaCO_3$ and $CaCl_2$ + NaCl as a function of temperature, time of pyrochemical treatment and the relative content of CaO. The main analytical methods for the characterisation of the quenched melts applied in the current stage of the study are X-Ray diffraction (XRD) and thermogravimetric analysis (TGA).

NFC-P10, (Id: 79)

THE EFFECT OF PH AND IONIC STRENGTH ON THE DISSOLUTION OF TCO$_2$ IN HYPERALKALINE ENVIRONMENTS

Nicholas Evans

Loughborough University
n.d.m.evans@lboro.ac.uk

The UK has a relatively high inventory of ^{99}Tc in the wastes to manage. Under the planned cementitious Geological Disposal facility (GDF) conditions of high pH and low Eh most Tc should be immobile as amorphous technetium dioxide. Nevertheless, not much is known about the behaviour of this solid phase. The Loughborough University task within work-package 3 was to investigate the dissolution behaviour of amorphous Tc (IV) oxide containing the isotope Tc-99 as a function of various parameters, viz. pH (10.5, 12.5 and 13.3), ionic strength (I = 1 mol/L and I = 3 mol/L), and the age of the solid phase (1 day to 1 year).

To this aim, fully-reduced, high purity ^{99}TcO$_2$(s) was produced electrochemically from ammonium pertechnetate. The ammonium pertechnetate solution was adjusted to pH 10.5, 12.5 or 13.3 and ionic strength 1.0 mol L^{-1} or 3.0 mol/L before reduction for 2 hours at 6 V in the presence of 0.01 mol/L sodium dithionite as a holding reductant. Five replicates of each system were set-up and kept in an anaerobic glove box for up to 12 months for sampling and counting by LSC.

Results and Discussion

Effect of ionic strength at pH 10.5

The steady-state aqueous concentration of Tc changed from 12.8 ± 1.0 nmol/L to 17.0 ± 2.1 nmol/L as the ionic strength rose from 1.0 to 3.0 mol/L in the presence of NaCl as a background electrolyte. This change has been investigated using the ANOVA single factor test and is significant at the 99 % confidence level. Therefore, it can be said that the change in ionic strength has affected the steady-state aqueous concentration of Tc. Until a new set of experiments has been set-up it is not possible to determine is this is due to changes in the solid phase of chloride complexation or some other factor(s).

Effect of ionic strength at pH 12.5
The data show that there is no effect of changing the ionic strength from 1.0 mol/L to 3.0 mol/L at pH 12.5

Effect of ionic strength at pH 13.3
The measured aqueous concentration of Tc changed from 175 ± 33 nmol/L to 356 ± 59 nmol/L as the ionic strength rose from 1.0 to 3.0 mol/L. As the pH 13.3, I = 3.0 mol/L system has not reached steady state, no firm conclusion can be drawn except to say that it appears as though the same ionic-strength-effect as at pH 10.5 is being observed. Table 1 summarises the final measured aqueous concentrations of Tc measured.

pH	Ionic Strength (mol/L)	Steady state [Tc] (nmol/L)
10.5	1	12.8 ± 1.0
10.5	3	17.0 ± 2.1
12.5	1	29.6 ± 3.1
12.5	3	30.3 ± 2.7
13.3	1	175 ± 33
13.3	3	356 ± 59*

Table 1: Steady-state supernatant concentration of 99Tc from pH 10.5 to 13.3 at ionic strengths of 1.0 and 3.0 mol/L, 5 replicates of each, errors ± 1 s.d. *Not at steady-state after 12 months

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NFC-P11, (Id: 98)

STUDY OF CARBON DIOXIDE SOLUBILITY IN NITRIC ACID AND METAL NITRATES SOLUTIONS FOR ESTIMATION OF CARBON-14 DISTRIBUTION BETWEEN GAS PHASE AND SOLUTION DURING DISSOLUTION OF SPENT NUCLEAR FUEL

Oleg Ustinov, Andrei Shadrin, Olga Shmidt, Olga Shudegova

JSC «VNIINM», Moscow, 5a Rogova st., Russian Federation
march@bochvar.ru

In the reprocessing of spent nuclear fuel (SNF) during proposed to oxidize completely to $^{14}CO_2$ with following release to the gas phase. Due to the probable dissolution of CO_2 in nitric acid solutions ^{14}C may partially remain in the liquid phase and transfer to the following SNF reprocessing operations. In this case contamination of technological media with ^{14}C will lead eventually to severe long term impact on environment in the reprocessing plant region. There is no accessible data on solubility of carbon dioxide in nitric acid and nitrate salt solutions. The laboratory installation and appropriate method have been developed In order to determine CO_2 solubility in nitric acid and metal nitrates. The obtained experimental data on CO_2 solubility and the estimations on ^{14}C capture with liquid phase are presented in the work.

NFC-P12, (Id: 104)

SELECTIVITY FOR ACTINIDES WITH N,N'-DIETHYL-N,N'-DITOLYL-2,9-DIAMIDE-1,10-PHENANTHROLINE LIGAND: A HARD-SOFT DONOR COMBINED STRATEGY

Weiqun Shi, Chengliang Xiao, Liyong Yuan, Yuliang Zhao, Zhifang Chai

Key Laboratory of Nuclear Radiation and Nuclear Energy Technology, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China
shiwq@ihep.ac.cn

MA(III) and Ln(III) have similar physicochemical properties, such as oxidation state, ionic radii, hydration, and complexation mode. Extractants containing soft sulfur or nitrogen atoms are preferred to recognize MA(III) over Ln(III). R-BTP, R-BTBP, and R-BTPhen ligands are the successful representatives for Ln(III)/MA(III) in the last 20 years [1-2]. However, light actinides (U, Np, Pu) normally favor ligands (alkylamide or alkylphosphate) containing hard oxygen atoms [3]. If we make sure the selectivity for light actinides using hard-atoms ligands, the separation of MA(III) from Ln(III) is difficult to achieve. To separate all the actinides from lanthanides, the synthesis, solvent extraction, and complexation behaviors of actinides and lanthanides by a novel phenanthroline-based tetradentate ligand with combined hard-soft atoms, N,N'-diethyl-N,N'-ditolyl-2,9-diamide-1,10-phenanthroline (Et-Tol-DAPhen, 1), are described in this work. The ligand exhibits excellent extraction ability and high selectivity of actinides over lanthanides from highly acidic solution. X-ray crystallographic structures of Et-Tol-DAPhen with thorium and uranyl ions are showed to be 1:1 complexation. The stability constants for some actinides and lanthanides complexes with Et-Tol-DAPhen are also determined in methanol by UV-Vis spectrometry. The results of density functional theory (DFT) calculation reveal that the An-N bonds have more covalent characters than that of Eu-N, which may dominate the selectivity of Et-Tol-DAPhen towards actinides. This work can shed light on the design of new ligands with combined soft-hard atoms for group separation of actinides from highly acidic nuclear waste.

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NFC-P13, (Id: 115)

SORPTION OF AMERICIUM(III) IONS ON THE BENTONITE OF THE VOLCLAY TYPE OR RED CLAY

Agata Oszczak[a], Agnieszka Gladysz-Płaska[b], Leon Fuks[a], Marek Majdan[b]

[a]Institute of Nuclear Chemistry and Technology
[b]Faculty of Chemistry, Maria Curie Skłodowska University
a.oszczak@ichtj.waw.pl

Storage of radioactive wastes requires various protective barriers against leaking of the stored radionuclides: metal canisters (tanks), buffers made of adsorbent of metal ions, and often the surrounding rocks. On the other hand, humidity from the outside may penetrate the storage tanks. Various biopolymers and naturally occurring inorganic adsorbents were intensively examined as inexpensive and abundant materials able to slow down to a significant degree the velocity of migration of the radionuclides [e.g. 1,2].

Commercial materials - Volclay MX80 bentonite, aluminum silicate clay formed from volcanic ash, and the mine red clay coming from the Palega clay pit in the vicinity of Kielce were used in presented study. All examinations were made in parallel: with normal adsorbent and with the irradiated material (dose of 100 kGy). The latter seems to be of interest because of its possible application as the engineered barrier in radioactive waste repositories. Powder X-ray diffraction studies revealed that the materials are of layered structure, both in natural and in the irradiated forms. A decrease in the distance between the layers occurs upon the irradiation.

Water was collected in the Institute of Nuclear Chemistry and Technology (Warsaw). Post-decontamination liquids were simulated by dissolving citric acid in the water to obtain 1 M solution prior to the radionuclide addition. Sorption of americium(III) was studied as a function of contact time, initial pH of water and mass of the sorbent, respectively. An attempt to revitalize of the Am(III)-loaded sorbents was done by shaking the material at room temperature with different types of desorbing agents.

Conclusions:

The experiments proved that both the red clay and the bentonite can adsorb efficiently Am(III) ions from aqueous solutions. They can be used for removing of radionuclides potentially contaminating water from aqueous solutions and they have been found suitable to make barriers in the National Radioactive Waste Repository in Rozan (Poland).

Studies were performed in frame of the Strategic Project Technologies Supporting Development of Safe Nuclear Power Engineering Domain 4 Development of spent nuclear fuel and radioactive waste management techniques and technologies.

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NFC-P14, (Id: 126)

DIFFUSION OF SELENIUM IN CRYSTALLINE ROCK

Jussi Ikonen[a], Mikko Voutilainen[a], Katja Hänninen[a], Andrew Martin[b], Marja Siitari-Kauppi[a]

[a] *University of Helsinki*
[b] *Nagra*
jussi.ikonen@helsinki.fi

In many countries, high-level radioactive waste is planned to be disposed of in deep-lying crystalline rock. The role of the geosphere as a safety barrier is one of the most important issues in repository performance assessment. Repository safety evaluation today requires going from the laboratory and surface-based field work to the underground repository level. The diffusion and sorption of radionuclides have been studied extensively in the laboratory, but only a few long-term in situ experiments have been carried out. In situ experiments are time consuming and cost intensive, and it is commonly accepted that laboratory scale tests are well-established approaches to characterizing the properties of geological media. In order to assess the relevance of laboratory experiments, the Swiss National Cooperative for Disposal of Radioactive Waste (Nagra) have been conducting extensive in situ experiments at the Grimsel Test Site (GTS) in order to study field scale radionuclide transport and retention. Two Long Term Diffusion (LTD) experiments have been performed since summer 2007. Amongst the elements used in these experiments is nonradioactive Selenium. It is used as an analog for the radiotoxic isotope Se-79, which is ubiquitous in nuclear waste.

In the Radiochemistry Laboratory, University of Helsinki, two laboratory scale selenium diffusion experiments have been carried out to support one of the above mentioned long term in situ experiments. The selenium through diffusion experiments are conducted in two rock blocks; Kuru grey granite and Grimsel granodiorite. Changes of the selenium concentration in the inlet and observation holes are followed using ICP-MS technology. Experiments are conducted under oxic conditions. Parallel to the diffusion experiments, selenium sorption onto Grimsel granodiorite and Kuru grey granite was studied with batch experiments and geochemical modelling. Sorption was studied as a function of grain size, pH, Se concentration and pE. Apparent diffusion coefficients (Da) of selenium were determined using a Time-Domain Diffusion (TDD) modelling tool. Da and distribution coefficients (Kd), acquired from batch sorption experiments, were used to calculate the effective diffusion coefficients (De).

Selenium Kd was higher in Kuru grey granite than in Grimsel granodiorite. Kd was also higher under anoxic conditions than under oxic conditions. Diffusion coefficients were higher for Grimsel granodiorite ($De = 3\times10^{-12}$ m^2/s) than for Kuru grey granite ($De = 2\times10^{-13}$ m^2/s). Selenium probably occurred as selenium (IV) oxide in the Kuru rock matrix judging by the higher Kd and the slower diffusion observed in the Kuru grey granite.

NFC-P15, (Id: 142)

RESEARCH ON PYROHYDROLYSIS OF FLUORIDE SALTS

Yuxia Liu, Xiaobei Zheng, Xiaoyu Dong, Yulong Song, Lan Zhang

Shanghai Institute of Applied Physics, Chinese Academy of Sciences
liuyuxia@sinap.ac.cn

TMSR (Thorium-based Molten Salt Reactor) is one of the “Strategic Priority Research Program” of Chinese Academy of Sciences[1]. It offers attractions as power producers because of fuel utilization and safety characteristics. The molten mixture of ThF_4, UF_4 and LiF-BeF_2 was used as fluid fuel in this reactor.

Now we are developing a totally new flow sheet for TMSR fuel cycle in which the pyrohydrolytic technology is included. This kind of technology was first introduced by Warf et al. in the 1950s[2], which convert insoluble halide salts into corresponding oxides under a high temperature. A new designed pyrohydrolysis equipment was used in this work. It consists of a muffle furnace, reaction tube, steam generator and gas collecting system.

Experiments on the different fluoride salts, such as ThF_4, UF_4 and SrF_3 et al, were carried out with this device. The structure of pyrohydrolysis products were studied by Fourier Transform Infrared (FT-IR) and x-ray diffraction (XRD).

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NFC-P16, (Id: 144)

PRELIMINARY RESEARCH ON MONITORING URANIUM FLUORIDE VOLATILITY PROCESS BY FOURIER TRANSFORM INFRARED SPECTROSCOPY

Lixin Sun, Yongsheng Niu, Qingnuan Li, Huanqi Zhang, Congwei Hu

The division of Radio Chemistry and Technology of Shanghai Institute of Applied Physics, Chinese Academy of Sciences
sunlixin@sinap.ac.cn

Fluoride volatility method is regarded as a promising pyrochemical reprocessing technology, which might be used to reprocess spent fuels. How to monitor fluorination process on time and precisely is very important. Currently, the methods of monitoring fluorination in industry are mostly the weighting the product and sampling then off-line analysis. The former is poor in the precision, and the latter cannot reflect the current situation. In this research, the Fourier transform infrared spectroscopy (FTIR) was used to detect components and concentration of the outlet gas from UF_4 and F_2 gas-solid reaction reactor on-line at different time points. From the spectrums, the starting point, end point and reaction rate could be determined. The results showed that UF_6 was detected 3min after the beginning of reaction; during the fluorination, the concentration of UF_6 in outlet gas increased with time, then maintained at a certain concentration, finally decreased; and the rate constant of fluorination was 0.0027 min^{-1} at 300 °C and 0.2L/min 5 $\%F_2$. In summary, FTIR might be used to monitor the uranium fluorination process with high precision and fast response. However the actual spent fuel is much more complicated compared to this experiment system. There are varied fission products, so that the products of fluorination might become more complex. More research will be carried out to determine whether FTIR can detect the process or not.

NFC-P17, (Id: 147)

THORIUM BASED MOLTEN SALT FUEL CYCLE

Qingnuan Li, Lan Zhang, Guozhong Wu

Shanghai Insititute of Applied Physics, CAS
liqingnuan@sinap.ac.cn

In 2011, Chinese Academy of Sciences (CAS), after discontinuing the research and development activity in nuclear energy for decades, started to implement Strategic Priority Research Program "Future Advanced Fission Nuclear Energy (FANE)". To perform this program, two sub-bases, the north and the south, were deployed in CAS. Shanghai Institute of applied physics (SINAP), as the south sub-base, is taking in charge of research and development of "Thorium-based Molten Salt Reactor Nuclear Energy System (TMSR)". According to this research plan, two kinds of molten salt nuclear reactors, i.e. 2MW pebble bed fluoride salt-cooled high temperature reactor with solid fuel (TMSR-SF1) and 2MW molten salt reactor with liquid fuel (TMSR-LF1), will be designed and developed. Three fuel cycle models will also be implemented orderly, one-through fuel cycle on TMSR-SF, modified open fuel cycle on TMSR-SF and TMSR-LF, and closed fuel cycle on TMSR-LF. Compared with ^{239}Np (half-life 2.35 days), an intermediate product in U-Pu fuel cycle, ^{233}Pa, an intermediate product in the conversion of ^{232}Th to fissionable ^{233}U) has β decay with half-life 27 days that is almost an order of magnitude longer, which indicates that the equilibrium concentration of ^{233}Pa in reactor is almost ten times of that of ^{239}Np. ^{233}Pa has relatively high thermal neutron capture cross section, and neutron capture of ^{233}Pa accumulating in reactor will reduce conversion ratio by consuming pioneer nuclide of fissionable ^{233}U and reactivity of the reactor which negatively influents the formation of ^{233}U indirectly. The operation of reactor at high efficiency and high breeding ratio requires the isolation of ^{233}Pa and rare-earth frequently, even continuously, which is the key issue in design and operation of thorium molten salt reactor (TMSR). The frequent fuel processing is feasible for MSR, and just feasible for MSR. Compared with other GIV reactors, the feasibility of on-line fuel processing is an unique merit for MSR. Therefore MSR is an optimal type to implement Th-U fuel cycle. Pyrochemical processing methods are judged to be the only technologies for the fuel of MSRs with integrated reprocessing technologies. Because the liquid fuel for MSR is a mixture of molten fluorides, the fuel processing and reprocessing technologies planned are pyrochemical or pyrometallurgical techniques, which are based on separation of ^{233}U and fission products in molten fluoride salt. Considering the special advantages of fluoride volatility and electrometallurgical techniques, a preliminary protocol based on closed fuel cycle has been proposed for the treatment of fuel from TMSR. The recycling techniques of fuels proposed in this protocol include fluoride volatilization, distillation of molten salt carriers, electrochemical deposition. The simple experimental devices for above techniques have been established, and the feasibility studies are ongoing in SINAP.

NFC-P18, (Id: 153)

SENSITIVITY ANALYSIS OF GEOLOGICAL PARAMETERS INFLUENCING A SOLUTE TRANSPORT FROM A DEEP REPOSITORY OF SPENT NUCLEAR FUEL

Josef Chudoba

Technical University of Liberec
josef.chudoba@tul.cz

When evaluating Nuclear Waste DGR Safety [1] it is necessary to confirm its safety in a long run and above all its safety towards the biosphere, more precisely that the biosphere will not be in any hazard caused by radioactive substances. With the aid of geologists a model of a hypothetical area (the Melechov Massif) was elaborated and described with the use of geological (38 types of rocks possessing different hydraulic conductivity depending on the depth) and hydrogeological parameters [2]. The model covered the area of about 100 km^2, the depth went up to 600m and it was mathematically meshed with 37 000 elements. The volume of isotopes released out of the massif at the borderline of the near/far field from the DGR was determined (according to the reference project - measurements of 40 isotopes had to be carried out). For the most critical isotopes were considered C14, Cl36, Sr90, I129, Cs135 and Ra226.

The paper results showed that ground water flow and transport of substances within the area were the first ones to be determined. The Flow123D SW [3] developed at the Technical University of Liberec was used for the determination. The SW allows flow and transport calculations in the 3D geometry (a feature that makes it different from the similar SW available at the market). The resulting outcome represents a determination of transported substances concentration (in particular elements within the area) depending on time and its “function” is shown graphically or in the map form. To model the transport it was necessary to do calculations of all isotopes particularly.

The disadvantage of the model is the fact that all the input parameters were set deterministically [4]. The problem is being solved using the sensitivity analysis (changing the input parameters) or using the Monte Carlo Method [5].

The sensitivity analysis changing the input parameters is based on the “defined change” of (given) input parameters, i.e. hydraulic conductivity of particular types of rocks or fissures, opening of fissures, porosity and sorption parameters of transported substances. A set of new functions has been reached and followed with transport calculations.

The sensitivity analysis using the Monte Carlo method is based on defined changes of input parameters that are supposed to be stochastic ones. In this case it was necessary to know the expected (mean) value, variance and the type of the expected statistical distribution describing the given parameter.

The major paper results are: (1) calculations of the radionuclide concentrations in the elements depending on time, (2) explanation of the (basic) principal of the sensitivity analysis applications in the particular model parameters and (3) determination of parameters that have the biggest impact on the sensitivity of the whole model.

NFC-P19, (Id: 158)

NEPTUNIUM EXTRACTION BEHAVIOR IN THE PLUTONIUM PURIFICATION PROCESS

GuoAn Ye, Hu Zhang

China Inetitute of Atomic Energy , under CNNC(China Nation Nuclear Corporation)

In order to control Np path-way in plutonium purification process,the extraction behavior of Np(IV) and Np(V) were invastigated with experiment and numerical simulation.

19 %-42 % Np can be extracted into organic phase in the co-extraction unit while using 1-3 mol/L nitric acid as scrubbing reagent, if Np(V) was added into feed solution,because of the oxidation of Np(V) to Np(VI) prompted by nitrous acid.Most of Np(V) is not oxidated timely at short residence time if using centrifugal contactor and leads Np goes into raffinate.On the contrary,above 90 % Np can be extracted into organic phase if Np(IV) was added into the feed solution.At this time,however Np(IV) is accumulated obviously at scruubing stage when the nitric acid concentration of scrubbing reagent is 1.5 mol/L.

NFC-P21, (Id: 168)

AMMONIUM NITRATE AND CHELATING AGENTS DECOMPOSITION IN AUTOCLAVE DURING ILW PROCESSING

Nadezhda Mishina, Anastasia Efremenko, Artem Vodkailo, Dmitry Ryabkov, Boris Zilberman, Andrey Murzin

mishina@khlopin.ru

A large amount of intermediate level waste (ILW) containing ammonium nitrate, as well as some chelating agents and precipitator, such as diethylene triamine pentaacetic acid (DTPA) is generated during spent nuclear fuel reprocessing which can not be included into vitrified HLW due to the presence of explosive components. ILW processing is proposed which includes ammonium nitrate significant decomposition using formalin during ILW evaporation with circulation of bottom product followed by autoclave treatment of the latter. The process was elaborated and tested with the use of the laboratory-scale automated rigs.

Autoclave decomposition of organic sorbents by HNO_3 [1] has been a base of the proposed procedure. The process of NH_4NO_3 decomposition in a batch mode with 30-50 % loading of auto-clave by volume with the stimulant containing 2-6 mol/dm^3 NH_4NO_3 and 2-6 mol/dm^3 HNO3 is car-ried out for 5-6 h with an 98 % efficiency at 180-210 °C generating vapour and gas pressure of 4.0-8.0 MPa. The main gaseous products are CO_2 and N_2O. The process could be performed at other component concentrations, depending on the conditions of the other reprocessing stages, particular-ly ILW evaporation, mentioned above.

DTPA degradation in autoclave is performed in 2 steps, the temperature of first and second stages are 130 °C and 210 °C respectively. This approach allowed us to reduce the sharp increase in pressure in the process and completely decompose both DTPA and the intermediate products of its decomposition.

The joint decomposition of NH_4NO_3 and DTPA in a two-step process has been also per-formed [2], indicating on decomposition of > 95 % NH_4NO_3 and > 98 % DTPA, respectively. How-ever, the working pressure during the process of joint ammonium nitrate and DTPA decomposition significantly exceed those of their individual decomposition and apparently is summed. The loading of the autoclave should be decreased to reduce the operating pressure in it.

The preliminary NH_4NO_3 decomposition by formalin during the evaporation is expedient-ly carried out at high NH_4NO_3 accumulation in ILW for its processing. The volume reduction factor during the testing of ILW stimulant evaporation has been [2]. Destruction efficiency has amounted to 91-93 % at a molar consumption ratio $CH_2O:NH_4NO_3 = 2$, while an amount of decomposed HNO_3 has been threefold greater. These characteristics should be reduced to the level of the similar batch process [3], i.e. $CH_2O:NH_4NO_3 \leq 1$ without significant HNO_3 decomposition.

Verification of the flowsheet as a whole confirmed that the above process characteristics are sufficient for commercial implementation.

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NFC-P22, (Id: 178)

STATISTICAL ANALYSIS METHODS APPLICATION FOR THE DETERMINATION OF THE RADIONUCLIDE MIGRATION IN THE NEAR-SURFACE STORAGE FACILITIES

Elena Veselova

Russia, Moscow, SIU "RADON"
veselradon@gmail.com

At the present moment the age of the most of near-surface waste storages is more than several decades and most of protective barriers have lost their original characteristics and are not able to provide necessary insulation. As a result, atmospheric precipitations penetrate into the storage and redistribution of radionuclides within the storage as well as their removal beyond the storage zone into the ground become possible. To evaluate the safety of the storage, first of all, it is necessary to determine the presence or absence of the storage tightness violation and, in case of need, try to evaluate its quantitatively and qualitatively. Examination of the storage facilities condition is effected by means of drilling of observation and research wells in the body of the storage and the ground of the nearby zone.

The results of the statistical evaluation of the geochemical studies of the geological objects has determined that as a rule the normal concentration distribution is typical for rock forming distributed elements and the concentration of rare chemical elements which quarks are less than 0.05 % are distributed by lognormal. Also it was indentified that the nature of the statistical distributions of the components in the array is connected with the genesis of this geological formation. Normal distribution involves the exposure of a number of factors that are in addition relations, while the lognormal distribution causes their multiplicative interaction. The same patterns are observed in the study of the technogenic pollution arising under the influence of industrial facilities for relatively small period of time.

For the near-surface RAW storage formation of a new geochemical solid field occurs under the conditions corresponding to the theoretical scheme of a lognormal distribution of radionuclides. It allows to conclude that there is connection between the intensity of migration and geochemical properties of the field, in particular, the statistical characteristics of the distribution of values of exposure rate.

The closeness of the empirical distribution to the theoretical lognormal distribution the exposure dose rate (EDR) values indicates the degree of conversion of geochemical field of the RAW array and the development of radionuclide migration. With the development of migration the shape of the distribution is changing. That allows us to estimate the intensity and dynamics of migration. Correspondence of the empirical distribution to the theoretical one is determined by Pearson criterion (2). This evaluation has been effected according to the results of several surveys of existing storage. First of all we should mention uneven distribution of the values of EDR and different nature of variability for different parts of the storage facilities. Clearly pronounced anisotropy of the geochemical fields of the RAW array points to the predominance of the horizontal migration of radionuclides. According to the results of the calculation of the coefficients of the correlation between neighbouring wells within the same section and on different sides of the walls, areas of probable destruction of the intersectional partitions inside the storage and availability of migration flows have been identified. The conformity of the statistical distribution of EDR for these sites (approximately at the depth of 2,0m) as well as the areas with a clear multimodal histogram which indicates the high heterogeneity of the studied complex has been determined. In these areas the RAW array has not been subject to the “smoothing” action of the migration and has kept the features of primary heterogeneity.

The proposed method of statistical studies of the geochemical structure of the RAW array provide the unique possibility to obtain more complete data on the state of the array RAW and to evaluate the presence and intensity of migration processes in different parts of the storage that allows to examine the degree of preservation of the stru

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CHANGE OF HYDRO-GEOLOGICAL AND GEOCHEMICAL CONDITIONS OF ROCKS OF A NEAR ZONE OF STORAGES

Evgeny Veselov, Elena Veselova

Russia, Moscow, SIU "RADON"
veselovradon@gmail.com

The construction and operation of storages of the radioactive waste brings indignations in structure and properties of containing rocks of a near zone of object. Containing rocks get new hydro-geological and geochemical parameters. Change of geochemical conditions in a zone of accommodation of storages defines speed of migration of components in rocks and parameters of process of degradation of a design of engineering barriers.

The degree of hazardous of radiating objects is defined by speed of development "technogenic" water horizon, size of water exchange, structure of an acting filtrate, quantity and forms of migrating substances, conditions of their migration and change of geochemical conditions in a zone of accommodation of storages of the radioactive waste Carrying out of researches on studying a geochemical condition of environment in a zone of accommodation is radioactive hazardous objects allows to analyze at early stages of development of processes a condition of constructive elements of a construction, development of processes of degradation of engineering barriers, migration and really to estimate ecological safety of similar constructions and operatively to spend the actions directed on increase of their reliability. Containing rocks of a near zone of object which should play a role of a hydro impenetrable barrier, as a result of building operations get the raised filtration properties. Increase of filtration properties of containing rocks of a near zone of storages of the radioactive waste will cause development of process of accumulation in broken rocks atmospheric precipitation. Researches have shown that for 20 years term of preservation of object the water level within the limits of broken rocks a near zone has raised on 5 m. Increase of a level of subsoil waters has occurred not in all territory of accommodation of object, but only in a near zone of a construction.

Formation of a file broken rocks within the limits of a near zone of storage and accumulation in them of atmospheric precipitation is the precondition for change of geochemical conditions of environment in immediate proximity from a construction.

Collecting in broken rocks atmospheric precipitation contain free oxygen and have neutral or poorly sour parameter pH (atmospheric precipitation can sometimes have size pH up to 4-4,5). Waters influence external constructive elements of storage, causing their hydration and chemical destruction.

The structure of a filtrate of a near zone substantially depends on age and a degree of degradation of storage. In an initial stage from concrete chemically active elements (such as, Na^+, K^+, etc.), and finally - Ca^{+2} are taken. Thus it is necessary to note, that shift pH environments in alkaline area in a near zone can be caused by process of chemical corrosion of a concrete design of storage or an output a solution from its volume. Therefore change of size pH environments of a near zone is reliable the indicator of process of destruction of designs of storage.

NFC-P24, (Id: 191)

SORPTION OF RADIONUCLIDES IN THE ENVIRONMENT OF URANIUM HEXAFLUORIDE

Oleg Gromov, Yury Torgunakov

ollgromov@mail.ru

Impurity $^{106}RuF_5$, $^{237}NpF_6$ and $^{99}TcF_6$ in regenerated of uranium hexafluoride are the most radiation-hazardous impurity. For decrease in a dose of radiation it is expedient to carry out extraction of these elements from UF_6 [1, 2]. Researches on catching of radionuclides from dividing streams raw and perfect of uranium hexafluoride are carried out on various fluoride adsorbents of I, II, III and VIII groups of the Mendeleyev's table at 25ºC and 115ºC. The maximum quantity $^{237}NpF_6$ is absorbed on MgF_2 and AlF_3, $^{106}RuF_5$ — AlF_3, $^{99}TcF_6$ — CaF_2. At an increased temperature extent of extraction of some required impurity on sorbents, for example, $^{99}TcF_6$ on CaF_2, $^{237}NpF_6$ on AlF_3 rather sharply decreases [3]. The analysis of results shows that selective concentration of impurity from a gas stream of uranium hexafluoride needs to be carried out via the cascade of consistently located fluoride adsorbents in strictly certain order: $FeF_3 \rightarrow LiF \rightarrow CaF_2 \rightarrow AlF_3$ at a temperature of 25 – 40ºC. At such arrangement of sorbents on head FeF_3 ruthenium will be occluded selectively ($K(Ru/\Sigma) = 36 - 45$), in a front layer of CaF_2 catch TcF_6 with small impurity of neptunium and ruthenium ($K(Tc/\Sigma) = 4{,}4$ — 8,2). For essential catching of neptunium and ruthenium before CaF_2 lithium fluoride need to place. Residual amounts of radionuclides are absorbed on AlF_3. The radiation background of pure UF_6 will be defined generally ^{237}Np.

As a result of the analysis of the present data, some regularities on behavior of RuF_5 is received. Taking into account all three types of periodic dependence of behavior of ruthenium pentafluoride in system of the considered fluorides, it is possible to assume that the most active adsorbent $^{106}RuF_5$ in the environment of uranium hexafluoride will be BeF_2.

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NFC-P25, (Id: 199)

DISSOLUTION STUDIES ON MOLYBDENUM-BASED INERT MATRIX FUEL TARGETS FOR THE TRANSMUTATION OF MINOR ACTINIDES

Elena Laura Ebert, Andrey Bukaemskiy, Felix Brandt, Giuseppe Modolo, Dirk Bosbach

Forschungszentrum Jülich GmbH IEK-6
e.ebert@fz-juelich.de

Plutonium and minor actinides (MA = Np, Am, and Cm) are of particular concern with respect to long term radio toxicity, heat load issues and proliferation risks. One possibility to cope with this problem may be the transmutation of plutonium and minor actinides in subcritical accelerator-driven reactors (ADS). Fuels with high Pu and MA contents are preferred for transmutation. To increase the burn-up of transuranium elements (TRU) and to reduce the formation of new TRU a non-fissile, inert matrix is added to the fuel to improve the thermal properties. These so-called inert matrix fuels (IMF) [1-3] contain ceramic substrates or metallic matrices with high thermal conductivity, which are free of uranium and neutron transparent. The reprocessability of (Pu,MA)-oxide within a metallic ^{92}Mo matrix (CERMET) is under investigation within the EU project ASGARD [4]. A major difficulty will be to optimize the dissolution process of the used fuel after ADS operation as a head-end step prior to partitioning by solvent extraction. Mo as an inert matrix poses additional challenges with respect to its REDOX-chemistry. Mo is soluble in nitric acid but is oxidized to MoO_3 which then precipitates.[5] There is a need to avoid coprecipitation with Pu, thus leading to Pu losses.

This work focuses on the dissolution kinetics of molybdenum as matrix material in nitric acid. Molybdenum pellets as well as Mo pellets containing different amounts of cerium dioxide (5, 10, 25, and 40 wt %), which serves as surrogate for plutonium dioxide, were produced. The pellets were compacted at 640 MPa and sintered at 1600 °C. The dissolution rate was investigated as a function of acid concentration and temperature.

The dissolution rate of the Mo-pellets strongly depends on the acid concentration. Higher acid concentrations result in faster dissolution but also in more precipitation. An increase in temperature also results in a faster dissolution and larger amount of precipitation. Iron (III) is known to significantly increase the solubility of uranyl molybdate in nitric acid. Anion exchange resin studies indicate that a negatively charged iron-molybdenum complex ion is present in such solutions. [6,7] The addition of ferric nitrate to the acid increases the dissolution rate of Mo-pellets in 1M HNO_3 due to complexation. The pellet can be completely dissolved in 1 mol/L HNO_3 containing two equivalents Fe(lll). An increase of temperature results in faster dissolution kinetics, but at temperatures above room temperature precipitates occur even in the precence of iron.

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NFC-P26, (Id: 201)

DISSOLUTION BEHAVIOR OF MGO BASED INERT MATRIX FUEL FOR THE TRANSMUTATION OF PLUTONIUM AND MINOR ACTINIDES

Elena Laura Ebert, Elena Lichte, Andrey Bukaemskiy, Felix Brandt, Giuseppe Modolo, Dirk Bosbach

Forschungszentrum Jülich GmbH IEK-6
e.ebert@fz-juelich.de

For the transmutation in accelerator-driven systems fuels with a high content of Pu and minor actinides (MA = Np, Am, and Cm) are favored. To increase the burn-up of transuranium elements (TRU) and to reduce the formation of new TRU inert matrix fuels (IMF)[1-3] are preferred. These are ceramic substrates or metallic matrices with high thermal conductivity, which are free of uranium and also have small cross sections for reactions with neutrons. Experimental work on the reprocessability of IMF is being performed within the EU project ASGARD[4]. (Pu,MA)-Oxide within a metallic ^{92}Mo matrix (CERMET) and (Pu,MA)-oxide within a ceramic MgO matrix (CERCER) are under investigation. The influence of the major amounts of matrix material on the reprocessing processes such as dissolution and different extraction steps needs to be investigated. A complete dissolution of the actinide oxide and the matrix material and the actinide oxide, or a selective dissolution, where the matrix remains undissolved, can be considered.

MgO pellets as well as MgO pellets containing different amounts of CeO_2 (5, 10, 25, and 40 wt %), which serves as surrogate for plutonium dioxide, were produced and characterized. Here, we present new experimental data on the dissolution kinetics of the matrix material in nitric acid as a head-end step prior to partitioning by solvent extraction. The dissolution rate was studied in macroscopic experiments as a function of acid concentration and volume, temperature, stirring velocity, and pellet density (85, 90, 96, and 99 %TD). MgO is soluble even under mild conditions (RT, 2.5 mol/L HNO_3). The dissolution rates of MgO at different acid concentrations are rather similar, whereas the dissolution rate is strongly dependent on the temperature. Additionally, the dissolution process was investigated following a microscopic approach. Detailed SEM investigations show a heterogeneous reactivity of the MgO pellet's surface. A model was developed to describe the evolution of the pellet surface area. The additional surface area of the pellets caused by the pores created during dissolution was estimated under the assumption that they are all cylindrical with a diameter equal to the height.[5] The obtained cylinder surfaces were summed up and related to the total geometrical surface area of the pellet. Considering the additional surface area obtained by estimation of the development of pores in the pellet surface resulted in a more or less constant dissolution rate of approximately 0.02 gs-1m-2. Moreover, dissolution rates of the inert matrix fuel containing CeO_2 as surrogate for the (Pu,MA)-oxide were determined as a function of the acid concentration and temperature. During the dissolution of MgO/CeO_2 pellets the MgO dissolves completely, while the bulk of CeO_2 (>99 %) remains undissolved.

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NFC-P27, (Id: 211)

CHARACTERIZATION OF CZECH BENTONITES B75 AND S65 AND MONTMORILLONITE SAz-1: DETERMINATION OF ACID/BASE TITRATION CURVES AND CEC

Rostislav Adam[a], Barbora Drtinová[a], Karel Štamberg[a], Dušan Vopálka[a], Radek Červinka[b]

[a]*CTU in Prague, Department of Nuclear Chemistry, Prague 1, Břehová 7, Czech Republic*
[b]*ÚJV Řež, a. s., Fuel Cycle Chemistry Department, Hlavní 130, Řež, Czech Republic*
adamrost@fjfi.cvut.c

Bentonite clay is proposed to be used as buffer material in final disposal of radioactive waste mainly because of its favorable swelling properties and significant sorption capacity for both cationic and anionic forms of many critical radionuclides present in spent fuel. The sorption properties of clay materials used to be described with two types of sorption sites: layer- and edge-sites. The layer-sites are characterized by their concentration and constants describing ion exchange on them, the edge-sites are characterized also by their concentration, further by two protonation constants.. These parameters, which knowledge will help for evaluation and modelling of interaction of radioactive contaminants with the clay surface, could be obtained by evaluation of acid-base titration curves. Our titration curves were obtained: (i) by semi-continual titration method on the assumption that the equilibrium is reached when the change of electrochemical potential, or pH, in given time-interval (between two sequential additions of titrant solution) is less than 2 mV between the readings after 5 and 10 minutes, (ii) by batch method. The semi-continual method was carried out by automatic titrator TIM 845 and as for the batch method, the influence of contact time (1 to 3 weeks) on the consumption of titrant was studied. In this case, the consumptions of titrant could be influenced by dissolution of the clay material, and therefore, this effect was checked up by back titrations.

Our experiments were carried out in suspension of bentonite in 0.1 M $NaNO_3$ with the initial phase ratio V/m = 250 ml/g. For example, the pretreated bentonite B75, characterized by the producer as a non-activated, was titrated with 0.1M HNO_3 and 0.1M NaOH. The pretreatment of bentonite was done mainly with the aim to eliminate the influence of carbonates on the consumption of titrants. For evaluation of titration curves we develop an original method based on the combination of codes UCODE_2005 and PHREEQCv3. The debugging of this new evaluation method was facilitated by comparison with former approach based on a code prepared in the FAMULUS environment. On the basis of discussion of experimental and calculated data, the recommendations, comprising the optimal experimental conditions for characterization of clay materials by acid-base titration, were formulated.

Dependences of total sorption capacity of bentonites B75, S65 and montmorillonite SAz-1 on pH were compared with values of cation-exchange capacity (CEC) obtained using standardized Cu-triethylenetetramine method. Generally, the CEC corresponds to the summation of two types of charges arising from: (i) isomorphous substitution of cations in the clay crystal structure (permanent charge of layer-sites), (ii) coordination of the cations at the edges of silicate layers (pH-dependent charge of edge-sites). In case of smectites, the pH-dependent charge varies between 10 and 20 % of the total charge.

NFC-P28, (Id: 216)

STEADY-STATE MODEL OF CARBON DIOXIDE ABSORPTION AS A PART OF MATHEMATHICAL DESCRIPTION OF ON-SITE NUCLEAR FUEL CYCLE

Vladimir Tkachenko, Vladimir Kashcheev, Oleg Ustinov, Sergey Yakunin

Bochvar Institute (VNIINM)
vl.a.tkachenko@yandex.ru

Nuclear fuel cycle (NFC) closure is significant objective for contemporary energetics. One of the perspective ways at this direction is closed NFC based on fast neutron reactors using nitride fuel. One of the problems of irradiated nitride fuel (INF) reprocessing is radioactive carbon-14 handling. Unlike oxide fuel nitride fuel will contain nitrogen-14, which partially will transform to carbon-14 during irradiation. Since INF dissolution operation is carried out in oxidative media, carbon-14 in the carbon dioxide form will enter gas purification system. Hence, gas stream should be cleaned up from carbon dioxide. The simplest way for capturing carbon dioxide is absorption by alkali solution in packed absorber.

The paper presents the mathematical model for simulation of carbon dioxide absorption by alkali solution in packed absorber. The model presented is designed for estimation of influence of different process parameters (i.e. temperature, pressure) on efficiency of carbon dioxide capture and absorber dimensions. At the same time model provides ability to perform balance calculation of absorbent regeneration. Optimization calculation and consideration of absorbent regeneration are the objective for model future development.

Scheme of absorption process, algorithm and results of calculation that can be used for calculation of dimensions of apparatus, process optimization and technical-economical estimation are provided in this paper.

NFC-P29, (Id: 225)

IMMOBILIZATION OF LONG-LIVED IODINE AFTER INCORPORATION INTO APATITE AND LAYERED DOUBLE HYDROXIDE MATRICES

Natallia Torapava[a], Clemens Walther[a], Luis Iglesias Pérez[b]

[a]Leibniz University of Hanover
[b]Rovira i Virgili University
torapava@irs.uni-hannover.de

Iodine-129 being long-lived volatile fission product, among with cesium-135 and technitium-99, represents a challenge for the design of repository-suited matrices [1]. The present study investigates a possibility of iodine incorporation in the forms of iodide and iodate into apatite and layered double hydroxide matrices. The matrice should meet certain requirements, i.e. being cheap, safe, easy to synthesize, stable and environmental friendly. Optimization of coprecipitation method for synthesis of iodine containing apatite and layered double hydroxide has been done. It was shown that iodide practically does not incorporate in case of apatite and that incorporation is lower in comparison to iodate in case of layered double hydroxide. However, apatite incorporates ca. 5 - 7 % of iodate. Obtained matrices are strucutrally characterized by XRD and EXAFS methods. EXAFS shows that the iodate-apatite obtained via coprecipitation has different structural iodine environment in comparison to apatite with adsorbed iodate. Thermogravometric analysis of the iodate-apatite showed the release of iodine at t > 550ºC.

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NFC-P30, (Id: 233)

THE PROCESS OF HIGH-TEMPERATURE SATURATION OF SORBENTS LIVED RADIO NUCLIDES FROM SOLUTIONS OF HIGHLY ACTIVE WASTE AND CONVERTED INTO MINERAL LIKE MATRICES

Maya Kalenova, Andre Koshcheev, Andre Shchepin, Alex Ananiev, Oleg Gromov

vgot@vniiht.ru

The concept of radioactive waste management of IAEA and State Corporation "Rosatom" is based on the principle of multilevel environmental protection, according to which the isolation of the waste will be provided by the system of engineering and natural barriers including inert matrix, sealed container, buffer (filler) and geological formation. The main objective of the first barrier is the containment of radionuclides in the solid phase, which prevents their transition into the environment.

The task was to develop a process of obtaining mineral like matrices (MLM) saturated by the highly active waste (HLW) imitators from nitric acid solutions. Ways to accomplish the task were: high-temperature saturation of the sorbents and their subsequent conversion to MLM.

Commercial sorbents “Termoxide-5”, “Termoxide-3” and active alumina were used as starting materials after a two-stage heat treatment. It has been established that the maximum saturation is reached when using the sorbent “Termoxide-5”. For the conversion of saturated and calcined sorbents to mineral like matrix the method of induction melting in a cold crucible on a hot support was used. The MLM samples of 200 g each without adding of the alloying components, as well as with additives of iron or/and manganese oxides were obtained and analyzed. The following techniques: X-ray phase analysis, scanning electron microscopy and X-ray fluorescence analysis were used to study the resulting materials. The estimated rate of the rare-earth elements leaching from samples of MLM does not exceed 10^{-7} g/cm^2 per day. It should be noted that the conversion of saturated sorbents in mineral like matrix by the method of induction melting in a cold crucible on a hot support has several advantages compared to pressing and sintering operations: higher productivity , the ability to organize the process in a continuous mode; less stringent requirements for the quality of the batch; reaching temperatures of 3000 °C or more, virtually eliminates restrictions on the choice of the MLM compositions; more stable composition and quality of the end product due to steady state that is provided by the required time of exposure in the molten state.

NFC-P31, (Id: 234)

ABOUT CHOICE OF INTERFACE LANGUAGE FOR THE SOLUTION OF PROBLEMS OF MATHEMATICAL MODELING OF CHEMICAL AND TECHNOLOGICAL PROCESSES

Sergey Travin, Petr Miheev, Oleg Gromov, Andre Bykov

travinso@yandex.ru

The vast majority of the known program complexes applied in simulation modeling uses this or that kind of language of very high level which allows to set computer procedures specific for the model without writing special program module for each kind of the systems of ordinary differential equations (SODE). Software for the solution of direct and reverse problems of chemical kinetics is no exception.

The authors are sure interface language most closely resembling to the notation accepted in chemistry to describe the mechanism of stepwise reactions corresponds to such tasks most accurately. Formation of the right parts of SODE on the assumption of the mass action law provides their accordance with Lipschitz's criterion and also gives a chance to calculate Jacobian determinants explicit that reduces operating time of the integrating units with implicit schemes by times and orders. The available operation algorithm of entry interface contains the main blocks:

1) All substances, including intermediate, are given in the form of the identification list in the convenient notation. The declaration of all significant substances makes it possible to avoid casual mistakes at the earliest stage and guarantees against appearance of "twins".

2) Initial concentrations of substances are determined as well. Default zero concentration are substituted for the final products of reaction and active intermediates. In the overwhelming majority of cases in most cases "in manual mode" nonzero concentrations of two or three initial substances are assigned.

3) The overall scheme or the mechanism of reagents interaction is formed in the standard for chemical kinetics notation. The choice of participants in the scheme is made strictly according to the identification list declared in item 1. Natural and obligatory restriction is that total number of involved particles can't exceed three neither among reagents, nor among products of the elementary act of interaction that follows from requirements of formal kinetics.

4) All introduced reactions have default zero specific reaction rate. Before the calculation it is necessary to insert reference or guess values. It’s never too late to remove reactions with zero rates, however in some cases it’s not unreasonable to reserve them in order to complicate and correct the model in future.

Examples of solution of "non-chemical" models using formal chemical and kinetic language are given.

NFC-P32, (Id: 244)

STUDY OF 85Sr TRANSPORT THROUGH CRUSHED GRANITE IN THE PRESENCE OF COLLOIDS PARTICLES

Kateřina Videnská, Radek Červinka, Václava Havlová

ÚJV Řež, a. s.
via@ujv.cz

The formation and stability of clay colloids from the engineered barrier system of deep geological repository for radioactive waste may have a direct impact on safety in two aspects: firstly, generation of colloids may degrade the engineered barrier and colloid transport of radionuclides may reduce the efficiency of the natural barrier.

The presented work is focused on the study of the effects of bentonite colloids on strontium ^{85}Sr transport through crushed granitic rock. The main aim of experiments was to compare strontium and bentonite colloids behavior passing through crushed granite and quantification the effect of bentonite colloids on strontium retardation. The strontium migration was investigated under dynamic conditions in column set-up which provides an approximation to real conditions, existing in the environment. Firstly, we studied the transport behavior of strontium through crushed granite without presence of clay colloids. Then we performed column experiment with colloid suspension without presence of radioactive tracer. Finally, we conducted column experiment with prepared suspension of bentonite colloids with sorbed strontium. The values of transport parameters such as the sorption and desorption retardation coefficients (R) or sorption and desorption distribution coefficients (Kd) were calculated from experimental breakthrough curves.

The transport experiments were carried out with 10-6 mol/l solution of $SrCl_2$ spiked by ^{85}Sr in deionized water. The carrier concentration, initial activity of aqueous phase (about 0,7 kBq/cm^3 of ^{85}Sr) and flow rate were constant during the experiments. The crushed granitic rock from Melechov massive (Czech Republic) was used as a solid phase, the grain size of granite was 0,125 – 0,63 mm. The purified bentonite B75 (commercial product, Keramost, a. s.) in Na^+ form was used for colloids preparation. Stable suspension of purified bentonite B75 and distilled water was prepared with concentration 100 mg/ml and clay particles volume mean diameter 396 nm.

The experimental suspension of radiocolloids was prepared by mixing $SrCl_2$ solution radiolabelled by ^{85}Sr and bentonite colloids solution. The contact time between strontium and the colloids before column experiments was five days. The percentage of initially adsorbed strontium ^{85}Sr onto bentonite colloids was approximately 90 %. The results showed completely different behaviour of strontium and colloids particles during transport through crushed granite. Regardless of the strontium presence in colloids suspension, the colloids particles passed through column without retardation and behaved as conservative non-sorbing tracer. On the other hand, the retention of strontium on granite was observed, which suggest higher affinity of strontium towards granitic rock than towards bentonite colloids and showed the reversibility of the sorption of strontium on bentonite colloids.

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NFC-P33, (Id: 259)

STANDARD THERMODYNAMIC FUNCTIONS AND CONDITIONAL ELECTROCHEMICAL POTENTIALS OF HYPOTHETICAL CRYSTALLINE U(II) AND Pu(II) CHLORIDES IN LiCl-KCl MELT

Evgeny Polyakov[a], **Nina Barysheva**[b], **Vadim Simonenko**[b]

[a]*Institute of Solid State Chemistry, UB RAS*
[b]*RFNC-VNIITF*
polyakov@ihim.uran.ru

Equilibrium electrochemical behavior of (U, Pu)N in LiCl–KCl eutectic melts is of great significance for computer modeling of high-temperature electrochemical reprocessing of fast reactors with nitride fuel and lead coolant (BREST) fuel [1]. We have carried out thermodynamic modeling of pyrochemical reprocessing of (U, Pu)N in LiCl-KCl eutectic melt by using software codes and databases HSC 7.1, OUTOTEC together with our own estimates of thermodynamic data. To estimate the thermodynamic characteristics of U, Pu, Am, as well as of numerous chemical analogs of fission products and to harmonize the latter with the databases in HSC 7.1, we used the well-known comparative physicochemical methods. In this work, we coupled comparative approach with system analysis of chemical properties of considered chemical elements. This allowed us to estimate also the thermodynamic functions for such hypothetical crystalline compounds as UCl_2 and $PuCl_2$. The Gibbs free energy of formation of these chlorides in standard conditions is estimated to be (-1196+/-15) and (-1129+/-15) kJ/mole respectively. By comparing the Gibbs free energies for lanthanides, actinides and transition element chlorides with the known conditional equilibrium electrochemical potentials (E*, V, vs. Cl02/Cl^-) of the same compounds in LiCl-KCl eutectic melts at 772 K [2], we have estimated E* for the hypothetical M^{2+}/M0 in chloride melt M = U, Pu to be -4.70 and -4.40 v respectively. The reliability and precision of the estimates for UCl2 and $PuCl_2$, as well as the impossibility to detect these species in the chloride melts are discussed in the presentation.

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NFC-P34, (Id: 263)

RADIATION-INDUCED MODIFICATIONS ON PHYSICO-CHEMICAL PROPERTIES OF DILUTED NITRIC ACID SOLUTIONS WITHIN ADVANCED SPENT NUCLEAR FUEL REPROCESSING

Eros Mossini, Elena Macerata, Marco Giola, Luigi Brambilla, Chiara Castiglioni, Mario Mariani

Politecnico di Milano
eros.mossini@polimi.it

The public acceptance of the nuclear energy depends on many aspects, such as safety, environmental impact and sustainability. In this direction, the Partitioning and Transmutation strategy is crucial for an optimal resources utilization and a preferable radioactive waste management. The removal of Minor Actinides from Spent Nuclear Fuel and their transmutation into short-lived or stable isotopes would reduce the long-term radiotoxicity and the isolation time enabling a safer storage of the remaining waste in dedicated repository. In order to perform an effective burning of Actinides, it is necessary to separate them from the rest of the elements present in the spent fuel, in particular from Lanthanides. In the last decades several hydrometallurgical processes based on liquid-liquid extraction have been proposed for this challenging task, even though the radiolytic degradation of the phases, mainly due to alpha-emitters present in the process streams, still needs to be completely understood. It is known from literature that most of the radiation damage falls on the diluent and, only indirectly, on the ligands. Therefore, it is paramount to study the effects of radiolysis on the diluents, in order to evaluate the changes of both the separation performances and the fluid dynamical properties of the extracting system, as well as to hypothesize the radiolytic degradation paths of the ligands.

The experimental work here presented aims to study the effects of radiation on some physico-chemical properties of capital interest for the application within the newest and promising i-SANEX (innovative Selective ActiNides EXtraction) and GANEX (Grouped ActiNides EXtraction) processes, where the selective An separation is performed by hydrophilic extractants in acidic aqueous solutions. Therefore, 0.25 - 1M HNO_3 solutions were prepared, stored in sealed glass vials, kept at 4 °C in the dark and irradiated at total absorbed doses ranging from 25 to 200 kGy using a ^{60}Co source with a dose rate of 2.5 kGy/h. The dose rate and the total absorbed doses considered are consistent with the annual use of the solvent in the reprocessing of spent LWR/FR fuels. Density, viscosity and acidity of the solutions were measured before and after irradiation. The preliminary results suggest that the macroscopic physico-chemical properties of the irradiated solutions do not show relevant modifications with increasing the total absorbed dose in the range considered. Thus, no significant modifications in the fluid dynamical behaviour of the extracting systems are expected. This result is very encouraging from the viewpoint of the industrial-scale development. Furthermore, irradiated solutions were analysed by UV-vis spectrophotometry to assess variations of the nitrate anion concentration and by RAMAN spectroscopy to identify changes in the spectra possibly related to the radiation-induced degradation at molecular level.

In conclusion, because of the lack of knowledge concerning the effects of radiation on physico-chemical properties of diluted HNO_3 solutions, the experimental work presented would contribute to provide physico-chemical data not well-known but necessary for the safe and reliable development of the advanced separative processes.

NFC-P35, (Id: 274)

PLUTONIUM SALT-FREE STRIPPING AGENTS - ADVANTAGES AND DISADVANTAGES

Andrey Murzin[a], Mikhail Logunov[b], Alexander Mashkin[b], Vasiliy Babain[a], Irina Blazheva[a], Mikhail Alyapyshev[a]

[a]*Khlopin Radium Institute*
[b]*PA "Mayak"*
aamurzin@khlopin.ru

Selective stripping of plutonium from the organic phase is the common way for separation of plutonium from uranium in the first cycle of PUREX-process. The goal of process is conversion of plutonium (IV) to not extractable by TBP plutonium (III). Iron (II) or uranium (IV), with hydrazine as stabilizer, are typically used as reductive agents. In this case stabilizer is responsible for stability of reducing forms of metals, preventing oxidation of one's by nitrous acid. Drawback of hydrazine as reducing agent is the possibility of obtaining of ammonium nitrate and hydrazoic acid as destruction products. In spite of many studied alternatives, most of industrial flowsheets of spent nuclear fuel processing are based on hydrazine nitrate use in plutonium stripping process. Use of salt-free reactants for reducing of secondary radioactive wastes volume is the main trend in the development of new flowsheets for SNF processing.

Reducing stripping as well as complexing stripping agents may be used for plutonium affinage. Key requirements are salt-free compounds and possibility of plutonium concentration in process.

Many classes of organic compounds – such as hydrazine derivatives, for example, ethanolhydrazine etc., hydroxamic acids, carbohydrazide, diglycolic acid monoamides etc., were proposed and studied as potential salt-free chelating and reducing agents for plutonium stripping.

The goal of proposed work is the review of varied methods of plutonium stripping from the technological point of view. Advantages and drawbacks of studied chelating and reducing agents are discussed as well.

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CESIUM CONTAINING Β-TRIDYMITE AND MARICITE TYPE PHOSPHATE CERAMICS: SYNTHESIS, STRUCTURE AND THERMOPHYSICAL PROPERTIES

Ivan Korchemkin, Vladimir Pet'kov

Lobachevsky State University of Nizhni Novgorod
ivans89@mail.ru

The family of phosphates with a general formula A(I)B(II)PO4 (A(I) − monovalent metal; B(II) − divalent metal with a tetrahedral coordination) includes the groups of compounds with different structure types: β-tridymite, arcanite, glaserite, maricite, olivine. The compounds of this family have been studied because of their ferroelectric, electrochemical and luminescent properties, catalytic activity. Interest in β-tridymite structure phosphates, containing cesium in a high concentration and possessing thermal, chemical and radiation stability, are conditioned by an opportunity to use them as ceramic for ^{137}Cs γ-radiation sources for commercial and medical applications. Data on thermodynamic properties of β-tridymite type phosphates are limited by compounds $CsZnPO_4$, $CsMgPO_4$. It is known, that some species of liquid radioactive wastes contain high concentrations of stable isotopes (sodium, nickel, iron, chromium) and radionuclide cesium ^{137}Cs. Investigations of hydrolytic stability of single-phase $CsMgPO_4$ ceramic, which was obtained by “hot” and “cold” pressure and spark plasma sintering method, were shown that these objects can be used as matrix for storage of cesium containing radioactive nuclear wastes. In this work we have studied phase formation regularities and thermophysical properties of phosphates system $CsMPO_4$ (M = Co, Mn), Cs1-xNaxNiPO_4 ($0 \leq x \leq 1$).

The samples were synthesized by the co-precipitation method. The aqueous solution of phosphoric acid taken in accordance with the stoichiometry sample was added to stoichiometric mixture of metal nitrate or chloride solutions. The reaction mixture was dried at 353 K and thermally treated at 873 and 973 K. All the thermal treatment stages were alternated with grinding. X-ray powder diffraction measurements indicated that limited solid solutions in Cs1-xNaxNiPO4 system of the tridymite and maricite structural types were obtained.

The samples of $CsMnPO_4$ and $CsCoPO_4$ were crystallized at ambient temperature in tridymite structural type. The samples were investigated by DTA method over the temperature range 298−1273 K. Thermal decomposition of $NaNiPO_4$ (x = 1) was researched.

Crystal structure of $CsNiPO_4$ and $NaNiPO_4$ were refined by Rietveld method at 298 K. $CsNiPO_4$ crystal structure is characterized by three-dimensional framework, which is formed six-membered rings of tetrahedra NiO_4 and PO_4, linked by common vertices, and by large cavities that are occupied by Cs cations. $NaNiPO_4$ crystal structure consists of edge-sharing chains of NiO_6 octahedra running parallel to the b axis, which are crossconnected by the PO_4 tetrahedra, giving rise to large ten-coordinate cavities in which the Na ions are located.

The heat capacity measurements of $CsMnPO_4$ and $CsCoPO_4$ crystalline phosphates were performed over the temperature range 5−650 K. The temperature dependence of the heat capacity of crystalline CsMnPO4 showed that for the phosphate two phase transitions were found at 6.86 K and 126.99 K. The temperature dependence of the heat capacity of crystalline $CsCoPO_4$ showed that for the phosphate three phase transitions were found at 311, 481 and 512 K. For the studied compounds the characteristics of phase transitions and the thermodynamic functions over the temperature range from T (0 to 650) K and standard entropy of formation at 298.15 K were calculated.

The thermal expansion behavior of $CsMPO_4$ (M = Ni, Co, Mn) and $NaNiPO_4$ was studied by high-temperature X-ray powder diffraction at the temperature range 298−973 K. The samples expand anisotropically and belong to high-thermal expansion materials. The prepared ceramics showed a volume thermal expansion coefficient of $(3\div7) \bullet 10^{-5}\ K^{-1}$. The high specific content of the cesium in β-tridymite structure some phosphates in combination with thermal and hydrolytic stability account for the prospects for their using as safe ceramic materials for cesium γ-radiation sources. This work was made using equipment Shimadzu Corp.

NFC-P37, (Id: 295)

CORROSION AND DISSOLUTION OF INTERMETALLIC COMPOUNDS OPd_3 AND URu_3 IN 0.5-6.0 M HNO_3

Semen Zavarzin, Alexandre Maslennikov

Federal State Budjetory Institution of Science A.N.Frumkin Institute of Physical Chemistry and Electrochemistry of Russian Academy of Sciences
mmgoblin@gmail.com

The intermetallic compounds (IMC) of uranium and plutonium with Ru-subgroup metals are expected to be as a principal chemical state of Ru, Rh and Pd in spent (U,Pu)N fuel (SNF) of fast breeder reactors. Their effective dissolution is required for quantitative recycling of fissile materials during the fuel reprocessing.

The corrosion and dissolution of IMC UPd_3 and URu_3 in 0.5 to 6 M HNO_3 electrolytes were studied using linear voltammetry (LV) and current controlled electrolysis (CCE). Corrosion potentials (Ecorr) and corrosion rates (vcorr) of UPd_3, determined from Tafel plots, were found to increase from 0.22 to 0.699 V / Ag/AgCl and from 0.07 to $1.2.10^4$ $g.cm^{-2}H^{-1}$ correspondingly with the increase of HNO_3 concentration from 0.5 to 6 M. The changes in Ecorr and vcorr for URu_3 had the same trend and increased from 0.314 to 0.702 V / Ag/AgCl and from 90 to $4.3.10^3$ g.cm-2H-1. Transpassivation potentials (Etr) of UPd_3 and URu_3 were found to increase slightly from 0.45 V to 0.55 V / Ag/AgCl and from 1.12 to 1.2 V / Ag/AgCl correspondingly with the increase of HNO_3 concentration from 0.5 to 6 M. The data of LV measurements indicate that UPd_3 may be dissolved in 6 M HNO_3 with the significant rate without application of external oxidation potential. The dissolution rate of UPd_3 obtained using quantitative determination of U(VI) and Pd(II) in the electrolyte increased from 2.16 to 45 $mg.cm^{-2}H^{-1}$ with the growth of HNO_3 concentration from 4 to 8 M. At the same time URu_3 dissolution with significant rates required the electrochemical techniques, for instance, the CCE.

The rate of URu_3 anodic dissolution in CCE conditions was practically independent on the HNO_3 concentration in the electrolyte but increased significantly with the increase of anodic current density. At current densities below 12.5 $mA.cm^{-2}$ (E = 1500 ± 40 mV / Ag/AgCl) the dissolution was slow and the accumulation of soluble U(VI) and Ru(IV) in the electrolyte was found to increase linearly in time. At greater anodic current densities the IMC dissolution was accompanied by the accumulation of a thick black film, apparently RuO_2, at the electrode surface and corresponding slowing down the uranium leaching rate. At current densities 100 – 180 mA cm^{-2} the part of Ru was oxidized with formation of the soluble species of Ru(IV) and Ru(VIII), confirmed by the measurements of UV-VIS spectra of the electrolyte. The part of Ru was found to be removed from the solution in a form of volatile RuO_4. The material balance of URu_3 dissolution in course of CCE in 6M HNO_3 at 180 mA cm^{-2} allowed to estimate the rate of U(VI) leaching as 34.6 mg cm^{-2} H^{-1}. The calculation of Ru content in the electrolyte based on the UV-VIS spectrophotometry shown that only 62±2 % of the metal were found in the solution, while the rest metal was distributed between gaseous stream and the solid film, covering the electrode surface.

The results of the presented research indicate that the retention of U and Pu in the insoluble residues of SNF dissolution could be determined by the Ru content in the IMC formed during fuel burn-up. To increase the rate of the IMC dissolution the electrochemical technique is proposed.

NFC-P38, (Id: 296)

ELECTROCHEMICAL DISSOLUTION OF U – 5 MASS. % ZR ALLOY, STEEL 316 AND ZIRCALLOY IN NITRIC ACID

Svyatoslav Nikitin, Alexandre Maslennikov

Federal State Budjetory Institution of Science A.N.Frumkin Institute of Physical Chemistry and Electrochemistry of Russian Academy of Sciences
nikitin-sa@bk.ru

The advantage of electrochemical dissolution of metal or alloy spent nuclear fuel (SNF) consists in the alloy surface oxidation by application of external oxidation potential without adding the chemicals complicating following recovery of fissile materials during SNF reprocessing. The present work deals with the study of electrochemical properties and dissolution of U – 5 mass. % Zr alloy simulating U – Zr alloy based SNF and the possible cladding materials, including steel 316 and zircalloy.

The principle dissolution characteristics of U – 5 mass. % Zr alloy in 0.5 – 6 M HNO_3 were determined using linear voltammetry technique. The corrosion potential (Ecorr) value of U – 5 mass. % Zr alloy electrode was found to increase with growth of HNO_3 concentration. Its value is expected to be determined by the formation of the passive film containing U(IV) and Zr(IV) hydroxides at the electrode surface and by the cathodic reduction of HNO_3. The overvoltage of the latter reaction at U – 5 mass. % Zr in 0,5 – 6,0 M HNO_3 was found to be high. The increase of HNO_2 yield due to the reduction of NO_3^- ions with the increase of HNO_3 concentration in the electrolyte results in the increase of alloy dissolution rate in absence of applied oxidation potential in the solutions containing more than 4 M HNO_3. At the potentials, exceeding 450 mV / Ag/AgCl (Etr), U – 5 mass. % Zr passed to the transpassive state. The data of potential controlled electrolysis (PCE) shown that at the potentials close to Etr and fixed HNO_3 concentration the increase of the electrode potential increased the alloy dissolution rate. The systematic study of U – 5 mass. % Zr alloy electrochemical dissolution during current controlled electrolysis in HNO_3 electrolytes revealed that the rate of anodic dissolution of this alloy reached 44 $mg.cm^{-2}.H^{-1}$ and slightly dependent on HNO_3 concentration in electrolyte. It was demonstrated, that maximum yields of soluble U(VI) during electrochemical dissolution were achieved in 2 M HNO_3 and current density less than 100 $mA.cm^{-2}$. Formation of a precipitate consisting of crystalline ZrO_2 and X-ray amorphous U compounds at the anode surface accompanied the process of U- 5 wt. % Zr alloy dissolution, causing the decrease of the dissolution current efficiency form 7,2 to 8,6 F/mol with the increase of anodic current density.

The process of electrochemical dissolution of claddings, consisting of stainless steel and zircalloy were studied in conditions of current controlled electrolysis. The rate of stainless steel electrochemical dissolution in 2-8 mol/l HNO_3 increased from 12±1 to 98±4 $mg.cm^{-2}.H^{-1}$ with the increase of current density from 23 to 160 $mA.cm^{-2}$. Current efficiency of a process was found to vary from 90 to 98 %. It was shown that the dissolution parameters had not depend on HNO_3 concentration. Rise of the electrolyte temperature to 80 °C was found to be necessary for the electrochemical destruction of Zr-1wt. % Nb claddings. The rate of anodic dissolution of latter alloy reached 44 $mg.cm^{-2}.H^{-1}$ and was slightly dependent on HNO_3 concentration in electrolyte.

NFC-P39, (Id: 306)

BEHAVIOR Ca, Sr, Ba TUNGSTATES IN ALKALI CHLORIDE MELTS LiCl-KCl

Ekaterina Potanina[a], Albina Orlova[a], Maya Kalenova[b]

[a]*Lobachevsky State University of Nizhni Novgorod*
[b]*JSC "Scientific Research Institute of Chemical Technology"*
ekaterina.potanina@list.ru

Promising technology of recycling spent nuclear fuel suggests dissolving it in melts chlorides of alkali elements, with extraction of valuable components (U, Pu, minor actinide, etc.) and the transferring of radioactive waste into insoluble compounds. Such technology is anhydrous, therefore, it is more advantageous environmentally compared to aqueous processes. Chloride melts are resistant to radiation and can be easily cleaned from impurities. At the same time relatively high working temperatures melts allow to concentrate and to transfer of radionuclides into stable chemical forms directly in the melt. In turn, the search of sustainable radioactive waste both in aqueous systems and in the melts chemical forms for consolidation is one of the main tasks of radiochemical science. Mineral-like compounds may be regarded as such forms. Among there are compounds with the structure of the mineral scheelite ($CaWO_4$), which are studied as forms of binding such fission products as alkaline earth elements (Sr, Ba) in some alkali chloride melts. In the present work, in order to develop technology concentration of strontium and barium, and their extraction from the molten LiCl-KCl, the purpose was to explore 1) the possibility of formation of strontium and barium tungstates (scheelite structure) due to the reactions in the melt, 2) stability of such phases in the melt and 3) kinetics of dissolving the formed precipitates at T = 450, 500, 600 °C. Samples were obtained by us using the precipitating processes in aqueous systems and characterized by X-ray diffraction (XRD).

XRD data of precipitates, which were formed in melts , confirm the formation of strontium and barium tungstates (tetragonal crystal system, s. g. I41/a). It was established that the alkaline earth element transition into the solid phase is ~ 98 - 99 % (at T = 600 °C).

Tungstates of calcium, strontium and barium remain stable in contact with melt LiCl-KCl to T = 600 °C (test time to 10 hours).

Based on the kinetics data were calculated solubility values tungstates at T = 450, 500 and 600 °C. It is established that an increase in temperature increases the solubility of 1.5 - 2 times.

Comparative analysis of solubility allows to do the prediction about the extraction of Sr and Ba in sorption processes (in addition to data on precipitation technology).

NFC-P40, (Id: 323)

PARAMETRIC SAFETY STUDY OF A COMPREHENSIVE MODEL OF DEEP GEOLOGICAL REPOSITORY IN THE CZECH REPUBLIC

Dagmar Trpkošová, Jiří Landa

UJV Řež, a. s.
dagmar.trpkosova@ujv.cz

For the safety assessment of the deep geological repository it is necessary to define scenarios of possible repositories development in order to evaluate all possible variants of its development. The present work is devoted to influence of the scenarios defined by the model geometry and model parameters on the development of the main safety indicator, which embedded in the Czech legislation . The main safety indicator is the optimization level. The influence of a hydraulic and migration parameter set, based on repositories barrier and surrounding geological environment parameters, the influence of the fuel cycle end, the influence of geosphere and the biosphere model geometry on the effective dose rate were studied in this particular case.

The results showed that the new obtained data for near and far field interactions had a significant effect only for ^{79}Se. This radionuclide in terms of long-term safety seems to be one of the most important. The chemical properties of selenium, especially the solubility and distribution coefficient in granitic environment can be very significant for the overall impact of a deep geological repository on the environment (see presentation K. Videnská et al., 2014, this conference).

Results for closed cycle with the reprocessed MOx fuel and other wastes arising from reprocessing UO_x spent fuel show almost an order of magnitude highereffective dose rate than for the open cycle with spent fuel UO_x only. This is caused by the radionuclides released from the cement matrix of intermediate-level waste. Spent fuel MO_x itself has lower effective dose rate than UO_x one.

The biosphere model "FARM", which was previously used in the safety analyses under Czech Republc environmental conditions has been supplemented and extended to cover biotopes of current Czech Republic. New calculations show that the fish ingestion can significantly affect the effective dose rate of ^{129}I; it furthermoreconfirmed the importance of ^{79}Se and showed the necessity to include the dust re-suspension in the intake of vegetables.

The results of sensitivity analyzes based on reason of a model deeper understanding and the determination of significance of individual model components and the importance of model parameters show a significant effect of groundwater flow rate and the geosphere total dilution ion the effective dose rate maximum. With regards to factors such as the flow time through the geosphere, it doesn't show to influence the maximum of effective dose rate directly, but it show the effect on its time course.

The research leading to these results has received from Ministry of Trade and Industry (MPO TIP FR-Tl1/362).

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NFC-P41, (Id: 327)

MIGRATION PARAMETER STUDIES OF CZECH GRANITIC ROCKS DETERMINED BY ELECTROMIGRATION METHODS

Petr Večerník[a], Václava Havlová[a], Eva Hofmanová[a], Jan Najser[b]

[a]*ÚJV Řež, a. s.*
[b]*ARCADIS CZ a.s.*
petr.vecernik@ujv.cz

In several concepts of deep geological repository (DGR) development granites are considered as potential host rocks (Sweden, Finland, Czech Republic). Safety calculations, evaluating safety functions of DGR engineered and natural barriers, require information about radionuclide migration in fractured rock, both by advection and by diffusion in rock matrix. These two processes are the most important for radionuclide activity decrease.

Radionuclide diffusion into rock matrix is namely studied in laboratory, nevertheless also in-situ experiments are performed (e.g., Long term diffusion project, Grimsel URL, Switzerland). However, due to the diffusion experiments velocity, such studies usually take rather long time (months or even years). The through electromigration method (TEM) can be used for diffusion parameter studies, especially due to speeding up the experimental work in comparison with standard through diffusion methods. In TEM experiments both formation factor (Ff) and effective diffusion coefficient (De) values could be obtained. The invented experimental cell for TEM experiments, based on the work of M. Löfgren (Löfgren, 2004) and further improved in ÚJV laboratories (Večerník, Brůha, 2012), was used. This experimental cell enables to use samples with diameter of 40–50 mm and lengths up to 100 mm. In this study, comparison of migration parameters on different Czech granitic rocks were performed not only for samples from different sites but also compared the archive and fresh drill core samples. Iodide anion as a tracer in sodium chloride background electrolyte was used in experiments. Samples from the same sites were also used in through diffusion studies with tritium as a tracer.

Based on obtained results, it can be seen, that the diffusion of iodide anion, as a tracer in electromigration experiments, is affected by anion exclusion in most samples. Migration of negatively charged anionic species in pore space is slower than neutral non-sorbing 3H. There are also noticeable relations between formation factor values obtained by TEM experiments and others parameters describing the rock sample properties (e. g. diffusivity, hydraulic conductivity).

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NFC-P42, (Id: 344)

EXPLOSION HAZARDS OF MIXTURES OF REDUCTANTS AND OXIDANTS USED IN REPROCESSING SNF

Alexey Rodin[a], Evgeniy Nazin[a], Elena Belova[b]

[a]*Scientific and Engineering Centre for Nuclear and Radiation Safety*
[b]*A.N. Frumkin Institute of Physical chemistry and Electrochemistry, Russian academy of sciences*
rodin@secnrs.ru

Mixtures of reductant with nitrate oxidant are widely used or produced in technological operations radiochemical reprocessing SNF. The potential danger of these mixtures consists in the possibility of oxidation that can occur with a high rate and accompanied by the release of heat and gases, which may lead to the release of the contents of the apparatus or its deformation.

Some of the more dangerous operations are those in which it is possible to drying nitric acid solutions containing reducing agents, as at a certain temperature such dried mixture erupt like pyrotechnic compositions or gunpowder. In the practice of the radiochemical plants are known cases of accidents caused by intense exothermic processes. By the consequences they are fairly weak, however they led to the destruction of equipment, release of radioactive materials and even fatal. The aggregate state of mixtures of reductants and nitrate oxidants can be divided into the following groups:

- nitrate solution (nitric acid and / or nitrates) with reducing agents;

- Mixtures of solid oxidizing and reducing agents (nitrates). The maximum heat release and gas mixtures is achieved when ratio of reductant and oxidant is stoichiometric and hydrogen with carbon are oxidised to H_2O and CO_2. During assessment of explosion risk of particular manufacturing operation at the presence of mixtures of reductants and oxidants need at least the following information:

- Temperature of the solution (mixture), at which in system begin interaction accompanied by the release of heat and gaseous products (Tonset);

- The rate of gas release (Wgaz)

- Pressure that can be created in the device upon completion of the interaction process of the oxidant and the reductant.

We believe that by using of these values can be estimated the major aspects of explosion safety of technological operations - safe working conditions, the probability of failure and the possible consequences of the accident. To assess the real hazard and consequences of accidents need both information about the characteristics of the oxidative processes in these mixtures and the characteristics of apparatus in which the mixtures are using. First of all it is necessary to know the temperature at which the exothermic oxidation process starts, accompanied by gas evolution. If these processes are inevitable, for gas pipe capacity estimation of apparatus must be known maximum gassing rate. In case of sealing the gas lines, the pressures in the closed apparatus can be estimated from the total amount of the reducing agent, the quantities of the specific volume (Vsp) and the size of the free volume. In our works, we study the basic aspects of interaction between oxidants with reductants in both conditions the approximate for normal operation, and with regard to possible violations. The perspective processes of reprocessing SNF provide for the use for different purposes a number of new reductants - carbohydrazide, acetohydroxamic acid, glycine, hydroxylamine, metilaminkarbonat. Planned to introduce new operations - the destruction of ammonium nitrate with the participation of formaldehyde, denitration of uranyl nitrate with formic acid. The potential and real explosion hazards (the ability to exothermic reactions) for these reductants - nitrate oxidants mixtures is not known and requires mandatory study.

NFC-P43, (Id: 346)

DEVELOPMENT AND TESTING OF ELECTROMIGRATION TECHNIQUE TO STUDY RADIONUCLIDE TRANSPORT IN COMPACTED BENTONITE

Eva Hofmanová[a], Norbert Maes[b]

[a]*Department of Nuclear Chemistry, Czech Technical University in Prague*
[b]*Expert Group Waste & Disposal, SCK●CEN*
hofmanova.eva@gmail.com

Diffusion and sorption parameters are needed to assess the performance of a deep geological repository for high level waste (HLWR). Classical migration experiments are used to obtain these parameters but require long experimental time periods (months to years). The electromigration (EM) technique uses an electrical gradient as driving force to force ionic species to move, hence these data can be obtained in days. This technique was developed to determine diffusive properties for different radionuclides in Boom Clay (e.g. Maes et al. (1999), Maes et al. (2002)), extended for use on compacted sodium montmorillonite by e.g. Higashihara et al. (2004), Tanaka et al. (2008), and in crystalline rocks by Löfgren and Neretnieks (2006). In many countries, compacted bentonite is considered as a part of the engineered barrier system in HWLR. The aim of this study was to develop an EM cell for compacted bentonite and to test the applicability of the EM technique to study radionuclide transport.

The EM cell design was based on a mix of the design of Higashihara et al. (2004) and Maes et al. (1999). Plugs of the Czech commercial bentonite B75 were compacted to a dry density of 1300 kg/m^3 and fully saturated with 0.033 M $CaCl_2$ (which suppresses the swelling). Two bentonite plugs were combined in an EM set-up and in between an aliquot of 125-I tracer was spiked.

When an electric field is applied, electrolysis of the electrolyte solution occurs with creation of protons and hydroxyls respectively at the anode and cathode sides which induces pH changes over the sample that can negatively influence the EM experiment. In order to mitigate these effects, different set-ups were tested (with intermixing both electrode sides in neutralisation reservoir, without intermixing and with salt bridges). For the optimal experimental condition found during testing phase, several electromigration experiments at different electrical potential gradients were performed. From the linear regression between the dispersion velocity and the dispersion coefficient, the apparent diffusion coefficient for iodide was evaluated. This value was compared with apparent diffusion coefficient obtained from classical through-diffusion experiments.

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NFC-P44, (Id: 372)

STABILITY OF SILICA-SUPPORTED MONOAMIDE RESINS WITH SELECTIVITY TO U(IV) AND U(VI) AGAINST γ-RAY IRRADIATION IN HNO_3

Masanobu Nogami[a], Daisuke Mori[a], Nobuhiro Sato[b]

[a]*Kinki University*
[b]*Kyoto University*
mnogami@ele.kindai.ac.jp

In order to develop resins with selectivity to U(VI) in HNO_3 media, we have synthesized several sili-ca-supported polymer beads with the structure of a monoamide as the functional group. The examination on their adsorptivities to various metal ions has clarified that among these resins those consisting of N,N-dimethyl- acrylamide (Silica-DMAA) and N-methyl-N-vinylbenzylacetamide(Silica-MVBAA) have selectivity to U(VI) and U(IV), respectively, where major fission product (FP) ions are found to show no or very little adsorption from HNO_3 ranging up to 6 mol/dm^3 (= M) [1, 2]. For wider applications of these resins including treatment of highly- radioactive solutions, it is necessary to investigate their stability under irradiation conditions. In this study, the above two resins were irradiated by γ-ray in HNO_3 and adsorptivities to FP ions were examined. The structure change in the resins by irradiation was also studied. Silica-DMAA and MVBAA resins were synthesized in a similar manner as previously reported[1, 3]. The resins and HNO_3 of up to 6 M were mixed in a Pyrex sample tube at a ratio of 5 cm^3/g, respectively, and used as the samples for γ-ray irradiation. Irradiation by the Co-60 source was performed at max. 16.3 kGy/h up to 1.6 MGy at room temperature under ambient atmosphere. The irradiated resins were separated from the supernatant and washed using distilled water to avoid further degradation of the resins by HNO_3. The resulting resins and the supernatants were analyzed by IR and 1H NMR (solvent : D_2O), respectively. Adsorptivities of the irradiated resins to FP ions were examined by the batch method similar to the previous studies[1-3].

For the IR analyses, a new peak generated at around 1700 cm-1 for DMAA irradiated in HNO_3 of higher concentration. While, no clear changes in the spectra were observed in the irradiated MVBAA. 1H NMR spectra of the supernatants after irradiation showed exclusively distinguished peaks which would be attributed to N,N-dimethylamine (ca. 2.7 ppm (vs. DSS), CH_3, singlet) for DMAA irradiated in 6 M HNO_3 at 1.6 MGy and acetic acid (ca. 2.1 ppm (ditto), CH_3, singlet) for MVBAA irradiated in 6 M HNO_3 at 0.90 MGy, respectively.

Based on the above results, it would be proposed that both two resins were mainly degraded simply by the break of each amide bond, followed by the formation of polyacrylic acid from DMAA and secondary-amine-type weakly-basic anion exchange resin from MVBAA, re-spectively. These degradation properties are similar to those of chain-type monoamide extractants[4], and are simpler than that of a cyclic monoamide resin[5]. Considering the degradation properties of these monoamide compounds, the two resins are expected to be stable against irradiation in HNO_3 of lower concentration such as 0.1 M.

The irradiated resins showed weak adsorptions for Zr(IV) and Pd(II) from HNO_3 of lower concentration ranges and no or little adsorptions were found for other FP ions, which was in accordance with the expected adsorptivities of the degraded resins. Besides, it is expected that the two irradiated resins keep the selectivity to U species, respectively, in HNO_3 of ca. 3 M and higher.

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TECHNOLOGICAL VERIFICIATION OF FLUORIDE VOLATILITY METHOD

Jan Škarohlíd, Jan Uhlíř

Research Centre Rez
jan.skarohlid@cvrez.cz

Fluoride Volatility Method is considered to be a prospective advanced reprocessing technology for spent nuclear fuels of FBR systems. The experimental verification of the Fluoride Volatility Method has played an important role in Czech R&D devoted to Partitioning and Transmutation. The goal of the experimental technological line FERDA (Fluoride Experimental Research and Development Assembly), constructed in Nuclear Research Institute Rez, is verification of technology of FVM for the requirements of pyrochemical partitioning. The technology is based on the flame fluorination of spent fuel, subsequent condensation and multistage distillation of formed volatile fluorides. The powdered fuel is fed into the flame fluorination reactor together with fluorine gas. A separation of volatile fluorides from non-volatile ones carries out in this reactor. A main goal of the partitioning of volatile and non-volatile products of fluorination is to separate uranium in the form of volatile UF_6 from plutonium, minor actinides and most of fission products that form predominantly non-volatile fluorides. UF_6 is then purified from rest of volatile flurides by distillation process. The short-term capacity of the fluorination reactor is 1 – 3 kg of spent fuel per hour, however the whole facility is constructed as a batch process. The paper describes the experience with design and construction of the FERDA facility and evaluates the results of the first experiments with simulated fuel. Proposal of detailed experimental programme for next years is described as well.

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INVESTIGATIONS OF THE URANYL AND NEODYMIUM(III) ADSORPTION BEHAVIOR ON ION EXCHANGE RESINS FOR THE WEAK-ACID RESIN PROCESS

Christian Schreinemachers, Ronald Middendorp, Stefan Neumeier, Giuseppe Modolo, Dirk Bosbach

Forschungszentrum Jülich GmbH
c.schreinemachers@fz-juelich.de

Partitioning and transmutation (P&T) is considered as one of the promising methods to safely handle minor actinides which origin from energy production by nuclear fission. Current focus is on the production of suitable particles which can be used for future fuels.

Promising types of particle fuels are Sphere-pac and Vipac fuels [1]. The Vipac method uses randomly shaped particles, whereas the Sphere-pac process requires spherical particles. By the use of different size classes a density equal to conventional pellet fuel can be achieved. In both processes, the particles can be loaded directly into the fuel rod. One of the considered particle types consist of a homogeneous mixture of uranium and minor actinide oxides. In framework of the ASGARD project [2], microspheres consisting of a homogeneous mixture of U and Nd have been prepared by the weak-acid resin process [3]. Neodymium acts as a surrogate for trivalent actinides, such as americium. During the process, weak-acid cation exchange resins are loaded with ions. After full loading the resin beads are thermally treated in various atmospheres to produce different microspheres, such as oxides, carbides and nitrides. In this work, the ion exchange resins Amberlite IRC-86 and Lewatit TP-207 are loaded with UO_2^{2+} and Nd^{3+}. Various parameters have been investigated to maximize the adsorption. The adsorption kinetics of UO_2^{2+}, Nd^{3+} and a mixture of both ions have been studied. In addition, the temperature influence and the effect of the pH on the adsorption of UO_2^{2+} and Nd^{3+} have been investigated.

Neodymium ions show significantly faster adsorption kinetics compared to uranyl. With a contacting time of 18 h, adsorption of both UO_2^{2+} and Nd^{3+} reaches equilibrium. An exchange of Nd^{3+} by UO_2^{2+} is observed for mixtures of UO_2^{2+} and Nd^{3+} for contacting times longer than 18 h. The difference of adsorption at various temperatures is negligible, while the pH of the solution plays an important role. A pH lower than 3 causes a decrease of the adsorption. Acid-deficient uranyl nitrate (ADUN) solutions can be used to maximize the pH of the uranyl nitrate solution without the introduction of foreign cations.

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LONG TERM DIFFUSION EXPERIMENT (LTD): ANALYSES OF ^{3}H, ^{22}Na AND ^{134}Cs DIFFUSION IN CRYSTALLINE ROCK UNDER REAL DEEP GEOLOGICAL REPOSITORY CONDITIONS

Václava Havlová[a], Martin Andrew J.[b], Siitari-Kauppi Marja[c], Tachi Yukio[d]

[a]*Nuclear Research Institute Řež plc.*
[b]*NAGRA, Wettingen, Switzerland*
[c]*University of Helsinki, Finland*
[d]*JAEA, Japan*
hvl@ujv.cz

The term matrix diffusion usually considers the process by which species, being transported in distinct flow paths, penetrate the surrounding rock through connected system of pores or microfractures. The importance of matrix diffusion is that it provides a mechanism for potential specie retention within enlarged area of rock surface in bulk rock pore network. This is especially crucial when considering the calculated contribution to dose for potential escaping radionuclides from deep geological repository (DGR).

The Long Tern Diffusion Project (LTD) is an international project consisting of a series of experiments that aim was to obtain quantitative information on matrix diffusion under in situ conditions.

The 1st phase of the project included an in-situ diffusion experiment where radionuclides (^{3}H, ^{22}Na, ^{134}Cs) were injected into the borehole in undisturbed rock matrix in Grimsel test site (Switzerland) for 800 days. Here the borehole was drilled up to 8 m into the granodiorite massive in the depth 400 m under surface. The experimental interval was left opened in the borehole packer system in order the injected radioactive cocktail got int the contact with undisturbed rock matrix. The activity decrease was observed by regular sampling of the experimental solution in the system. The radionuclide tracer activity was measured by liquid scintilation spectrometry (LSC, ^{3}H) and gamma spectrometry (^{22}Na, ^{134}Cs). After 24 month the system was closed and the borehole was overcored. The active rock, surrounding the experimental interval, was then sawed and the tracer profiles were measured in the rock samples in order to determine the diffusion extent. ^{3}H content in pore water in each subsample was measure by LSC after pore water destillation and condensation. ^{22}Na and ^{134}Cs was measured by standard gamma spectroscopy.

Eventough it had been envisaged that ^{3}H might be undetectable in the rock, the methodology used enabled to determine that the tracer, being concerned as conservative non sorbing one, migrated up to 17 cm into the rock matrix. ^{22}Na as slightly sorbing tracer migrated up to 7 cm. Finally, sorbing ^{134}Cs migrated surprisingly up to 1,5 cm, instead expected several mms. The analyses results were afterwards used as a base for post mortem modelling.

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USE OF ^{3}H FOR CHARACTERISATION OF CRYSTALLINNE ROCK MIGRATION PROPERTIES

Václava Havlová[a], Najser Jan[b], Gvoždík Libor[c], Večerník Petr[a], Sosna Karel[b], Záruba Jiří[b], Dobeš Petr[d]

[a]*ÚJV Řež, a.s.*
[b]*Arcadis Geotechnika Inc., Geologická 4, Prague*
[c]*Progeo, spol. s.r.o, Roztoky u Prahy*
[d]*Czech Geological Survey, Prague*
vaclava.havlova@ujv.cz

Crystalline rocks are considered as potential host rock for deep geology repository (DGR) of radioactive waste in many countries. In order to define safety functions of host rock and gained performance assessment relevant input data, detailed examination of rock migration parameters, for relevant radionuclides has to be performed. DGR is usually planned to be constructed at the depth 400 – 600 m below the surface within as the least heterogeneous and fractured rock segment. The main processes that radionuclide might undergo during their potential way from the repository towards human and biota are advection in rock fracture, diffusion into the rock matrix and sorption onto fracture mineral surfaces. Therefore, the aim of the presented project was to determine relevant migration properties (porosity, diffusivity and formation factor) for Czech crystalline rock samples. The migration properties were determined in relation with several other parameters (hydraulic conductivity K, sampling depth, sample age, hydraulic conductivity).

102 granitic samples from ten different granitic bodies, comprising rock material of different structure and grain size, were subjected to test in order to determine porosity ( ), effective diffusion coefficients (De), formation factor (Ff) and hydraulic conductivity (K).

Porosity was determined using water-saturation method [1]. The effective diffusion coefficient De was measured using 3H as a tracer in through-diffusion experiments. The activities in both input and output reservoirs were regularly monitored using liquid scintillation spectrometry (LSC). Hydraulic conductivity K was measured in pressure cells. Porosity values differed from 0.3 – 2.7 %; while the effective diffusion coefficient De ranged from 1.6×10^{-13} to 7.41×10^{-12} $m^2.s^{-1}$, eventhough samples with De of 10^{-11} $m^2.s^{-1}$ were also found (namely altered by metasomatosis). On the other hand, several low-grade metamorphosed samples proved lower diffusion rates than undisturbed samples. General positive trend of De dependence on porosity was spotted with the major cluster of De and porosity values. The trends between De and K, however, were not so clear.

In order to put the measured values of hydraulic conductivity K and effective diffusion coefficient De into relation, numerical simulations of both through-diffusion and pressure cell experiments were undertaken using finite-element code NAPSAC. A discrete fracture network approach with stochastically generated microcracks was used for constructing granite rock matrix.

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STANDARD THERMODYNAMIC FUNCTIONS AND CONDITIONAL ELECTROCHEMICAL POTENTIALS OF HYPOTHETICAL CRYSTALLINE U(II) AND Pu(II) CHLORIDES IN LiCl-KCl MELT

Evgeny Polyakov[a], **Nina Barysheva**[b], **Vadim Simonenko**[b]

[a]*Institute of Solid State Chemistry, UB RAS*
[b]*RFNC-VNIITF*
polyakov@ihim.uran.ru

Equilibrium electrochemical behavior of (U, Pu)N in LiCl–KCl eutectic melts is of great significance for computer modeling of high-temperature electrochemical reprocessing of fast reactors with nitride fuel and lead coolant (BREST) fuel [1]. We have carried out thermodynamic modeling of pyrochemical reprocessing of (U, Pu)N in LiCl-KCl eutectic melt by using software codes and databases HSC 7.1, OUTOTEC together with our own estimates of thermodynamic data. To estimate the thermodynamic characteristics of U, Pu, Am, as well as of numerous chemical analogs of fission products and to harmonize the latter with the databases in HSC 7.1, we used the well-known comparative physicochemical methods. In this work, we coupled comparative approach with system analysis of chemical properties of considered chemical elements. This allowed us to estimate also the thermodynamic functions for such hypothetical crystalline compounds as UCl_2 and $PuCl_2$. The Gibbs free energy of formation of these chlorides in standard conditions is estimated to be (-1196+/-15) and (-1129+/-15) kJ/mole respectively. By comparing the Gibbs free energies for lanthanides, actinides and transition element chlorides with the known conditional equilibrium electrochemical potentials (E*, V, vs. $Cl0_2$/Cl-) of the same compounds in LiCl-KCl eutectic melts at 772 K [2], we have estimated E* for the hypothetical M2+/M0 in chloride melt M = U, Pu to be -4.70 and -4.40 v respectively. The reliability and precision of the estimates for UCl_2 and $PuCl_2$, as well as the impossibility to detect these species in the chloride melts are discussed in the presentation. This work was supported by RFNC-VNIITF.

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Radiopharmaceutical Chemistry, Labelled Compounds (RPH)

Verbal presentations

RPH-V02, (Id: 180)

MODIFIED INORGANIC NANOPARTICLES AS A VEHICLES FOR ALPHA EMITTERS IN RADIONUCLIDE THERAPY

Aleksander Bilewicz[a], Agata Piotrowska[a], Edyta Leszczuk[a], Przemysław Koźmiński[a], Frank Bruchertseifer[b], Alfred Morgenstern[b]

[a]*Institute of Nuclear Chemistry and Technology*
[b]*Institute for Transuranium Elements, Joint Research, Karlsruhe*
a.bilewicz@ichtj.waw.pl

Alpha particle emitting isotopes are in considerable interest for radionuclide therapy because of their high cytotoxicity and short path length [1]. Unfortunately, all available emitters have serious disadvantages: ^{211}At forms weak bond with carbon atoms in the biomolecule and in the case of ^{212}Bi, ^{213}Bi and ^{226}Th short half-life often limits the application of these nuclides. However, the short half-life of ^{212}Bi and ^{213}Bi could be effectively lengthened by binding the parent radionuclide ^{212}Pb ($T_{1/2}$ = 10.6 h) or ^{225}Ac ($T_{1/2}$ = 10 d) to a biomolecule, thereby effectively extending the use of short half-life ^{212}Bi and ^{213}Bi. In addition, in vivo generator delivers much greater dose per unit of administered activity compared to ^{212}Bi and ^{213}Bi alone. Also three radium radionuclides ^{223}Ra, ^{224}Ra and ^{225}Ra exhibit very attractive nuclear properties for radiotherapy, but the lack of appropriate bifunctional ligand for radium was the reason why these radionuclides did not find application in receptor targeted therapy. In our studies we investigated the use of TiO_2 nanoparticles as potential carriers for ^{225}Ac/^{213}Bi in vivo generator and nanozeolite particles as vehicles for ^{223,225}Ra radionuclides.

The TiO_2 nanoparticles have unique properties like: high specific surface, high affinity for multivalent cations and simple way of synthesis, which are useful in the process of labelling. Commercially available (e.g. P-25 Degussa) and synthesised in our laboratory nanoparticles were used in experiments. The nanoparticles were characterized by TEM, SEM, DLS and NanoSight techniques. In our experiments we tested two different methods of labeling. The first one was based on the possibility of formation strong bonds with certain cations on the surface of the nanopraticles. In the second one, TiO_2 nanoparticles were doped with ^{225}Ac during the process of synthesis. In both cases we obtained high yields of labelling (>99 %).

Afterwards, the stability of labelled nanoparticles was examined in 0.9 % NaCl, 10^{-3} M EDTA, solutions of biologically active substances (cysteine, glutathione) and human serum. In case of TiO_2 nanoparticles labelled with Ac-225, which was built in the crystalline structure, the leakage of ^{225}Ac and its daughter radionuclides was not significant in any of solutions, even when the incubation time was extended to 10 days. In the case of nanoparticles with adsorbed ^{225}Ac on surface the leakage in serum was slightly higher, but still insignificant. Also the NaA nanozeolite as a carrier for radium radionuclides has been studied. ^{223}Ra, and ^{225}Ra, the α-particle emitting radionuclides, have been absorbed in the nanometer-sized NaA zeolite through simple ion-exchange. ^{223,225}Ra-nanozeolites have shown very good stability in solutions containing: physiological salt, EDTA, amino acid and human serum. To make NaA nanozeolite particles dispersed in water their surface has been modified with silane coupling agent containing poly(ethylene glycol) (PEG) molecules.

To obtain conjugates specific for receptors on glioma cancer cells short peptide substance P were covalently attached to the PEG-TiO_2 and PEG-nanozeolite surface. The obtained bioconjugate were labeled with ^{225}Ac and ^{223}Ra respectively. The serum stability of labelled biconjugates was similar or little better than unmodified nanoparticles. The cell affinity, cytotoxicity and biodistribution studies of the obtained radiobioconjugate are in progress.

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RPH-V03, (Id: 68)

DETERMINING THE RETENTION OF RECOILING DAUGHTER NUCLIDES OF ^{225}Ac IN POLYMERIC NANO-CARRIERS

Guanglin Wang[a], Antonia Denkova[a], Robin De Kruijff[a], Alex Rol[a], Eduardo Mendes[a], Elisabeth Thijssen[a], Alfred Morgenstern[b], Frank Bruchertseifer[b], Bert Wolterbeek[a]

[a]*TU Delft*
[b]*ITU, Karlsruhe*
guanglin.wang@tudelft.nl

Alpha radionuclide therapy has a great potential in the fight against cancer as proven by a large number of pre-clinical and clinical studies. In vivo generators capable of delivering a highly efficient cascade of alpha particles are also steadily gaining importance. At the moment ^{225}Ac is the most relevant radionuclide that can serve as an in vivo generator, providing four alpha particles with a total energy of 28 MeV. However, due to the recoil effects the daughter recoil atoms, most of which are alpha emitters as well, receive energies that are much higher (> 100 keV) than the energies of chemical bonds (typically around 2- 8 eV) resulting in decoupling of the radionuclide from common targeting agents such as antibodies. The escaped daughter atoms are free to spread in the body and can cause severe harm to healthy tissue, which is considered to be the major challenge in alpha radionuclide therapy. Here, we demonstrate that polymer vesicles (i.e. polymersomes) can retain recoiling daughter nuclei based on an experimental study examining the retention of ^{221}Fr and ^{213}Bi when encapsulating ^{225}Ac. Furthermore, we examined the retention of ^{209}Pb, the daughter nuclide of ^{213}Po, when enclosing ^{213}Bi in the vesicles.

Polymersomes composed of poly(butadiene-b-ethylene oxide) were successfully loaded with ^{225}Ac and ^{213}Bi reaching an efficiency of more than 60 % in both cases with negligible loss. The recoil retention of ^{221}Fr and ^{213}Bi were found to increase with the size of the polymersomes, reaching respectively 69 ± 1.5 % and 53 ± 4 for polymersomes having a diameter of 800 nm. The retention of ^{209}Pb subsequent to a single recoil step (i.e. ^{213}Po decaying to ^{209}Pb) was found to be 59 % ± 17 in the case of polymersomes having the same diameter as reported above. Finally, the polymersomes were found to accumulate around the nucleus in tumor cells (HeLa cell line) which is expected to further reduce the harm caused by recoiling alpha emitters, provided that the nano-carriers have favorable pharmacokinetics.

RPH-V04, (Id: 58)

IN VIVO STUDY OF ^{111}In-LOADED POLYMERSOMES

Robin de Kruijff[a], **Antonia Denkova**[a], **Guanglin Wang**[a], **Eduardo Mendes**[a], **Bert Wolterbeek**[a], **Diane Abou**[b]

[a]*Delft University of Technology*
[b]*Johns Hopkins Hospital*
r.m.dekruijff@tudelft.nl

In the fight against cancer, it is of utmost importance to damage diseased cells whilst leaving healthy tissue unaffected. Vesicles composed of amphiphilic block copolymers have been proven to be promising nano-carriers, which are capable of transporting a variety of pharmaceuticals to tumour sites [1]. Their application can be extended to the field of nuclear medicine by designing ultra stable polymersomes, although such studies are scarce. Here, we present a study demonstrating the radiolabeling of polymer vesicles with the molecular imaging agent ^{111}In, and their in vivo pharmacokinetics in mice. This has been examined using microSPECT, the most powerful pre- clinical imaging technique in terms of spatial resolution.

The vesicles are composed of poly(butadiene-b-ethylene oxide) block copolymers, and the labelling has been achieved by transportation of the radionuclide, complexed to a lipophilic ligand, through the hydrophobic bilayer into the aqueous cavity containing a strong hydrophilic chelate [2]. A sufficient amount of the radionuclides was successfully encapsulated in the polymersomes (>90 % loading efficiency) with a negligible loss of radiolabel upon incubation in serum (<5 % in 24 hours at 37 ˚C), allowing their safe application in in vivo studies. The ^{111}In containing 80 nm polymersomes have been subsequently used in pharmacokinetic and bio-distribution studies using microSPECT. Both healthy and tumour bearing female Ncr nude mice were injected intravenously or subcutaneously with 80 nm polymersomes loaded with 20 MBq ^{111}In. Periodic microSPECT images were taken, and a biodistribution was performed 24 and 48 h p.i.

The polymersomes have been observed to circulate a considerable time in vivo (longer than 6 h) in healthy mice, and are primarily cleared by the spleen, which complies with the circulation time obtained in other in vivo polymersome studies [3]. This in contrast to a much shorter circulation time observed for polymersomes intravenously injected in tumour bearing mice, where the liver and spleen removed the polymersomes from circulation within 1.5 h. Saturation of the RES by saturation with a higher polymersome concentration is expected to prolong the blood circulation time of the vesicles. Very promising results were obtained for subcutaneously injected mice, where a high retention rate of polymersomes in the interstitial tissue surrounding the tumour site was observed, whereas unencapsulated ^{111}In-DTPA was cleared immediately. This makes subcutaneously injected polymersomes a valuable option for loco-regionally targeted tumour therapy.

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INVESTIGATION OF ASTATINE CHEMISTRY IN SOLUTION

Gilles Montavon[a], Andréa Sabatié-Gogova[b], Ning GUO[a], Remi Maurice[a], Florent Réal[c], Nicolas Galland[d], Fadel Bassal[d], Tahra Ayed[d], Eric Renault[d], Julien Plimé[e], Cyrille Alliot[b], David Deniaud[d], Julie Champion[d], David Teze[d]

[a]SUBATECH
[b]GIP Arronax
[c]PHLAM
[d]CEISAM
[e]LCT-Paris
montavon@subatech.in2p3.fr

Astatine 211 is considered to be one of the most promising candidates for targeted alpha therapy (TAT)[1,2] and it is the subject of a wide research program in Nantes (France). A carrier molecule should transport At-211 to the cancer cells where alpha-particles emitted by the radionuclide would destroy the target. However binding astatine to cancer selective carrier molecules remains a difficult task. It is recognized that many of the basic chemical studies with astatine (At) have unfortunately been set aside, which currently hinders the development of radiotherapeutic agents [3] At-211 is produced in cyclotrons and all investigations were consequently derived from radiochemical studies at ultra-trace concentrations (typically smaller than 10^{-10}mol.L^{-1}). Therefore no spectroscopic tools can be used to assess At chemistry at the molecular level. These two points clearly limit the investigations of its chemistry, and consequently the development of efficient labelling protocols.

Based on these considerations, a research program has started to explore the fundamental properties of At using a multi-disciplinary approach combining radiochemistry, analytical chemistry and molecular modelling competences. The object of this contribution is to present the main advances obtained during the past 10 years as regards especially to the particular metallic character of astatine. Our methodology enabled to define a Pourbaix diagram (Eh/pH diagram) for At in non-complexing acidic aqueous medium. In addition to At^- species, the experiments and quantum calculations highlighted the existence of two stable At^+ and AtO^+ cationic forms of astatine [4, 5]. This truly contrasts with others halogens. Recent results on the chemical reactivity of AtO^+ demonstrate the potentiality to form both coordination and covalent bonds with organic and inorganic ligands [6-8]. The peculiarity of the AtO^+ behaviour in water solvent will be also discussed [9,10].

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RADIOACTIVE GOLD NANOPARTICLES IN NANOMEDICINE: NEUTRON ACTIVATION AND RADIOCHEMICAL APPROACHES IN GREEN NANOTECHNOLOGY

Kattesh Katti

University of Missouri
kattik@health.missouri.edu

Effective delivery of radiopharmaceuticals, chemotherapeutic, hormonal and biological pharmaceuticals to the tumor tissue and cancer cells selectively continue to be the most vexing problems in cancer oncology. Radioactive nanoparticles with diagnostic and therapeutic capabilities provide intelligent drug delivery systems to maximize therapeutic activity and to minimize undesirable side-effects. For example the radioisotope of gold metal, Au-198, provides a desirable beta energy emission and half-life that destroys tumor cells/tumor tissue (β_{max} = 0.96 MeV; half-life of 2.7 days). Its penetration range (up to 4 mm in tissue or up to 1100 cell diameters) is sufficiently long to provide cross-fire effects to destroy tumor cells/tissue, but short enough to minimize radiation exposure to adjacent tissues. One particularly attractive feature of radioactive gold nanoparticles is that it does not have to be incorporated into every tumor cell to have a therapeutic effect. The path length of the emitted radiation is sufficient to allow effective therapy following uptake into a subpopulation of tumor cells. It is this feature that has attracted recent attention to apply nanotechnology for the effective delivery of therapeutic doses of beta emitting nanoparticles selectively to tumor tissue and tumor cells. We have recently carried out extensive in vitro and in vivo investigations to validate the hypothesis that glyco protein (gum Arabic) functionalized radioactive Au-198 nanoparticles are stable and biocompatible under in vivo conditions. Our research efforts have demonstrated that the complex polysaccharides and protein structures within the GA backbone can effectively lock gold nanoparticles on the protein matrix to produce non-toxic gold nanoparticulate constructs (GA-AuNP) which are stable under in vivo conditions for potential applications in tumor therapy [1]. Our detailed in vivo studies, through intratumoral administration of GA-^{198}AuNP (1.5 Ci/tumor), in SCID mice bearing human prostate cancer xenografts, have demonstrated retention of over 154.05 ±40.7 %ID/gm within the tumor at 30 min that declined to 87.0±16.9 %ID/gm by 24 h. The overall reduction in tumor volume was 80 % three weeks after a single dose intratumoral administration of GA-^{198}AuNP (408µCi).

In our continued efforts to apply Green Nanotechnology for the development of therapeutic radioactive gold nanoparticles, recently we have discovered that the high antioxidant capacity of Epigallocatechin gallate (EGCG), which is the most abundant catechin polyphenol in tea, can be used to convert radioactive Gold-198 precursor to the corresponding biocompatible radioactive gold nanoparticles functionalized with Laminin receptor specific EGCG. Laminin receptors are overexpressed in a large number of human tumors and the high in vivo affinity of EGCG toward Laminin receptors has allowed to develop Laminin receptor specific radioactive gold nanoparticles to achieve tumor specificity [2,3]. This lecture will provide: (a) scope and prospects of beta emitting radioisotopes in nanomedicine; (b) details on the intervention of nuclear activation analysis and various radioanalytical approaches for the production of tumor specific radioactive gold-198 nanoparticles; and (c) full in vivo investigations on therapeutic properties of EGCG-198-AuNP agent in treating prostate tumors and (d) the overall implications of Green Nanotechnology of therapeutic beta emitting nanoparticles in oncology.

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RPH-V07, (Id: 262)

PRE-CLINICAL EVALUATION OF DOTA-CONJUGATED PSMA-INHIBITORS AND THEIR COMPARISON WITH STANDARD REFERENCE Glu-urea-Lys-(Ahx)-HBED-CC

Martina Benešová[a], Martin Schäfer[a], Ulrike Bauder-Wüst[a], Walter Mier[b], Uwe Haberkorn[b], Klaus Kopka[a], Matthias Eder[a]

[a]*DKFZ Heidelberg*
[b]*University Hospital Heidelberg*
m.benesova@dkfz-heidelberg.de

New theranostic radiopharmaceuticals for rapid visualisation of prostate cancer and the highly effective radioendotherapy are of utmost clinical interest. Since the Prostate-specific membrane antigen (PSMA) is upregulated in nearly all prostate cancers compared with the rather low expression levels in normal tissue, PSMA can be considered as an attractive target for the diagnosis and therapy of prostate cancer. This project is focused on the development and evaluation of a series of linker variations of DOTA conjugated ^{68}Ga-PSMA-PET imaging agents. These ligands consist of three principle components: the PSMA binding motif (Glu-urea-Lys pharmacophore), a variable linker and the DOTA chelator. The combination of DOTA with the PSMA targeting inhibitors might open the possibility of using the same vector molecule for imaging and therapeutic purposes due to the similarity of the coordination chemistry of ^{68}Ga and that of therapeutic radionuclides such as ^{90}Y or ^{177}Lu. All studied compounds were compared with the clinically used reference Glu-NH-CO-NH-Lys-(Ahx)-HBED-CC. It was reported that the chelator HBED-CC seems to interact advantageously with the binding pocket. The here aimed linker region is designed in order to elucidate the structure-activity relationships (SAR) and to compensate binding potential of HBED-CC. After the formation of the resin immobilized Glu-urea-Lys, the further synthesis of the PSMA binding motif and linker region was performed by solid-phase peptide chemistry. The resulting product was coupled by using the active ester of DOTA. All compounds were analysed using RP-HPLC, MALDI-MS, and NMR. Subsequent ^{68}Ga-labeling resulted in a radiochemical yield (RCY) of >97 % after 15 minutes at 95 °C for DOTA-conjugated compounds and in a RCY of more than 99 % in less than 2 min for the HBED-CC-based compound. In order to select the most promising precursors, *in vitro* cell binding properties (competitive binding affinity and specific internalization) were studied using the PSMA expressing cell line LNCaP. The tumor-targeting and pharmacokinetic properties were further investigated through *in vivo* biodistribution studies and dynamic small animal microPET imaging. PET scans and biodistribution data were obtained 1 or 2 hours after injection in BALB/c nu/nu mice bearing LNCaP tumor xenografts. All prepared compounds revealed a high affinity for PSMA on the human prostate cancer cell line LNCaP. Of the library of 25 targeted probes synthesised two were found to bind the cells with low subnanomolar affinity (Ki = 0.07 ± 0.02 nM, and 0.49 ± 0.09 nM, respectively) which was significantly improved in comparison with the HBED-CC-based standard compound (Ki = 12.1 ± 2.1 nM). The inhibition potency investigated by the enzyme-based NAALADase assay confirmed these results. Both mentioned DOTA-conjugated imaging agents showed a higher specific internalisation of up to 48 % ID/106 cells which is crucial in respect to the tumor targeting properties. Taken together, these two substances showed improved cellular uptake compared to the reference Glu-urea-Lys-(Ahx)-HBED-CC. In addition, differences between the HBED-CC and the DOTA derivatives were observed also in the*in vivo* organ distribution studies. The lower kidney, liver and spleen values together with the higher tumor uptake were in favor of the DOTA compounds. Time-activity curves obtained from dynamic PET measurements showed prolonged tumor uptake and a faster clearance from the kidneys. Finally, the interaction with the binding pocket and the in vivo tumor-targeting and the pharmacokinetic properties of the DOTA-conjugated compounds were significantly optimized by modification of the linker region. This approach could lead to an improved management of recurrent prostate cancer with one and the same precursor for diagnostic and therapeutic purpose.

RPH-V08, (Id: 331)

AN ASYMMETRIC APPROACH TO THE SYNTHESIS OF A CARBON-11 LABELLED GLIOTRANSMITTER D-SERINE

Alexander Popkov[a], Oleksiy Itsenko[b]

[a] *Department of cognitive research and tomographic imaging methods, Samo University*
[b] *MFT, Sahlgrenska University Hospital*
sasha.samouni@gmail.com

Endogenous D-serine is a co-transmitter of glutamate for synaptic N-methyl-D-aspartate receptors (NMDARs). Receptor affinity for binding D-serine versus glycine depends on its GluN2 subunit composition. For the activation of NMDARs glutamate binds to the GluN2 subunit of the receptor and a second ligand binds to the GluN1 subunit. D-serine is an endogenous ligand for the glycine site of the GluN1 subunit receptors in the brain in the case when NMDARs composed of the GluN1 and the GluN2A subunits. NMDARs composed of the GluN1 and the GluN2B subunits preferentially bind glycine at GluN1 sites [Madry, 2007]. Biosynthesis of D-serine requires epimerisation of L-serine in neurones by serine racemase. Resulting D-serine is transported into astrocites for storage. Na^+-independent alanine–serine–cystein transporter-1 is found exclusively in neurons, Na+-dependent ASCT1 and ASCT2 are present in both neurons and astrocites. It was demonstrated D-serine plays an important role in the formation and maturation of synaptic contacts and in earlier stages of neuronal circuit construction, as a regulator of neuroblast migration in the developing brain. It has been tested as a therapeutic agent for the treatment of schizophrenia, depression, Parkinson disease and post traumatic stress disorder (PTSD) [Van Horn, 2013].

We performed a key step in the synthesis of carbon-11 labelled D-serine: creation of the chiral centre by the condensation of carbon-11 labelled formaldehyde [Hooker, 2008] with a glycine synthon [Popkov, 2012]. Decay corrected radiochemical yield of the hydroxymethylated complex was above 20 %. The observed ratio of diastereomers vary; in the best experiments the d. e. was above 90 %. Purification of the L,D diastereomer on a C18 HPLC column takes 8 min. Optimisation of SPE purification is in progress. Hydrolysis of the complex will take up to 3 min.

Literature

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RPH-V09, (Id: 321)

^{18}F FLUMANEZIL, RADIOLIGNAD OF THE CENTRAL BENDODIAZEPINE RECEPTORS: A SYSTEMATIC STUDY OF SYNTHESIS AND PURIFICATION PARAMETERS

Natalia Gomzina, Daria Vaulina, Olga Kuznetsova, Morteza Nasirzadeh

N.P.Bechtereva Institute of the Human Brain, Russian Academy of Sciences (IHB RAS), St. Petersburg, Russia
gomzina@ihb.spb.ru

Positron emission tomography (PET) is an imaging modality that allows in-vivo studies of physiological and biochemical processes on molecular level. Radiolabeled flumazenil analogues are important radiopharmaceuticals for the assessment of the central benzodiazepine receptors (cBZR) density by PET. These receptors play an important role in many neurological and psychiatric disorders, such as epilepsy, panic disorder, dementia, acute stroke, alcoholism. [^{11}C]Flumazenil is a gold standard radioligand for cBZR, however due to the short half-life of carbon-11 (20.4 min) its application is limited by cyclotron-equipped centers.

The fluorine-18 labeled analogue, [^{18}F]flumazenil ([^{18}F]FMZ) presents an advantage due to a longer half-life of radionuclide (109.8 min). Synthesis of [^{18}F]flumazenil by nucleophilic substitution of nitro group of Ro 15-2344 with [^{18}F]fluoride in the presence of phase transfer catalyst (PTC) has been suggested. Using 6-8 mg of labeling precursor provided by Hoffmann La Roche the ^{18}F-incorportaion rate achieved 60 % (DMF, 180 °C, 30 min) [1]. Selective binding of [^{18}F]flumazenil to cBZR in monkey and human brain has been further demonstrated [1,2]. The factors limiting clinical application of [^{18}F]FMZ belong to relatively low ^{18}F incorporation yield using commercially available nitro-precursors and the losses on the HPLC purification and post-formulation steps, both lowering the radioactivity produced. The aim of this study was to investigate ^{18}F-fluorination step under different conditions and suggest the SPE purification method avoiding time-consuming HPLC purification. [^{18}F]Fluoride was produced via ^{18}O (p,n)^{18}F nuclear reaction in [^{18}O]H_2O water target of GE PETtrace cyclotron and synthesis was operated by home-made remote controlled apparatus. [^{18}F]Flumazenil was prepared by heating of 1-4 mg of Ro 15-2344 (Syncom, the Netherlands) in DMF, DMSO or o-DCB at 140-160 °C in the presence of different PTC and bases (kryptofix 2.2.2/K_2CO_3, kryptofix 2.2.2BB/K_2CO_3 or $TBAHCO_3$). The highest incorporation rate of more than 40 % was obtained using kryptofix 2.2.2/K_2CO_3 (DMF, 15 min) and only 1 mg of Ro 15-2344. In the attempted study using combination of different commercially available SPE cartridges/resins and solvents the conditions to separate both radiochemical and chemical impurities have been identified. As a result the principal possibility to replace HPLC purification with more attractive for automated SPE procedure has been demonstrated. At present the substitution of HPLC by suitable SPE approaches can be considered as a milestone for PET radiochemistry Work is now in progress to optimize all the developed procedures.

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RPH-V10, (Id: 438)

PROSPECTIVE CARRIERS OF 223-RA FOR TARGETED ALPHA PARTICLE THERAPY

Jan Kozempel[a], Martin Vlk[a], Ralph Santos-Oliveira[b], Eva Málková[a], Anna Bajzíková[a]

[a] *FJFI CVUT*
[b] *Universidade Estadual da Zona Oeste, Brazil*
jan.kozempel@fjfi.cvut.czmartin.vlk@fjfi.cvut.cz

Targeted alpha particle therapy (TAT) is very powerfull tool against cancer, since DNA double-strand breaks caused by alpha radiation induce cells death. Main advantage of radionuclides decaying by alpha particle cascade in a short-lived chain is the deposition of high energy in very small volume (approx. 27 MeV in the case of 223-Ra). However main disadvantage of such in vivo generator is the release of daughter hot atoms from all chemical bonds. Energy of chemical bond is just several few eV compared to recoil energy of daughter atom that typically ranges to about 100 keV. We report here on basic aspects that have to be addressed in TAT systems and describe our experimens with prospective carriers of 223-Ra intended for bone therapy. Preparation, labelling yelds and in vitro stabilities are given.

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Radiopharmaceutical Chemistry, Labelled Compounds (RPH)

Posters

RPH-P01, (Id: 64)

NUCLEAR-CHEMICAL METHOD – NEW OPPORTUNITIES FOR SYNTHESIS OF UNKNOWN BIOLOGICALLY ACTIVE DIAZINIUM STRUCTURES

Nadezhda Shchepina[a], **Viktor Avrorin**[b], **Gennadii Badun**[c], **Irina Agafonova**[d]

[a]*Head of the laboratory of Radiochemistry*
[b]*Research Scientist St-Petersburg State University, St-Petersburg, Russia*
[c]*Professor Moscow State University, Moscow, Russia*
[d]*Post-graduate student Natural Sciences Institute Perm State University, Russia*
neshchepina@mail.ru

Nuclear-chemical method, based on tritium β-decay in hydrocarbons, gives chemists unique opportunity of carbocations generation. Nucleogenic phenyl cations (cations generated by β-decay) and their further ion-molecular reactions with different nucleophiles have been used previously by us for the preparation of unknown and hardly available biologically active monoazine derivatives [1-5]. 1,4-Diazines and condensed quinoxaline systems are known as an important type of heterocyclic derivatives with high biological activity, they exhibit a wide range of physiological activities including antibacterial, antimycobacterial, antiprotozoal and antitumor. Unfortunately, N-phenyl derivatives of 1,4-diazines haven't been obtained by any methods of classical chemistry yet. We have prolonged the nuclear-chemical method for the synthesis of several new N-phenylsubstituted diazinium derivatives by ion-molecular reactions of the nucleogenic phenyl cations obtained by tritium β-decay in double labeled benzene with unshared electron pair of nitrogen atom of heterocyclic compounds.

Carried out investigations revealed not existed in classic organic chemistry direct phenylation of nitrogen atom in 1,4-diazine substrates and one-step formation of unknown N-phenyl onium derivatives of pyrazine, quinoxaline and 2,3-dimethylquinoxaline.Synthesized compounds may be used as effective tritium labeled biological markers.

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RPH-P02, (Id: 91)

CHARACTERIZATION OF Re/^{99}Tc KYCAR COMPLEXES FOR RADIOPHARMACEUTICALS

Vanessa Sanders[a], **Lynn Francesconi**[b], **Kenneth Czerwinski**[a]

[a]*University of Nevada Las Vegas*
[b]*Hunter College*
vsndrs1@aol.com

Radiopharmaceuticals are very powerful diagnostic tools for evaluation of a host of medical conditions. These drugs are labeled with radioactive isotopes which are utilized to create pictures of areas of interest through absorption of the drug. They are currently in high demand due to their ability to image areas that traditional imaging devices cannot. The main differences between radiopharmaceuticals and other imaging methods are how the tissue in question is imaged and how the information is obtained. The radioisotope ^{99m}Tc, with a half-life of 6.01 hour and a 140 keV gamma emission, is central to many radiopharmaceutical compounds. This isotope is easily obtained from a ^{99}Mo^{-} ^{99m}Tc generator, through beta decay and column chromatography separations. Very little technetium, less than 6 ng, is need to label the pharmaceuticals for use in-vivo. Another radioisotope ^{188}Re is also important due to its ability to be used for therapy while being tracked throughout the body. One of the main reasons there is interest in rhenium pharmaceuticals is the chemical similarity between it and technetium. The ^{188}Re isotope also has a considerably short half–life of approximately 17 hours and has emission energy of 155 KeV. The ^{188}Re isotope is separated from 188W-^{188}Re generator, analogously to the ^{99}Mo^{-} ^{99m}Tc generator.

Radiotherapy gives radiopharmaceuticals a huge advantage by their ability to destroy rapidly growing cells. The ligand used in this work is a pentapepetide macrocyclic ligand. This ligand, also called KYCAR (lysyl-tyrosyl-cystyl-alanyl-arginine), has been designed for the possible application for tumor imaging for breast cancer. Ligands are chosen based on their in-situ biological behavior, and are used in the complexation with technetium and rhenium. Understanding and exploiting technetium and rhenium chemistry can provide insight into the reaction mechanisms and coordination chemistry of these compounds. The exploration of various oxidation states as a function of the ligands used and the reaction conditions can help develop novel radiopharmaceuticals. The investigations of the manipulation of oxidation states have the possible application to simplify the synthesis of the pharmaceutical. The versatility of the oxidation states of these metals leads to numerous possibilities in developing new radiopharmaceuticals. The coordination chemistry and reaction mechanisms must be efficiently characterized to ensure the reproducibility of the radiopharmaceutical. The current study focuses on technetium and rhenium complexes with peptides. These complexes have become increasing interesting for their use in diagnostic and therapeutic radiopharmaceuticals. The characterization of the complexation of Tc(V), and Rh(V) with the pentapeptide KYCAR (lysyl-tyrosyl-cystyl-alanyl-arginine) will be discussed. Complexes will be characterized by High Purity Liquid Chromatography (HPLC), UV-Visible Spectroscopy, Proton NMR, Circular Dichroism (CD), Electrospray Ionization Mass Spectroscopy, Single-crystal x-ray diffraction, and x-ray absorption fine structure spectroscopy, to compare them to current radiopharmaceuticals. Information on the underlying reactions and coordination will be discussed.

RPH-P03, (Id: 97)

ISOLATION OF GENERATOR-PRODUCED ^{223}Ra IN NACL ISOTONIC SOLUTIONS CONTAINING EDTA FOR RADIOTHERAPEUTIC STUDIES

Olga Mokhodoeva, Lidiya Guseva

Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences
olga.mokhodoeva@mail.ru

The short range of α-particles (<100 μm) and high linear energy transfer (LET) in tissue make α-particle emitting radionuclides an ideal tool for targeted radiotherapy of cancer. A number of preclinical and clinical studies have shown the advantages of ^{223}Ra for treatment of bone tumor and skeletal metastases due to its chemical similarity to calcium [1]. Therefore, Ra injected intravenously in isotonic solution is retained in skeletal metastases realizing in vivo generator for short-lived α-emitters of the decay chain:

^{223}Ra(11.4d) α → ^{219}Rn(3.9s) α → ^{215}Po(1.78ms) α → ^{211}Pb(36.1m) β → ^{211}Bi(2.14m) β → ^{211}Po(0.52s) and α → ^{207}Tl(4.77m) β → ^{207}Pb stab.

The first two ultra short-lived α-emitters are formed within four seconds of ^{223}Ra decay and probably rest in the site of mother radionuclide. The more long-lived radionuclides, primary ^{211}Pb and its α-emitting daughters ^{211}Bi/^{211}Po can be escaped from mother vicinity and transferred to another site. Obviously that strong chelating agents, which are able to form stable complexes with all radionuclides of the decay chain, could retain the daughters together with mother radionuclide. Furthermore, the Ra chelates attached to antibody or proteins could be used for targeted radiotherapy or preparation of novel radiopharmaceuticals. The goal of the present work was to determine the conditions for formation of stable Ra/Pb-EDTA complexes in NaCl isotonic solutions using cation-exchange method. ^{223}Ra was produced from ^{227}Ac/^{223}Ra generator developed earlier [2]. We studied in details the cation-exchange behavior of ^{211}Pb and ^{223}Ra in NaCl solutions in dependence on composition of solution, concentration of EDTA, pH and other factors. Optimal conditions for elution of the ^{223}Ra/^{211}Pb EDTA complexes in 0.9 % NaCl solutions were found. More than 90 % of ^{223}Ra can be eluted in a volume 1 mL of NaCl isotonic solution containing 0.05M Na2EDTA at pH = 7-7.5.

A simple and efficient method for isolation of ^{223}Ra in the form suitable for biomedical studies has been developed. The method is adaptable to automation for the routine clinical process, eliminates the need of evaporation of the solutions of high radioactivity that reduce the dangerous radiation to technical staff.

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RPH-P04, (Id: 227)

THE SYNTHESIS OF THE NEW PHOSPHONATES AND STUDY OF THEIR ^{68}Ga COMPLEXES AS THE PROMISING AGENTS FOR BONE IMAGING

Tatyana Khaustova[a], Vladimir Baulin[b], Alesya Maruk[a], Irirna Kalashnikova[b], Valery Ragulin[b], Alexander Bruskin[a], Galina Kodina[a]

[a]Burnasyan FMBC
[b]Institute of Physiologically Active Compounds of the RAS
tanyaha-89@mail.ru

At present a large attention is given to the synthesis and study of new organic compounds as the potential components of bone imaging agents. Phosphonates are promising class of organic compounds for these purposes. Their ^{99m}Tc-based derivates are used for bone imaging with the Single Photon Emission Computed Tomography (SPECT) [1]. Imaging with ^{68}Ga-labeled radiopharmaceuticals have gained growing interest, and they play an increasing role in nuclear medicine.

In this work we developed an original and useful synthetic approaches for the production of phosphonates derivatives of acyclic analogs of crown-ethers-podands [2] (I-II) and new of cyclene derivatives (III-IV). The structures and purity of I-IV were confirmed by the NMR ^{1}H, ^{13}C and ^{31}P spectroscopy and of complexes of phosphonates I-IV were investigated as the promising agents for bone imaging with the Positron Emission Tomography (PET).

Thin layer chromatography (TLC) systems was used for the analysis of ^{68}Ga-labeling reaction products. Two systems were found to be the best. First system comprises silica gel instant TLC (ITLC) plates with the 0.1 M citric acid solution as mobile phase. Second system comprises aluminum backed silica gel plates with the mixture of acetonitrile/water at a ratio of 1:1 as mobile phase. The effect of conditions on the labeling process was studied. The influence of the pH, concentration of the ligand and the reaction temperature on the yield of labeling was examined.

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RPH-P05, (Id: 230)

Ga-68 CITRATE AS PROMISING AGENT FOR PET

Tatyana Khaustova, Maria Zhukova, Alexander Lunev, Anton Larenkov, Alexander Bruskin, Olga Klementieva, Galina Kodina, Ekaterina Lesik

Burnasyan FMBC
tanyaha-89@mail.ru

Ga-67 citrate has large clinical application in imaging of infection and inflammation focal sites using SPECT. For today there is a possibility of creation of its PET-analogue due to commercial availability of Ga-68 generator.

As a consequence, the researches of various scientific and medical centers all around the world were aimed at assessing the suitability of diagnostic Ga-68 citrate for PET imaging of infection and inflammation focal sites. First of all, the composition of lyophilized product was optimized. The content of sodium citrate should correspond to the concentration of 0.08±0.01 M in the final solution of the product (Ga-68 citrate). RPh was prepared by introducing of concentrated and purified eluate (2 mL) of Ge-68/Ga-68 generator (Ga-68 chloride complex solution in 0.1 M HCl) into the vial with lyophilized composition. Then the vial was incubated at room temperature for 10 min.

Another way of RPh preparation was mixing the eluate of Ge-68/Ga-68 generator with an aqueous solution of sodium citrate (the citrate concentration in the final solution was 0.08 M). The radiochemical purity of these RPhs was determined by thin layer chromatography using cellulose (Merck 5574) and silica gel (Merck 5553) on aluminum plate and the mixture of acetonitrile-water (1:1) as a the mobile phase. The value of the radiochemical purity was not less than 90 % in both cases.

Experiments to study the biodistribution of Ga-68 citrate were also carried out. The results showed that the use of transferrin receptor blockade achieves much more acceptable biodistribution results. Studies on pharmaceutical development of this RPh will be continued.

RPH-P06, (Id: 242)

CHROMATOGRAPHIC SEPARATION OF ^{111}In FROM IRRADIATED CADMIUM BY USING AMPHOLYTE CHELEX–100 AND CARBON SORBENT

Aleksandr Zverev[a], **Oleg Andreev**[a], **Galina Kodina**[b]

[a] *Federal Center of Nuclear Medicine Projects Design and Development, Moscow, Russia*
[b] *Burnazyan Federal Medical Biophysical Center, Moscow, Russia*
zverev@fcpr.ru

Early diagnosis of malignant tumors remains one of the urgent problems of the modern medicine. To create a new generation of radiopharmaceuticals on the base of In-111, it is necessary to use solutions with a minimum of chemical and radionuclide impurities. In this context becomes more urgent the search of the new modern sorbents with high affinity for indium and with good kinetic characteristics.

The distribution of carrier-free In-111 between aqueous solutions (chloride – acetate) and chelating ion exchange resin Chelex-100 and also the carbon sorbent SKN-1K, which is used for hemosorption in medicine, was studied in static and dynamic conditions. The dependences of static distribution coefficients of In-111 from the acidity of the solution contacting with sorbent, were determined. It was found for both sorbents that the optimum conditions of sorption were in the range of pH 4-7. The influence of macro amounts of cadmium and flow rate of the solution on the completeness of the radionuclide recovery was studied in dynamic conditions. The modes of subsequent desorption of In-111 with solutions of hydrochloric acid and its purification from the trace amounts of cadmium on the anion exchange resin BioRad AG1x8 were worked-out. The purification coefficient for cadmium was $1{,}5 \times 10^3$.

The results of the investigation indicate the prospects of application of the studied sorbents in radiochemical separation of carrier-free ^{111}In from macro amounts of cadmium and purification of radionuclide from chemical and radionuclide impurities.

RPH-P07, (Id: 270)

SYNTHESIS, RADIOLABELLING, IN VITRO AND VIVO BEHAVIOUR OF TACRINE DERIVATIVES

Ewa Gniazdowska[a], Przemysław Koźmiński[a], Elżbieta Mikiciuk-Olasik[b], Joanna Sikora[b], Paweł Szymański[b]

[a]*Institute of Nuclear Chemistry and Technology*
[b]*Department of Pharmaceutical Chemistry and Drug Analyses, Medical University of Lodz*
e.gniazdowska@ichtj.waw.pl

There are around 36 million people in the world with Alzheimer's disease and up to now here is no cure for this ailment. Alzheimer's disease is the most common form of dementia. One of the drugs used for the treatment of Alzheimer's disease is tacrine - the inhibitor of cholinesterase. The aim of this work was to label with technetium-99m the different analogue of tacrine (containing different number of CH_2 groups in the aliphatic chain, $n = 2 \div 9$) and to select the best one which potentially would be a tool for early diagnosis of Alzheimer's disease.

In the presented work we have synthesized with good yield and purity eight 99mTc-labelling tacrine derivatives. The technetium-99m complex, of type '4+1' used for labelling procedure, contained tetradentate tripodal chelator tris(2-mercaptoethyl)-amine (NS3) and monodentate isocyanide ligand previously coupled with tacrine derivative (CN-tacrine). The synthesized conjugates were isolated from the reaction mixture using semi-preparative HPLC for all physicochemical and biological studies.

The lipophilicity of the conjugates was characterized by the determination of the logarithm of their partition coefficients, log D, in the n-octanol/PBS (pH 7.40) system, which mimics the physiological conditions. Stability of the complexes has been investigated in a function of time, in challenge experiments (by incubation at 37 °C with 10 mM solutions of histidine or cysteine) and in human serum. Biological activity of the conjugate characterized by the highest lipophilicity was estimated by means of Ellman's method and preliminary biodistribution studies done in mice.

All conjugates studied showed high stability in all tests. The following distribution coefficients were determined between 0.92- 1.56 (the average values from three independent measurements) depending on the length of the aliphatic chain. The compound having 7 carbon atoms in the aliphatic chain ($n = 7$) have the highest lipophilicity ($\log D = 1.56$) and satisfactory biological activity (IC50 = 30.4 nM). Biodistribution studies in mice shoved for this conjugate rapid decrease of radioactivity in blood, the clearance mainly through the hepatic route and, unfortunately, relatively low radioactivity concentration in the brain.

RPH-P08, (Id: 345)

COMPLEXATION OF YTTRIUM, LUTETIUM, ACTINIUM AND BISMUTH BY NEW BENZO-DIAZA-CROWN ETHER LIGAND IN AQUEOUS SOLUTIONS

Bayirta Egorova[a], Maxim Oshchepkov[b], Yuri Fedorov[b], Stepan Kalmykov[a], Olga Fedorova[b]

[a]*Lomonosov Moscow state university*
[b]*A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences*
Bayirta Egorova bayirta.egorova@gmail.com Lomonosov Moscow state university a , 1

The complexation of alpha- beta- and Auger- emitting radionuclides is under investigation for the target delivery of them to tumor cells. The search of new effective binding chelating molecules with fast kinetics of complex formation should be carried out among H4DOTA analogs as it is currently used for radiopharmaceuticals. Water soluble new azamacrocyclic compounds show not only thermodynamic affinity for metal cations but also demonstrate very fast complex formation. This work presents complexation study of Y(3+), Lu(3+), Ac(3+) and Bi(3+) by new benzo-diaza-crown ether ligand, L.

Stability constants of ML complexes (M = Y(3+), Lu(3+), Ac(3+) and Bi(3+)) are presented in the table. Potentiometric titration of aqueous solutions of ligand in the absence and presence of cations was performed in water-jacketed titration vessel maintained at 25.0±0.1 °C. The formation of 1:1 ML complex was established. The protonation constants of the ligand L and the stability constants of the complexes were calculated from the electromotive force titration data applying Hyperquad software. Distribution of cation in solution shows than >50 % of M(3+) are bound at pH>6.5. For complexation constant determination with Ac(3+), Bi(3+) and Y(3+) competitive complexation technique was used. Free Ac(3+) and Y(3+) are completely sorbed by cellulose and uncomplexed Bi(3+) is precipitated. Ligand sorption onto cellulose is negligible as determined in separate experiments.

Table. Stability constants of ML complexes determined in the present work and reference data

M(3+) Y(3+) Lu(3+) Ac(3+) Bi(3+)

Reaction L+M(3+) ↔ L(M(3+))

lgK(ML), potentiometrically 5.94(1) 5.87(1) - -

lgK(ML), competitive 6.90(1) - 7.02(2) 10.1(1)

lgK(MDOTA) [1] 24.3 25.5 - 30.3

R (CN6), A [2] 0.900 0.861 1.12 1.03

Addition of M(3+) to aqueous solution of ligand leads to hypsochromic shift of band in UV-vis absorption spectra. This could be the consequence of crown ether-fragment participation in complexation process. The observed spectral change proceeds within 1-2 minutes and is not changing within days that confirm fast complex formation.

Obtained stability constant values are still less than for M-DOTA complexes but complexation rate is quite fast. Larger values of Bi-L complexes are in agreement with M-DOTA complexes. This fact could be associated with smaller coordination number for Bi(3+) than for rare earths. That leads to deeper location of bismuth than yttrium in the cavity formed by carboxylate and macrocyclic oxygens and nitrogens of the ligand while rare earths usually have capping water molecule to complete coordination sphere. Some deviation in stability constants calculated from different methods could be associated with different ionic media: KNO_3, $NaNO_3$ or $NaClO_4$

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RPH-P09, (Id: 361)

CHEMICAL AND BIOLOGICAL STUDIES ON ^{105}Rh-LABELLED TETRATHIOETHERS CONJUGATED TO TATE

Seweryn Krajewski[a], Urszula Karczmarczyk[b], Piotr Garnuszek[b], Wioletta Wojdowska[b], Ewa Laszuk[b], Renata Mikołajczak[b], Marek Pruszyński[a], Aleksander Bilewicz[a]

[a]Institute of Nuclear Chemistry and Technology, Warsaw, Poland
[b]National Centre for Nuclear Research, Świerk, Poland
s.krajewski@ichtj.waw.pl

Objectives: In clinical practice, there is a demand for no-carrier-added radionuclides emitting particles of short range that demonstrate a therapeutic effect on small neoplastic lesions diffuse over a large area of tissue or tumour metastases. Rhodium-105 meets all requirements for application in radionuclide therapy [1] and might be an alternative to ^{177}Lu. Tetrathioether crown complexes with ^{105}Rh have been generally considered as candidates for radiopharmaceutical precursors to be combined with carrier biomolecules. The aims of our work were: (i) synthesis of ^{105}Rh labelled bioconjugates with bifunctional acyclic ($^{333}S_4$diAcOH) and cyclic ($^{16}S_4$COOH) tetrathioether ligands conjugated to [Tyr3]octreotate, (ii) studies of their properties and (iii) conduction of in vitro experiments on cell line AR42J.

Methods: Rhodium-105 was obtained by neutron activation of ruthenium salt, $(NH_4)2[Ru(H_2O)Cl_5]$, for 8 h with flux of $7 \cdot 10^{13}$ $n \cdot cm^{-2} \cdot s^{-1}$ in the Maria reactor in Świerk, Poland. 105Rh was separated from the ruthenium target material by method described previously [2]. Acyclic ligand was synthesised through 1,5,9,13-tetrathiatridecane intermediate and 16S4COOH by method previously described [3]. The ligands were combined with N-hydroxysuccinimide to obtain active esters, which were subsequently conjugated with N-terminus of TATE. The respective products were isolated and analyzed by MS, NMR and elemental analysis.

Results: The bifunctional ligands were synthesized with total reaction yield of 21 % and 1 % for 333S4diAcOH and $^{16}S_4$COOH, respectively. The active esters and bioconjugates were obtained in high yield. The last step of synthesis was cleavage of Dde protecting group from Lys.

The complex $[RhCl_2(^{16}S_4COTATE)]^+$ was obtained as reference material for HPLC. The bioconjugates were labelled with ^{105}Rh, their distribution coefficients were measured. For bioconjugate $[^{105}Rh(^{16}S_4COTATE)]$+, the stability in PBS, Cys, GSH and human serum was examined, and the kinetics of internalization into AR42J cells was set.

Conclusions: The use of 105Rh-labelled tetrathioether precursors conjugated to peptides in radionuclide therapy seems possible, but requires further biological studies. Good stability of ^{105}Rh-labelled bioconjugate $^{16}S_4$COTATE in human serum with a high degree of its internalization meet the requirements for potential receptor radiopharmaceuticals.

Research Support: The work has been carried out within the system project “The scientific potential as support to the economy of Mazovia - scholarships for doctoral students” under Sub-measure 8.2.2 Human Capital Operational Programme 2007-2013.

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RPH-P10, (Id: 414)

SYNTHESIS OF INDOLE-3-ACETIC ACID DERIVATIVES FOR SELECTIVE TRITIATION.

Martin Vlk[a], Libor Havlíček[b], Bohuslav Černý[b]

[a]*Department of Nuclear Chemistry, Faculty of Nuclear Sciences and Physical Engineering, CTU Prague*
[b]*Isotope Laboratory, Institute of Experimental Botany AS CR, v.v.i., Vídeňská 1083, 142 20 Prague 4*
martin.vlk@fjfi.cvut.cz

Series of indole-3-acetic acid derivatives substituted in the benzene ring belongs to the natural plant growth hormone – auxines, with interesting biological activities (e.g. specific antigen stimulation in atopic allergic disease by interleukin 4 and 5). They have recently been made via Fisher ring closure of the succin-aldehydic acid phenylhydrazones obtained from glutamic acid or direct method where intermediate phenylhydrazones cary out the cyclization in one step employing corresponding acetals (e.g. ethyl γ,γ-dimethoxybutyrate) as a starting material. Herein, synthesis of indole-3-acetic acid derivatives and its labeled analogues was described via cyclization of substituted phenylhydrazine with methyl 4,4-dimethoxybutyrate in two step: the first is addition of acetal on phenylhydrazine in acetic acid the second is intramolecular cyclization of intermediate in ethanol catalyzed by addition of concentrated sulphuric acid. Both steps were also carried out in microwave reactor with focused power. Obtained esters were hydrolyzed and optimal conditions of dehalogenation were studied. Conditions for selective deuteration/tritiation were studied. All prepared compound were characterized by spectral data.

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RPH-P11, (Id: 418)

BIOLOGICALLY DEGRADABLE LABELLED ESTERS OF TRITERPENIC ACIDS

Petra Mičolová[a], Martin Vlk[a], Jan Šarek[b], Tomáš Elbert[c], Marián Hajdúch[d]

[a]*Department of Nuclear Chemistry, Faculty of Nuclear Science and Physical Engineering, Czech Technical University, Brehova 7, 115 19 Prague 1, Czech Republic*
[b]*Department of Organic Chemistry, IMTM, Faculty of Science, Palacky University in Olomouc, 17. listopadu 1192/12, 771 46 Olomouc, Czech Republic*
[c]*Institute of Organic Chemistry and Biochemistry, Academy of Science, Flemingovo n. 2, 116 10 Prague 6, Czech Republic*
[d]*IMTM, Faculty of Medicine and Dentistry, Palacky Univerzity in Olomouc, Hnevotinska 5, 779 00 Olomouc, Czech Republic*
micolova.petra@gmail.com

Triterpenes are natural substances obtained by isolation from common species of plants and fruits. Together with its semisynthetic derivatives, have different biological effects such as analgesic, antibacterial, antiosteoporotic, antihypertensive, antimicrobial, diuretic, antiviral, hepatoprotective, anti-inflammatory or a wide range of antitumor activities.

From this perspective are interesting lupane, oleanane, ursane and taraxastane derivatives. The well-known representatives of these compounds are betulin and betulinic acid. In order to increase the cytotoxic activity and retain good chemical and pharmacological properties of these compounds were prepared their esters. As most beneficial appears acetoxymethyl-esteric group because the cytotoxic activity of these compounds is comparable or even higher than the starting acid. For these reasons could be acetoxymethyl esters suitable prodrug and suitable candidates for the selective labelling.[1]

In this work were selective labelled acetoxymethylesters of oleanolic, ursolic, morolic and heterobetulinic acids. For this labelling were used hydrogen isotopes and was accomplished by reduction of ketones of previously prepared acetoxymethylesters using NaB$[^2H]_4$ or NaB$[^3H]_4$.[2]

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RPH-P12, (Id: 419)

LABELLED ESTERS OF CYTOTOXIC TRITERPENES

Martin Vlk[a], Petra Micolova[a], Milan Urban[b], Jan Šarek[b]

[a]Department of Nuclear Chemistry, Faculty of Nuclear Sciences and Physical Engineering, CTU Prague
[b]Department of Organic Chemistry, IMTM, Faculty of Science, Palacky University in Olomouc
martin.vlk@fjfi.cvut.cz

Natural triterpenoids together with their semisynthetic derivatives form basis for extensive medicinal research, because they have shown various biological activities [1], e.g.: antineoplastic, antiviral, anti-inflammatory, antimicrobial activities, hepato- and cardioprotective effects; and reveal a great potential for pharmaceutical applications when their cytotoxic and anti-HIV activities were described [1,2,3]. Betulinines, as we named the group of semisynthetic derivatives, have proved multispectral cytotoxic activity on the panel of several cell tumor lines of different histogenetical origin, including multidrug resistance [1,2,3]. One of our leading compoud 3β,28-diacetoxy-18-oxo-19,20,21,29,30-pentanorlupan-22-oic acid fast and selective apoptosis of tumor cells [3], comparable to conventional anticancer drugs – paclitaxel.

Synthesis of various esters of active triterpenic acids has been described previously to improve cytotoxicity and PK parametres. Group of methyl, ethyl, acetoxymethyl, pivaloyloxymethyl and benzyl esters were described and their cytotoxicity has been studied in vitro. Selectively labelled analogues of the most cytotoxic active compounds are used for the investigation of mechanism of action and binding interactions. As a standard for mass spectroscopy together 33 deuterated and C-13 labelled methyl esters were synthesized and fully characterized by spectral data.

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RPH-P13, (Id: 421)

SYNTHESIS OF COMPLEXES BASED ON PLATINUM

Ekaterina Kukleva[a], Nikolay Aksenov[b], Jan Kozempel[a], Martin Vlk[a]

[a]Czech Technical University in Prague, Faculty of Nuclear Sciences and Physical Engineering
[b]Radiochemistry Lab, Flerov Lab of Nuclear Reactions Joint Institute for Nuclear Research, Dubna, Russia
kate.kukleva@gmail.com

Main aim of this study was the revision of the synthetic methods of cisplatin, or cis-diamminedichloroplatinum(II) with an outlook to the preparation of 195mPt-labelled complex. [1]

Historically it was the first member of platinum-containing cytostatic drug. Nowadays carboplatin and oxaliplatin are also being used as the non-specific anticancer drugs. Cisplatin reacts with nitrogen in purine and pyrimidine bases of DNA molecule, what causes the inhibition of cell division and leads to apoptosis. Cisplatin is used widely especially in the combination with other drugs in the treatment of testicular cancer, ovaria cancer, bladder cancer, breast cancer, osteosarcoma etc. Since cisplatin acts non-specifically its use is universal, however it has several drawbacks and side effects such as nephrotoxicity and sickness. [1]

Chemically cisplatin is not very stable compound. It is less stable than carboplatin and hydrolyzes in aqueous solutions. This can be inhibited by adding excess chloride ions. Also transformation from cis to trans isomer is possible due to light sensitivity. The trans isomer has mutagenic properties. [1-4]

Several articles with detailed synthesis description were found. There are two methods of synthesis and both methods were examined. However only one of them was successful. In the future this method will be used in synthesis of cisplatin and other platinum complexes with radioactive Pt-195m, which can increase cancer toxicity of studied drugs. [2-5]

The key step in the synthesis of all platinum complexes is the reduction of Pt(IV) to Pt(II), which can be made e.g. with hydrazine in aqueous solution of chloroplatinic acid (H_2PtCl_6) [2-4]. Main reactant for following reactions is potassium tertachloroplatinate (K_2PtCl_4) obtained after reduction. Based on this compound any other platinum complexes can be easily prepared. For cisplatin synthesis ammonia solution was used. Difference between two methods is in substitution step. To increase the yield of the cis isomer chloride ion can be replaced by iodide. Next step is to substitute iodide ions with ammonia. After that iodide should be replaced by chloride by adding silver nitrate. Silver iodide precipitate can however cause contamination of the product. [2,4]

Another method eliminates the step with chloride replacement, but cis and trans isomers are obtained after adding of ammonia solution. This isomers can be successfully separated, because of different solubility of cis and trans isomers in 0.1M hydrochloric acid.[3] The second method for synthesis was successful. Structure analysis of obtained product was performed by MS spectrometry. Yields of this synthesis was not satisfactory, mainly because of problematic reduction of Pt(IV). Platinum(II) is unstable compared to metallic platinum and platinum(IV). The reduction step is being optimized. Obtained yield was 35 %, what is smaller than published results of 43 % [2], 95 % [3] and 50 % [4], but the work was made with micro amounts of platinum (about 20 mg), what made synthesis more complicated.

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RPH-P14, (Id: 452)

MICROFLUIDS SYSTEMS FOR RADIOFHARMACEUTICALS

Daniel Seifert, Ondřej Lebeda

Nuclear Physics Institute of CAS
Department of Radiopharmaceuticals, Czech Republic
Seifert@ujf.cas.cz

In the last two decades, microfluidics and lab-on-a-chip (LOC) technologies have emerged as powerful tool in organic chemistry. It shows characteristics like enhanced heat and mass transfer, reduction of reagent consumption, hazardous waste and shortening reaction time. Some of them are potentially very favourable also for radiopharmaceutical chemistry, and, indeed, their applications in preparing labelled compounds have been attracting more and more attention [1-5].

Our project supported by the Technology agency of the Czech Republic (no. TA02010797) is focused on development of PMMA chip and operational platform denoted as AMfS (Automated Microfluidic System). The PMMA chip is designed as multi-port inlet and outlet unit consisting of pre-mass heating, channels, mixers and separation layer. The objects placed on the PMMA chip are of micrometre dimensions. Fabrication structures of such dimensions can be achieved by various methods. We have investigated two of them: the Ion beam writing and CNC machine engraving. The latter method allow for easy production of structures on the area of several square centimeters with channels of 100–1000 µm width and of 10–100 µm depth. The former method using ion beam writing results in structures located on smaller area of units or of tens of square millimetres, while channel width and depth can be as low as 5 µm. The AMfS is a sort of “infrastructure” for operation variable chips consisted of pumps, injectors, selectors and chip manifold. The whole system can be operated up to 40 bars pressure, however, the PMMA chip and manifold is designed and tested for operational pressure of more than 125 bars. Flow-rate can be set in a wide range (units of µl to units of ml per minute). The final goal is to provide new versatile microfluidic system for radiopharmaceutical research and development.

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Education / Coordination (EDU)

Verbal presentations

EDU-I01, (Id: 428)

COOPERATION IN EDUCATION AND TRAINING IN NUCLEAR- AND RADIOCHEMISTRY IN EUROPE

Jan John

CTU in Prague, FNSPE, Department of Nuclear Chemistry
jan.john@fjfi.cvut.cz

Any of the potential options for the nuclear power – both the renaissance, if any, or the phase out – will require significant numbers of the respective specialists, amongst others the nuclear and/or radiochemists. In parallel, a significant demand exists for these specialists in non-energy fields, such as environmental protection, radiopharmacy, nuclear medicine, biology, authorities, etc. Since the numbers of staff in teaching and the number of universities with facilities licensed for the work with open sources of ionizing radiation has decreased on or sometimes even below the critical level, coordination and collaboration are required to maintain the necessary teaching and training capabilities.

In this paper, the motivation, history and status of coordination of education and training in nuclear- and radiochemistry in Europe will be reviewed and correlated to similar activities in other nuclear fields such as the nuclear engineering of radiological protection. The achievements of the Euratom FP7 project "Cooperation In education in Nuclear CHemistry (CINCH)" will be described in detail. This description will cover both the status review and the development activities of this Collaboration. The proposed long term sustainable strategy for nuclear- and radiochemistry education in Europe will be presented. Its main aim is to create conditions for coordination of the current fragmented and diverse activities in both the education and training field at both the Ph.D. and undergraduate levels. In the education field, the aim is to introduce the EuroMaster in Nuclear and- Radiochemistry quality label recognized and guaranteed by EuCheMS - European Association for Chemical and Molecular Sciences. In the training field formation of a long-term Euratom Fission Training Scheme (EFTS) is the ultimate goal that should ensure availability and quality of the training in this field. These measures are currently under development in a follow-on Euratom FP7 project "Cooperation In education and training in Nuclear CHemistry (CINCH-II)". They are hoped to contribute to moving the education and training in nuclear chemistry to a steady and qualitatively new level.

EDU-I02, (Id: 400)

EUROMASTER DEGREE IN NUCLEAR AND RADIOCHEMISTRY

Jukka Lehto

Laboratory of Radiochemistry, Department of Chemistry, University of Helsinki
jukka.lehto@helsinki.fi

The first EU project CINCH (Cooperation in education in nuclear chemistry) 2010-2013 was planning the Euromaster degree in nuclear and radiochemistry. The second CINCH project 2013-2016 will implement the degree. According to present plans a consortium of European universities will apply for the NRC Euromaster label from the European Chemistry Thematic Network (ECTN) which is the body granting Euromaster status labels. The consortium is open for all European universities and those universities not participating in the application can join the consortium at a later phase. The educational content of the common NRC Euromaster degree will be based on the minimum requirements planned out in the first CINCH project (see http://cinch-project.eu/). According to this plan a master's program eligible to NRC Euromaster label should have at least 50 % (60 cu) of its master's studies on nuclear and radiochemistry. Of this 60 credit units at least 10 credit units should be practical exercises and at least 30 credit units should comprise of master's thesis and project work. The educational program should cover most relevant aspects from the following five topic areas

- Radioactivity, radionuclides and radiation
- Radiation safety
- Detection and measurement of radiation
- Chemistry and analysis of radionuclides
- Nuclear reactions and production of radionuclides

According to ECTN requirements the content of the educational programs in the NRC Euromaster consortium should be similar. Exchange of students between partner universities and organization of common courses, such as summer schools, would be required as well.

EDU-I03, (Id: 434)

CURRENT STATUS OF NUCLEAR AND RADIOCHEMISTRY EDUCATION IN EUROPE

Teija Koivula, Jukka Lehto

teija.s.koivula@helsinki.fi

Cooperation in education and training In Nuclear Chemistry - CINCH-II project - aims at coordination of education and training schemes in nuclear and radiochemistry (NRC). One of the specific objectives of the project is therefore to identify the current level of NRC education in Europe. Surveying universities and various educational programmes was started under CINCH-I during the years 2010-2011. Results were published in a report “Nuclear and radiochemistry curricula in the European universities” and a list of contact information to the universities/departments that were included in the study (http://www.cinch-project.eu/); altogether 69 universities in 22 countries participated in this survey. The results showed diversity of the NRC education in Europe. At BSc level NRC is mainly taught in basic courses under various educational programmes such as chemistry or environmental sciences. There are only few complete programmes, i.e. BSc/MSc degrees in NRC; however, education in the same extent can be attained in various specializations under e.g. the degrees MSc in Chemistry or Chemical/Environmental engineering. Majority of these specializations are general NRC, one large specified topic is environmental radiochemistry/radioecology. Research training and diploma work have a strong role in specialization; however, the extent of specialization varies significantly in different educational systems. Furthermore, some countries/universities are only on their way to accreditation of the Bologna system. Curriculum in NRC typically reflects research interests of the department. Many universities have high level of research and offer possibility to do PhD-work in NRC related fields but have only limited education at lower level(s). Collaboration between universities and industry/research units brings education and training closer to each other and also effects development of the academic programmes. To have an up-to-date view on the current status of the education in NRC the survey is now continued under the CINCH-II project. Universities/departments already included in the first report are therefore asked (via their contact persons) to update relevant information on their unit, especially concerning changes in the curricula and focus of education in NRC. Other interested units can join the survey by sending free-form e-mail or by answering short questions in a questionnaire on the project web page. CINCH project partners will also contribute on the current situation in their respective countries. Perspectives on the current status of NRC education in Europe will be presented in this talk. Report from the overall survey will be published on the project web page by the end of 2015.

EDU-I04, (Id: 430)

NUCWIK - NUCLEAR AND RADIOCHEMISTRY TEACHING MATERIAL WiKi

Jon Petter Omtvedt, Hans V. Lerum

University of Oslo, Department of Chemistry
j.p.omtvedt@kjemi.uio.no

An open access database, implemented as a "Wiki" (same technology as e.g. used by Wikipedia [1]) was set up to enable university teachers and others to share teaching material and experiences. The basic idea is that teachers and institutions will share and co-develop teaching material for Nuclear and Radiochemistry use, in particular calculation and laboratory exercises. Furthermore, the Wiki – named NucWik [2] – is an ideal place for sharing experiences and discussing how to improve the material further. In this way a lot of work can be saved when setting up a new exercise or course: If someone already developed something similar it can either be directly used or at least provide a very good starting point for a local implementation. It should be made clear that

NucWik is not a site intended to be directly used by students. Instead, teachers use it to put together material for their teaching. As a long-term goal we also intend to put together a complete Radiochemistry course book, which will be freely available from NucWik. NucWik was created as part of the CINCH [3] EU-project, headed by Prof. Jan John, with a goal to strengthen training and education in nuclear and radiochemistry in Europe. However, the NucWik service is freely available for everybody, regardless if they are outside or inside Europe.

For any Wiki to be successful, including NucWik, it heavily depends on user participation. Thus, we strongly urge teachers to actively contribute with material and input to discussions. Currently (April 2014) only a limited amount of material has been uploaded, primarily to demonstrate NucWik's potential and encourage teachers to contribute.

An important issue with any database or wiki where material can be freely uploaded is quality control. For NucWik this is addressed by implementing a quality control system where we differentiate between documents that has been simply uploaded and those that have been "peer reviewed". Peer reviewed documents have been review by two independent scientists from a group appointed by the CINCH consortium. Such documents will be stamped with "CINCH approved" and cannot be edited (without undergoing another peer review). In this way NucWik will provide an easy and quick way to share and co-develop documents, but also include mechanisms to ensure that trustworthy and scientifically sound material can be downloaded with confidence.

At RadChem'2014 possible uses of NucWik will be demonstrated and its potential as a site for active teaching collaboration highlighted. Discussion of and ideas for possible use and future development will be welcomed both after the presentation and later.

[1] Wikipedia® is a registered trademark of the Wikimedia Foundation, Inc., a non-profit organization. Access is through http://wikipedia.org.
[2] http://nucwik.wikispaces.com
[3] CINCH – "Cooperation in Education and Training in Nuclear Chemistry" is a FP7 EU-funded coordinated action supported by the European Atomic Energy Community's 7th Framework Program (EURATOM FP7 2007-2011) under grant agreement No. 605173, see http://cinch-project.eu for details.

EDU-V05, (Id: 363)

RADIOCHEMISTRY EDUCATION: COMBINING FUNDAMENTAL AND APPLIED STUDIES

Kenneth Czerwinski

University of Nevada, Las Vegas
czerwin2@unlv.nevada.edu

Technetium and the actinides are radioelements of importance to the nuclear fuel cycle. Compounds composed of these elements are used in nuclear fuel, separations, safeguard applications, and isotope utilization. These radioelements also represent an underexplored section of the periodic table. Studies on compounds with technetium and the actinides provide opportunities to expand basic chemical knowledge, particularly when coupled with computational studies. Performing experiments with these elements requires specialized facilities and radiochemical expertise. The training of students and scientific rewards for examining this relatively unexplored area of the periodic table are worth the intrinsic difficulties associated with experiments using these elements. The radiochemistry program at the University of Nevada, Las Vegas is described, with emphasis given to the facilities, education mission, and collaborations. The linkage of the UNLV radiochemistry program with DOE and international research efforts is presented. Examples are provided on separations, fuel synthesis, and waste form studies. The incorporation of internet lectures with a laboratory intensive program for undergraduates is also described. The undergraduate program has been demonstrated as an effective pipeline for student recruitment to graduate programs.

Education / Coordination (EDU)

Posters

EDU-P01, (Id: 14)

PRACTICAL EXPERIENCE IN THE SCIENTIFIC AND EDUCATIONAL ACTIVITIES OF RADIOACTIVE WASTE MANAGEMENT AT FSUE "RADON"

Olga Gorbunova, Olga Karlina, Elena Diordii, Irina Semenova, Aneliya Vitanova

FSUE "RADON"
olg-gorbunova@yandex.ru

Federal State Unitary Enterprise (FSUE) "RADON" is a multifunctional scientific-industrial complex, meeting the international standards of Quality Management System ISO 9001 and Environmental Management Systems 14001. More than 50 years, the enterprise successfully carries out the entire technological complex of services on radiation monitoring, decontamination of contaminated areas, collection, transportation, processing, conditioning, long-term storage (disposal) of radioactive waste of low and intermediate level of radioactivity, and the safety assurance of near-surface storage of radioactive waste. FSUE "Radon" has a unique research-industrial, industrial, experimental and laboratory equipment to carry out education as training courses on the technological processes, covering all stages of radioactive waste treatment The value of the technological support of the educational process in FSUE "RADON" is in the continuous improvement of the equipment and technology in the center of Research and Development, and in the scientific development and implementation of new methods and devices. It is not less important that the lectures and practical sessions involved staff members of the FSUE "RADON", and as a rule, they are developers representing the technologies and authors of the regulations, procedures, patents. In the late 90's under the IAEA guidance on the basis of the Scientific and Production complex of the enterprise «RADON» in Sergiev Posad Moscow region was established an inter-regional Educational Center for training specialists from Eastern Europe and former CIS countries in the field of radioactive waste treatment. With time the "geography" of students has been extended, and for 20 years of research and technical training, theoretical and practical training courses took place more than 500 specialists. The IAEA representatives put forward the requirements for the organization of courses, which includes defined themes, visa support, transport services, accommodation, food and cultural program. Our Educational and Training Center perfectly meet these requirements, what brought us the reputation of a reliable partner and a wealth of experience in organizing large-scale multidisciplinary educational activities. The FSUE "RADON" holds scientific and practical training for the employees working in the nuclear industry of Russia, as well as training for improving the skills of their own staff and for adaptation of the young professionals to the specifics of the production. Adaptive introductory courses not directly associated with the processing of radioactive waste are held for the personnel. They include a tour to the technological installations and storage of radioactive waste and lectures by leading experts on technology of radioactive waste treatment. Over the past decade, the company has managed to reach the leading positions in the country in the field of radioactive waste treatment. Today, the FSUE "RADON" is a competence center of the State Corporation "ROSATOM" in the field of radioactive waste management, with a high level team of specialists, including 11 doctors and 65 candidates of science. The specialists of the company are actively engaged as experts for solving various technical problems and expertise of international projects. Having a unique research and industrial complex and high-level specialists, the FSUE "Radon" successfully performs the task of advanced training and professional retraining of domestic industry specialists and foreign students.

EDU-P02, (Id: 80)

A LABORATORY EXERCISE ON SYSTEMATIC EFFECTS IN GAMMA SPECTROMETRY

Henrik Ramebäck[a], Sofia Jonsson[b], Stefan Allard[c], Christican Ekberg[c], Tim Vidmar[d]

[a]Swedish Defence Research Agency, FOI, division of CBRN Defence and Security, SE-901 82 Umeå, Sweden
[b]Chalmers University of Technology, Department of Chemical and Biological Engineering, Nuclear Chemistry, SE-412 96 Göteborg, Sweden
[d]SCK-CEN, Belgian Nuclear Research Centre, Boeretang 200, ^{240}0 Mol, Belgium
henrik.ramebeck@foi.se

High resolution gamma spectrometry is a powerful method for the measurement of gamma emitting radionuclides. It requires most often only a minimum of sample pre-treatment. Moreover, gamma spectrometry is often considered as a transparent measurement method and is for that reason well understood by the users. However, often sample density and composition is different compared to standards used for the calibration of the measurement system. Another example of deviations between the calibration standard and the sample is when the sample container not can be filled to the same volume as the standard. Moreover, measurement of radionuclides emitting gamma photons in cascade, such as 134Cs, will suffer from true coincidence summing (TCS) effects when the samples are measured close to the detector. These systematic effects will often be significant, and have therefore to be corrected.

Everyday users of gamma spectrometry, at measurement laboratories such as within the nuclear industry, might be aware of these situations causing systematic effects and therefore deviations in the measurement results. However, methods for the correction of systematic effects are still rarely implemented in routine laboratories. One attempt to improve this situation was to develop a laboratory exercise for students in a master's course in nuclear chemistry. A spectrum containing peaks from ^{137}Cs and ^{134}Cs with an activity ratio of one was given to the students. The task comprised to evaluate the spectrum with respect to activity of the two radionuclides as well as their activity ratio. First this was done without correction. With the use of a program, EFFTRAN, for calculation of e.g. efficiency transfer factors and correction factors for true coincidence summing effects (TCS), the students could thereafter calculate the corrected activity of ^{134}Cs as well the corrected activity ratio. Moreover, the effect of sample-to-endcap distance on TCS was also evaluated. A third and last task in the exercise was to perform efficiency transfer for cases when volume differed between calibration standard and sample. The use of a calculation program, such as EFFTRAN, enables to illustrate the impact from the systematic effects on measurements with gamma spectrometry. The programs also allow the students to gain a deeper understanding regarding which parameters has the greatest influence on different effects and in which energy regions.

EDU-P03, (Id: 239)

RADIOCHEMISTRY COURSES IN THE NUCLEAR SCIENCE PROGRAM AT UNIVERSITI KEBANGSAAN MALAYSIA

Sukiman Sarmani[a], R. B Yahya[b], M. S Yasir[a], I. A Rahman[a], K. S Khoo[a]

[a]*National University of Malaysia*
[b]*national University of Malaysia*
sukiman@ukm.my

Universiti Kebangsaan Malaysia (UKM)also known as the National University of Malaysia offered an undergraduate and postgraduate degree programmes in Nuclear Science since 1983. The program has undergone several modifications due to changes in national policy and priority. The program covers nuclear sub-disciplines such as nuclear physic, radiobiology, radiochemistry, radiation chemistry and radiation safety. To graduate with a Bachelor of Science in Nuclear Science students are required to pass a total of at least 120 credits comprising of 20 credits of university courses and 100 credits of compulsory courses or core courses and electives. The radiochemistry component of the programme consists of radiochemistry, chemistry in nuclear industry, radiochemical analysis laboratory, radiopharmaceutical chemistry, and mini research project in radiochemistry. The radiochemistry components of the graduate programme cover specific topics on radiochemical separation, radioactive waste management, transuranium chemistry and environmental radioactivity. Radiochemistry research projects for PhD or MSc degrees include development of radiochemical neutron activation analysis, application of neutron activation, radioisotope production and radiopharmaceutical synthesis.

EDU-P04, (Id: 424)

NUCLEAR CHEMISTRY IN THE CENTRAL EUROPEAN ENERGY INSTITUTE

Katerina Cubova

Department of Nuclear Chemistry, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University, 115 19 Prague, Czech Republic
katerina.cubova@fjfi.cvut.cz

The lack of the technically educated specialists is the problem concerning the whole Europe. The problem is strongly felt in the field of nuclear power engineering. There are for two main reasons responsible for the current situation. The first is lack of interest of the potential students in the study in technical fields. The second one is the long term problem related to the generation exchange of the specialists. Taking into account the problems mentioned, Czech technical universities decided to establish a Central European Energy Institute which is aiming at providing a sustainable, interdisciplinary and practical teaching programme for highly educated specialists in nuclear power engineering. Such concept is supported in the framework of Operation Programme Education for Competitiveness supported by the Czech Ministry of Education Youth and Sports. Key activity of the project is to ensure the innovation of the nuclear power engineering study programmes in all three levels (Bc, MSc and PhD study programme) including formation of new educational materials and introduction of E-learning system. An integral part of the educational programmes of the Institute will be curriculum in nuclear chemistry. It will aim to give the students – future engineers – indispensable radiochemical background with the emphasis on the chemistry of operation of nuclear power plants, technology of the fuel cycle of nuclear power stations and the waste management and treatment.

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