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Determination of ^{93}Zr in nuclear power plant wastes

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Abstract

A radioanalytical method (based on separation using UTEVA columns and ICP-MS measurement) has been used for determination of ^{93}Zr in 37 nuclear power plant samples. As ^{93}Nb might affect the detection of ^{93}Zr, Monte Carlo activation model was used to calculate the expected ^{93}Zr/^{nat}Zr mass ratio, which was compared to measured ones. It was found, that a decontamination factor of 10^3 is sufficient to get a measurement uncertainty of less than 10%.

Keywords

^{93}Zr, nuclear power plant waste, UTEVA, ICP-MS, Monte Carlo simulation, LSC

Introduction

^{93}Zr is one of the few radionuclides (among other isotopes of Zr as well as those of Nb and Sn) that are produced in nuclear power plants (NPP) by two processes: nuclear fission of nuclear fuel (by ca. 6.3% yield from ^{235}U) and neutron activation of structural components (from stable ^{92}Zr). This is why it is very difficult to predict its activity concentration in NPP wastes. According to most recent reports, its half-life is $(1.13 \pm 0.11) \times 10^6$ years [1] or $(1.64 \pm 0.06) \times 10^6$ years [2]. Due to its long half-life, after 1000 years it is the second significant contributor (after ^{99}Tc) to the fission products activity of NPP wastes [2].

It is a pure β^--emitter ($E_{\beta,\text{max}} = 60$ keV [3]), and can be detected via β-radiation by liquid scintillation counting (LSC) or directly by MS (nowadays exclusively by inductively coupled plasma mass spectrometry, ICP-MS). When measuring it by LSC, complete separation from β-emitting and X-ray emitting radionuclides (e.g. ^{3}H, ^{14}C, ^{54}Mn, ^{55}Fe, ^{60}Co, ^{63}Ni, ^{65}Zn, ^{90}Sr, ^{90}Y, ^{93m}Nb, ^{94}Nb, ^{93}Mo, ^{133}Ba, ^{137}Cs, ^{152}Eu, ^{239}Np, ^{241}Pu) is necessary [4]. When measuring it by ICP-MS, isobaric (^{93}Nb, ^{93m}Nb and ^{93}Mo) and polyatomic (e.g., ^{92}Zr^{1}H) interferences as well as abundance sensitivity affect the results [5, 6]. Among these, the isobaric interference due to ^{93}Nb is critical, as Nb is always present in NPP wastes as component of Zr-Nb alloys, and ^{93}Nb is its only natural isotope.

Separation methods of ^{93}Zr

The chemical separation prior to measurement of ^{93}Zr can be based on liquid-liquid extraction, ion exchange or extraction chromatography.

A typical chelating agent used in these liquid-liquid extraction procedures is 1-(2'-thenoyl)-3,3,3-trifluoroacetone (TTA or HTTA). The method described by Remenec [7] is based on extraction from 2 M HNO_3 using 0.5 M TTA and re-extraction of Zr with 2 M HF. Espartero et al. [4] performed extraction from 4 M HCl / 1 M $AlCl_3$ using 0.50 M TTA in p-xylene and re-extraction of Zr with 0.25 M HNO_3 / 0.25 M HF. Using this method, the recovery of Zr achieved 80% and the separation factor of ^{94}Nb exceeded 99.987%. (The latter corresponds to a decontamination factor ($DF = A_{\text{initial}}/A_{\text{final}}$) of 7692.) Another possible reagent for liquid-liquid extraction of Zr is (2E)-2-hydroxyimino-1,2-di(phenyl)ethanol (aka α-benzoinoxime, ABO) [8].

These methods are sometimes combined with pre-concentration steps, such as formation of $BaZrF_6$ or ZrO_2*nH_2O precipitates [6, 7].

Dulanská et al. [9, 10] used a combination of ion exchange columns to separate Zr. Sample was loaded onto a cation exchanger in 0.5 M HF and column was washed with 0.5 M HF. The eluate was loaded onto an anion exchange resin and it was washed with 0.5 M HF. Zr was eluted with 11.3 M HCl / 0.0575 M HF, recoveries over 76.7 % were achieved and "no contamination from ^{94}Nb" was observed. (Unfortunately no exact DF was reported.)

As of extraction chromatographic materials, Zr has affinity for phosphoric acid derivatives such as bis(2-ethylhexyl) hydrogen phosphate (HDEHP), phosphine oxides (e. g. trioctyl phosphine oxide, TOPO) and tributyl phosphate (TBP) [11]. Excoffier et al. [5] used a resin impregnated with TBP as extraction chromatographic material. Load solution was 7 M HNO_3 and Zr was eluted with 0.3 M HNO_3. Recovery was 60%, Nb contamination was <0.1%.

Bombard [8] combined the liquid-liquid extraction developed by Espartero et al. [4] with separation on TEVA column (extraction chromatographic resin that contains trioctyl methyl ammonium chloride, manufactured by TrisKem International). Column was conditioned with 8 M $LiNO_3$ / 0.01 M HNO_3, load solution was 9 M HCl. Zr fraction (which was eluted with H_2O) was contaminated by 0.17% of Nb and 0.094% of Mo. (These correspond to DFs of 588 and 1064, respectively.)

Shimada [12] used TEVA column for separation of Zr, Mo and Nb. Sample in 0.1 M or 0.01 M HF was loaded, then column was washed with HF of the same concentration. Zr was eluted with 0.5 M HF / 7 M HCl, Mo with 4 M HF, and Nb with 1 M HNO_3. According to the author, the influence of ^{93}Mo and ^{93}Nb on the ICP-MS measurement of ^{93}Zr was excluded.

Oliveira et al. [13, 14] tested a procedure combining ion exchange chromatography on Dowex resin, liquid-liquid extraction using TTA and extraction chromatography on TRU resin (which contains octylphenyl N,N'-di-isobutyl carbamoyl phosphine oxide, CMPO and TBP, manufactured by TrisKem International). Sample was loaded onto Dowex ion exchange column in 9 M HNO_3 and column was washed with 9 M HNO_3, then the liquid-liquid extraction developed by Espartero at al. [4] was performed. Load solution of TRU column was 4 M HCl, and column was washed with 2 M HCl. As of the whole procedure, ~68% recovery of Zr and ~99% separation factor of Nb were reported. Instead of TRU, TEVA was also tested (according to Bombard's method [8]), and similar results (~65% recovery of Zr and ~99% separation factor of Nb) were found.

Behavior of ^{93}Zr on UTEVA

Among methods for separation of Zr, only few are based on usage of extraction chromatographic material UTEVA (supported di-pentyl pentyl phosphonate, manufactured by TrisKem International). The extraction behavior of Zr (and Hf) on UTEVA has been studied in detail by Alfonso et al. [15]. Below 4 M HCl, Zr (and Hf) do not have any affinity for UTEVA, but from 8 M to concentrated (12 M) HCl, the retention of Zr (and Hf) by UTEVA is consistently 100%. In H_2SO_4, the affinity of Zr for UTEVA is much lower; the uptake does not reach even 75%. In HNO_3, above 8 M concentration, UTEVA has complete retention of Zr (and Hf).

According to Maxwell et al. [16], the majority of elements are not retained on UTEVA from 8 M HNO_3, but Zr and Nb (such as Hf and Ta) are exemptions. However, in the presence of F^--ions (from 8 M HNO_3 / 0.2 M HF) these elements are also not retained. This special behavior can be used to separate these elements on UTEVA. Makishima et al. [17] retained Zr and Hf on UTEVA using 8 M HNO_3 / 0.1% H_2O_2 to separate Ti from them. Analyzing geological samples, Le Fevre et al. [18, 19] isolated Zr, Hf, Th and U from matrix elements using UTEVA. Using 0.3 M HNO_3 / 0.3 M H_2O_2 as load solution and 0.5 M HF as eluent, “100-104% recovery” was achieved.

Measurement techniques of ^{93}Zr

When using LSC, standard solution of ^{63}Ni is typically used for calibration, i. e. for optimization of the energy window and for determination of detection efficiency, as ^{63}Ni is a β^--emitter with $E_{\beta,\max}$ (66 keV) similar to that of ^{93}Zr [7, 9, 14, 20]. When using ICP-MS, standard solution of natural Zr (containing ^{92}Zr and ^{94}Zr) is typically used for calibration and calculation of the detection limits. Natural Nb (^{93}Nb) can be used as well, as ionization energies of Zr (6.63 eV) and ^{93}Nb (6.76 eV) are similar [14].

Detection limits or minimal detectable activities (MDA) reported in recent papers are summarized in Table 1.

The total number of reported activity concentrations above MDA is under 10 [7, 8, 13, 14, 21]. Although scaling factor methodology is widely used to estimate the activity concentrations of difficult to determine radionuclides [22], no such results according to ^{93}Zr were found in the literature. This is without fail due to the low number of data. However, after analyzing radioactive waste samples, Remenec [7] compared the activity concentrations of ^{93}Zr to those of ^{137}Cs (another fission product) and ^{241}Am (another activation product). In his conclusion the ^{93}Zr/^{241}Am ratio showed that Am was the most suitable activity indicator for Zr. (His samples were from Unit A1 of Bohunice NPP (Jaslovské Bohunice, Slovakia), which suffered an INES-4 rated core meltdown accident in 1977. [Silvia Dulanská and Boris Remenec, personal communication])

Present work

A method for determination of ^{93}Zr in NPP plant wastes was developed in our laboratory earlier [21, 23]. Since then, it has been used to analyze 37 samples (evaporator concentrates of a NPP equipped with WWER-440 reactors); among them 33 had activity concentration of ^{93}Zr over MDA. Evaporator concentrates originate from mixed liquid wastes, collected as "organized" and "non-organized" leakages of the primary system of the NPP. They have been concentrated by evaporation and addition of NaOH to pH 12-13 to increase the solubility of boric acid. The major components of the evaporation concentrates are boric acid (180-200 g/L) and Na^{+}-ions (90-100 g/L); while radioactive components (activation, corrosion and fission products) are included in various amounts depending on the technology and the fuel performance.

As mentioned above, when measuring ^{93}Zr by ICP-MS, the isobaric interference due to ^{93}Nb is most problematic. In order to estimate this effect and to confirm the reliability of our analytical results, an activation model was developed to calculate the theoretical ratios of ^{93}Zr/^{nat}Zr (based on the ratios of ^{93}Zr/^{92}Zr and ^{93}Zr/^{94}Zr) and ^{93}Zr/^{93}Nb in NPP wastes. Additionally, a few samples have also been measured by an independent analytical technique, i.e. by LSC.

This paper discusses the method for separation of ^{93}Zr from NPP wastes. Activity concentrations determined by ICP-MS and LSC are presented, and compared with calculated data originating from the activation model.

Experimental

Reagents

Analytical grade chemicals and certified radioactive materials were used.

The extraction chromatographic material UTEVA resin® was purchased from TrisKem International. Column sizes were 34 mm length and 7 mm inner diameter.

Carrier-free ^{95}Zr tracer was produced from ^{235}U by thermal neutron fission. After 1 minute long irradiation of about 5 mg uranyl-nitrate in the Budapest Research Reactor (thermal neutron flux: 2×10^{13} n cm^{-2} s^{-1}) the sample was dissolved in 5-10 mL 10 M HCl and loaded on a UTEVA column (conditioned with 10 mL 10 M HCl). The column was washed with 20 mL 9 M HCl, and Zr was stripped with 20 mL 4 M HCl.

Gamma-spectrometer

The γ-ray spectrometric measurements were performed using a calibrated PC-based 8k multichannel analyzer (MCA) with Intertechnique high-purity (HP) Ge detector (relative efficiency 12.8%) and Canberra Genie-2000 software.

Radiochemical separation

The radioanalytical method used in present work was originally developed for separation of actinoids, and then it was improved for determination of ^{93}Zr. It was described in more detail elsewhere [21, 23].

After acquiring the γ spectrum of a 100 mL aliquot of the liquid radioactive waste sample or 0.1 g spent resin (to determine the activity concentrations of the γ-emitting radionuclides, such as ^{58}Co, ^{60}Co, ^{134}Cs, ^{137}Cs, ^{152}Eu), about 100 Bq carrier-free ^{95}Zr were added to it as tracer. The sample was digested by evaporating with 3 × 30 mL 65% HNO_3, 3 × 30 mL 37% HCl and taken up in 100 mL 1 M HNO_3.

Zr was pre-concentrated by $Fe(OH)_2/ZrO_2$ co-precipitation. About 0.5 g $Fe(NH_4)_2(SO_4)_2$ and 2 mL hydrazine were added to the solution and the pH was adjusted to 9-10 using 25% NH_3. The precipitate was filtered using a vacuum filtration apparatus and a 50 mm diameter 0.45 μm pore size cellulose-nitrate membrane. The precipitate was dissolved with the mixture of 65% HNO_3, 37% HCl and 40% HF; then evaporated to dryness. The residue was taken up in 10 mL 1 M HNO_3 and 0.2 g H_3BO_3 was added.

0.22 g $(NH_4)_2S_2O_8$, 5 mg $AgNO_3$ and 100 µL 0.01 M $KMnO_4$ were added to the sample and it was slightly warmed for half an hour. (This oxidation state adjusting step can be skipped, if Pu and Np are not to be analyzed.) Sample was cooled down, and its acid concentration was adjusted to 8 M by adding 10 mL 65% HNO_3. The solution was loaded on a UTEVA column conditioned with 10 mL 8 M HNO_3. The column was washed with 5 mL 8 M HNO_3 containing 0.5 g $Fe(NO_3)_3 * 9H_2O$ and 2 mL 9 M HCl. The column was eluted with 10 mL 9 M HCl / 0.1 M NH_4I to strip Pu. Zr together with Np was eluted with 10 mL 4 M HCl, and U was stripped with 15 mL 0.1 M HCl.

The hydrochloric acid concentration of the Zr/Np fraction was adjusted to 9 M by adding 15 mL 37% HCl. The solution was loaded on a second UTEVA column (conditioned with 10 mL 9 M HCl). The column was washed with 5 mL 9 M HCl, Zr and Np were eluted with 10 mL 4 M HCl. After evaporation to dryness, the residue of this Zr/Np fraction was taken up in a mixture of 5 mL 0.1 M HCl and 10 µL 40% HF. During the procedure, the presence of Zr in the required fractions was controlled by repeated γ spectrometric measurements to avoid possible adsorption of hydrolyzed Zr species on walls of the equipment, on the filter or the resin.

The γ spectrum of the solution was acquired to determine chemical recovery. The ^{93}Zr and ^{237}Np content of a sample aliquot was determined after appropriate dilution by ICP-MS.

ICP-MS measurement

Before ICP-MS measurement, a known amount of Rh (internal standard, 1 ppb) was added to the sample.

For ICP-MS measurements, two instruments were used. The first one (at the Nuclear Security Department, Centre for Energy Research, Hungarian Academy of Science) was a double-focusing magnetic sector ICP-MS equipped with a single electron multiplier (ELEMENT2, Thermo Electron Corp., Bremen, Germany). Measurements were carried out in low resolution mode ($R = 300$) using a low flow nebulizer in self aspirating mode (flow rate 100 µL min^{-1}). Sensitivity for ^{93}Zr was about $2.5\text{-}2.9 \times 10^5$ cps ppb^{-1} (it was determined by measuring a standard solution of natural Zr and interpolating sensitivities for ^{92}Zr and ^{94}Zr), abundance sensitivity was 7.70 × 10^{-2}. The nuclides of interest were measured in peak hopping mode by changing the accelerator voltage (E-scan) in order to measure each nuclide.

The other instrument (at Isotoptech Zrt.) was an Agilent Technologies 8800 ICP-MS Triple Quad ICP-MS-MS with reaction cell. Sensitivity for ^{93}Zr was 5.5 × 10^{3} cps ppb^{-1}, abundance sensitivity was 1.60 × 10^{-4}.

To decrease uncertainties, isotope dilution technique could have been used [2, 6].

LS measurement

LS measurements were performed with a Perkin Elmer TriCarb 2800 LS counter.

A 2 mL aliquot of the purified Zr solution was mixed with 10 mL ProSafe LS cocktail (Meridian Biotechnologies Ltd.) and counted for 200 minutes together with blank samples containing known amount of tracer. The typical cooling time of the samples before LS measurement was about 6 months. β spectra were visually inspected, and those showing an anomalous shape due to contamination were dropped. Net counts in the low energy region of the β spectra (ROI 3-100 keV) were evaluated as ^{93}Zr. Counting efficiency was determined using ^{63}Ni standard solution as a function of quench.

Activation model

Calculation of the activity of ^{93}Zr by activation of Zr in case of a fuel rod cladding and an assembly wrapper was performed using the MCNP5 general-purpose Monte Carlo code. A detailed model of a WWER-440 fuel assembly was built (see Supplementary information), and the reaction rates and fluxes were calculated in infinite lattice geometry with track length estimator tallies using the ENDF/B-VII.0 cross-section library. The activity of ^{93}Zr referring to total mass of Zr was calculated analytically by solving the corresponding nuclide chain equation. The simulation does not address the production of ^{93}Zr via fission in the fuel, only via neutron capture of ^{92}Zr in the fuel rod cladding and the assembly wrapper.

Results

Using the radiochemical method described above, 37 evaporator concentrate samples were analyzed. Activity concentrations of ^{93}Zr measured by ICP-MS are presented in second column of Table 2. In order to improve their reliability, some samples were measured by LSC as well; these data are reported in fourth column of Table 2.

Comparing the ICP-MS and the LS results, an “acceptable” correlation (where results are in the same order of magnitude) can be observed. Measurement uncertainty of LSC is significantly higher, probably as a consequence of lower sensitivity. In three cases, ICP-MS results are significantly higher than LS ones, probably due to insufficient Nb decontamination and hence an overestimation of the ICP-MS data. On the other hand, LS measurements are subjected to contamination hazard due to any radionuclide impurities left in the Zr fraction. Comparative evaluation of the ^{93}Zr results using ICP-MS and LSC techniques helps avoid misinterpretation of the measured data.

Discussion

Production of ^{93}Zr

Alloys used for rod cladding and assembly wrapper are both called Zr1%Nb, but their Nb contents are slightly different: 1.2% in rod cladding and 2.8% in assembly wrapper.

Rod cladding of a typical WWER-440 assembly consists of 33.72 kg natural Zr (including 5.78 kg ^{92}Zr as well as 5.86 kg ^{94}Zr) and 0.41 kg Nb (^{93}Nb). According to our calculations mentioned in *Experimental – Activation model*, 8.89 g (8.23×10^{8} Bq) ^{93}Zr is produced during a typical 1340 day long (ca. 4 years) irradiation. Therefore, at the end of the irradiation period, the ^{93}Zr/^{nat}Zr and ^{93}Zr/^{93}Nb mass ratios are 2.64×10^{-4} and 2.17×10^{-2}, respectively.

These ratios refer to the spent fuel assembly; but assuming the corrosion rates of Zr and Nb being the same, these ratios refer to primary water and evaporator concentrate as well. [As the area of cladding contacting with primary water and therefore its corrosion rate is much bigger than those of wrapping; we assume ratios in primary water and evaporator concentrate being closer to ratios in cladding than ratios in wrapping. However, ratios in wrapping were also calculated. Wrapper of a typical WWER-440 assembly consists of 11.48 kg Zr (including 1.97 kg ^{92}Zr as well as 2.00 kg ^{94}Zr) and 0.33 kg Nb (^{93}Nb). From this, 0.0228 g

(2.11×10^{6} Bq) ^{93}Zr is produced during a 1340 day long irradiation, resulting 1.99×10^{-6} and 6.91×10^{-5} mass ratios (^{93}Zr/^{nat}Zr and ^{93}Zr/^{93}Nb, respectively).]

The ^{93}Zr/^{nat}Zr mass ratios measured in our samples are presented in third column of Table 2. Among them, some are in good agreement with the estimated value (2.64×10^{-4}), but others are too high. These might be caused by insufficient separation of Zr from Nb (and misinterpretation of ^{93}Nb at ICP-MS measurement – see *next chapters*), or by ^{93}Zr produced by fission of ^{235}U (or both). (Although the activity concentrations based on LSC measurements are sometimes in poor agreement with the activity concentrations based on ICP-MS measurements, they indicate that their orders of magnitude are correct.)

According to our calculations, in one assembly 1.43×10^{10} Bq ^{93}Zr is produced by fission, while only 8.23×10^{8} Bq is produced by activation. In general, the former cannot get into primary water (except in case of damage of cladding). However, a thin layer of UO_2 is always present on the outer surface of cladding (the so called tramp uranium; ca. 10^{-9} g cm^{-2} ^{235}U), and fission products of that UO_2 can easily dissolve into primary water. Unfortunately, the quantity of this fission-produced ^{93}Zr in primary water cannot be estimated (although its quantity in a fuel rod can easily be estimated), as its dissolution rate is unknown. Neither can be determined the total amount of Zr corrosion products in the coolant.

Separation of ^{93}Zr from Nb, DFs of Nb

When sampling and analyzing evaporator concentrates, the ^{93}Zr/^{93}Nb ratio is changed by the radiochemical process used for separation of Zr. According to our earlier results, the average recovery of ^{93}Zr is 65% and the DF of Nb over Zr is about 100 [21]. Using these values, the ^{93}Zr/^{93}Nb mass ratio at the ICP-MS measurement turns out to be 1.41. In this example only 58.5% of the counts at $m/z = 93$ can be interpreted as ^{93}Zr. Assuming the Nb/Zr "reduction factor" being 1000 [24], the ratio is 14.1, and 93.4% of the counts correspond to ^{93}Zr, increasing the uncertainty of results by 6.6%. A hypothetical DF of 10^{4} would increase the uncertainty by ca. 1%. These calculations emphasize the importance of separation of Zr from Nb, but unfortunately, such results are scarce in literature.

This is why model experiments were performed to determine the DFs of Nb in the 3 main separation steps of our procedure (co-precipitation on $Fe(OH)_2/ZrO_2$, extraction chromatography using UTEVA and HNO_3 as well as UTEVA and HCl). Each step was performed using model samples containing known amounts of ^{nat}Zr and Nb. Model samples before and after separation steps were analyzed by ICP-MS to determine their Zr and Nb content. Results are summarized in Table 3.

Analyzing real samples, DFs of Nb over Zr were found to be between 100 and 3000. This means, that the orders of magnitude of activity concentrations of ^{93}Zr are correct, although the values can have (in worst case) a ca. 45% uncertainty.

Conclusions

Radioanalysis of ^{93}Zr in radioactive waste is an important issue and a challenge for the analysts. An effective method based on radiochemical separation of Zr followed by measurement of ^{93}Zr by ICP-MS has been used for analyzing 37 NPP samples. Measurement of a few samples by LSC confirmed the accuracy of the results. Reliability of results was checked by comparing the measured ^{93}Zr/^{nat}Zr mass ratios with values calculated using a Monte Carlo activation model. Excess ^{93}Zr might originate from fission, but further investigation is needed to clarify this. Separation of Nb is a critical issue, a DF of at least 10^3 is necessary to get a measurement uncertainty of less than 10%.

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Tables

Table 1 Summary of detection limits or MDAs reported in recent papers presenting methods for determination of ^{93}Zr in NPP wastes. Take care, that 1 µg ^{93}Zr corresponds to 92.6 Bq

Detection Technique	Detection limit or MDA	Reference	Remark
LSC	0.067 Bq	Espartero, 2002 [4]	all samples below MDA
LSC	not reported	Remenec, 2008 [7]	-
LSC	0.05 Bq L^{-1}	Oliveira, 2011 [13]	-
LSC	0.061 Bq	Osváth, 2011 [21]	all samples below MDA
LSC	24-83 Bq kg^{-1}	Dulanská, 2012 [9]	all samples below MDA
LSC	0.05 Bq L^{-1}	Oliveira, 2014 [14]	-
LSC	9-67 Bq g^{-1}	Remenec, 2014 [20]	all samples below MDA
LSC	0.05-0.5 Bq g^{-1}	Dulanská, 2016 [10]	all samples below MDA
ICP-MS^{a}	0.02 Bq L^{-1}	Osváth, 2011 [21]	-
ICP-MS^{b}	0.01 µg L^{-1} (0.93 Bq L^{-1})	Dulanská, 2012 [9]	all samples below MDA
ICP-MS^{c}	0.045 µg L^{-1} (4.2 Bq L^{-1})	Oliveira, 2014 [14]	-
ICP-MS^{d}	200 Bq L^{-1}	Shimada, 2016 [12]	all samples below MDA

[a] Double-focusing magnetic sector ELEMENT2 from Thermo Electron Corp.

[b] Quadrupole Perkin-Elmer Sciex Elan 6000

[c] X series II 0 Quadrupole from Thermo Scientific

[d] Perkin Elmer Co.

Table 2 Measured activity concentrations (Bq L^{-1}) of ^{93}Zr in some NPP wastes (evaporator concentrates) as well as the ^{93}Zr/^{nat}Zr mass ratios. The uncertainty is given using a coverage factor of 1 (k=1)

Sample code	Activity concentration of ^{93}Zr [Bq L^{-1}] determined by ICP-MS	^{93}Zr/^{nat}Zr mass ratio from ICP-MS measurement	Activity concentration of ^{93}Zr [Bq L^{-1}] determined by LSC
2010/4	0.23 ± 0.14	-	-
2010/5	0.79 ± 0.19	-	-
2010/7	< 0.24	-	-
2012/6	803 ± 24	$(2.82 \pm 0.14) \times 10^{-3}$	-
2012/9	50.6 ± 1.4	$(2.09 \pm 0.10) \times 10^{-3}$	-
2012/15	352 ± 9	$(1.66 \pm 0.08) \times 10^{-2}$	-
2013/1	< 39	$< 9.6 \times 10^{-5}$	-
2013/2	0.15 ± 0.06	$(8.0 \pm 3.4) \times 10^{-5}$	-
2013/3	466 ± 11	$(1.17 \pm 0.05) \times 10^{-2}$	-
2013/6	< 0.56	$< 1.0 \times 10^{-4}$	-
2014/3	6.3 ± 1.2	$(2.0 \pm 0.4) \times 10^{-4}$	-
2014/4	14.5 ± 5.0	$(2.1 \pm 0.8) \times 10^{-4}$	-
2014/6	13 ± 5	$(1.7 \pm 0.7) \times 10^{-4}$	-
2015/1A	310 ± 50	$(7.1 \pm 1.3) \times 10^{-3}$	-
2015/1B	940 ± 80	$(2.35 \pm 0.20) \times 10^{-2}$	-
2015/2	1660 ± 140	$(8.7 \pm 0.7) \times 10^{-3}$	-
2015/3	350 ± 30	$(8.5 \pm 0.8) \times 10^{-3}$	-
2015/4	470 ± 50	$(8.7 \pm 0.8) \times 10^{-4}$	-
2015/5	68 ± 10	$(1.30 \pm 0.19) \times 10^{-4}$	-
2015/6	112 ± 14	$(2.5 \pm 0.3) \times 10^{-4}$	-
2015/7	167 ± 15	$(1.18 \pm 0.11) \times 10^{-3}$	-
2015/8	226 ± 23	$(2.42 \pm 0.25) \times 10^{-3}$	-
2015/9	930 ± 100	$(9.0 \pm 1.0) \times 10^{-3}$	-
2015/B56	253 ± 25	$(1.92 \pm 0.19) \times 10^{-3}$	-
2015B61	370 ± 30	$(2.73 \pm 0.24) \times 10^{-3}$	-
2015/B70	600 ± 50	$(3.5 \pm 0.3) \times 10^{-3}$	-
2016/1	53 ± 5	$(2.06 \pm 0.18) \times 10^{-4}$	78 ± 20
2016/2	137 ± 4	$(1.49 \pm 0.05) \times 10^{-3}$	76 ± 17
2016/3	55.7 ± 1.7	$(4.40 \pm 0.05) \times 10^{-3}$	-[a]
2016/4	327 ± 9 [b]	$(3.56 \pm 0.11) \times 10^{-3}$	45 ± 5
2016/5	118 ± 4 [b]	$(7.4 \pm 0.4) \times 10^{-3}$	50 ± 15
2016/6	1200 ± 40	$(8.7 \pm 0.3) \times 10^{-4}$	920 ± 90
2016/7	336 ± 10	$(4.69 \pm 0.17) \times 10^{-3}$	-[a]
2016/8	109 ± 3 [b]	$(1.12 \pm 0.04) \times 10^{-3}$	48 ± 5
2016/9	71.0 ± 2.8	$(5.99 \pm 0.24) \times 10^{-4}$	58 ± 6
2016/10	20.0 ± 1.2	$(3.14 \pm 0.19) \times 10^{-4}$	51 ± 5
2016/vak	64.0 ± 2.1	$(1.01 \pm 0.04) \times 10^{-3}$	66 ± 8

[a] Presence of some contaminant is clearly visible from the shape of the LS spectrum.

[b] Overestimation of ICP-MS result due to insufficient removal of Nb is likely.

Table 3 DFs of Nb in each step of the procedure used in present work

Steps of procedure	DFs
Co-precipitation on $Fe(OH)_2/ZrO_2$	≈ 1[a]
UTEVA / HNO_3	10 < DF < 400[b]
UTEVA / HCl	100
Whole procedure	1000 < DF < 10000

[a] No separation

[b] Difficult to reproduce

Supplementary information

Detailed description of the activation model

The activation calculations were performed for the fuel assembly of the WWER-440/V 213 type pressurized water reactor, where the analyzed samples are originated from. The detailed MCNP5 model of the WWER-440 fuel assembly is based on the Gd-2n type fuel assembly, which has been introduced at the NPP in 2010. The average enrichment of the fuel in the assembly is 4.2%, containing 81 fuel rods with 4.4% enrichment, 24 fuel rods with 4.0% enrichment, as well as 18 rods with 3.6% and 3 with 4.0% enrichment, of which the latter also contains 3.35% Gd burnable poison. The radial structure of the fuel assembly, including the position of the different types of fuel rods can be seen in the assembly layout depicted in Figure 1 [25]. The axial structure of the fuel assembly was also taken into account, including simplified models of the top and bottom nozzles, which consisted of concentric water and steel cylinders and hexagons. Some important parameters of the reactor and the fuel assembly can be found in Table 1 [25, 26].

As the variations of the neutron spectrum during burn-up is not expected to have significant effect on the activation of the fuel rod cladding and the assembly wrapper, the reaction rates and fluxes were determined for the fresh fuel assembly. The calculations were performed in infinite lattice geometry with track length estimator tallies (F4 tallies) using the ENDF/B-VII.0 cross-section library. In order to decrease computational time, the 120° symmetry of the fuel assembly was taken advantage of, and only one third of the assembly was modeled with reflective boundary conditions on the sides of the geometry (see Figure 2). The results of the MCNP5 simulations were the reaction rates and fluxes normalized to one fission neutron. The one-group microscopic cross-sections were calculated from the results, and in knowledge of the average assembly power, the one-group integrated neutron flux was also determined. The activities of the different Zr isotopes, including ^{93}Zr were calculated analytically by solving the corresponding nuclide chain equations and referred to the total Zr mass. The simulation does not address the production of ^{93}Zr via fission in the fuel, only via neutron capture of ^{92}Zr in the fuel rod cladding and the assembly wrapper.

Tables

Table 1 Important parameters of the WWER-440 reactor and the MCNP5 model of the Gd-2n fuel assembly [25, 26]

Thermal power [MW]	1485
Electrical power [MW]	500
Thermal efficiency	34%
Number of fuel assemblies	349
Number of rods / assembly	126
Cycle length [days]	4x335
Central hole radius [cm]	0.06
Fuel pellet radius [cm]	0.38
Cladding inner radius [cm]	0.39
Cladding outer radius [cm]	0.45
Lattice pitch [cm]	1.23
Active height [cm]	248

Figures

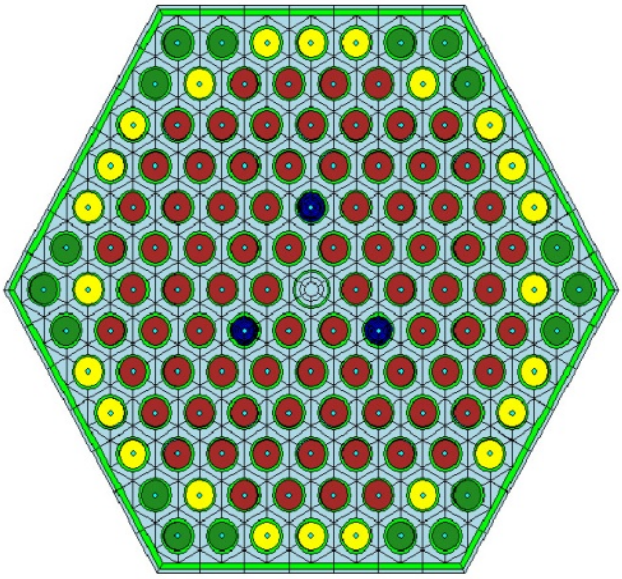

Figure 1 Fuel assembly layout of the WWER-440 Gd-2n fuel assembly (green and yellow rods: 3.6% and 4.0% enriched UO_2, red and blue rods: 4.4% enriched UO_2 and 4.0% enriched UO_2 + 3.35% Gd burnable poison) [25]

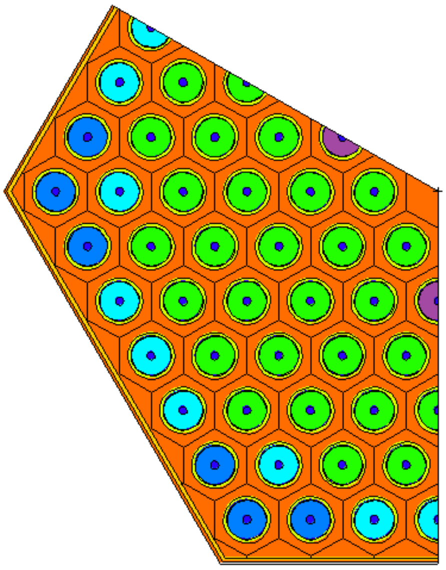

Figure 2 MCNP5 model of the WWER-440 Gd-2n fuel assembly (blue and light blue rods: 3.6% and 4.0% enriched UO_2, green and purple rods: 4.4% enriched UO_2 and 4.0% enriched UO_2 + 3.35% Gd burnable poison)

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