Capability assessment for application of clay mixture as barrier material for irradiated zirconium alloy structure elements long-term processing for storage during decommissioning of uranium-graphite nuclear reactors

S G Kotlyarevskiy[1], A O Pavliuk[1,2], E V Zakharova[3] and A G Volkova[3]
[1] Pilot & Demonstration Center for Decommissioning of Uranium-Graphite Nuclear Reactors, Seversk, Tomsk region, Russia
[2] Tomsk polytechnic university, Tomsk, Russia
[3] Frumkin IPCE RAS, Moscow, Russia

E-mail: seversknet@rambler.ru

Abstract. The radionuclide composition and the activity level of the irradiated zirconium alloy E110, the radionuclide immobilization strength and the retention properties of the mixed clay barrier material with respect to the radionuclides identified in the alloy were investigated to perform the safety assessment of handling structural units of zirconium alloy used for the technological channels in uranium-graphite reactors. The irradiated zirconium alloy waste contained the following activation products: ^{93m}Nb and the long-lived ^{94}Nb, ^{93}Zr radionuclides. Radionuclides of ^{60}Co, ^{137}Cs, ^{90}Sr, and actinides were also present in the alloy. In the course of the runs no leaching of niobium and zirconium isotopes from the E110 alloy was detected. Leach rates were observed merely for ^{60}Co and ^{137}Cs present in the deposits formed on the internal surface of technological channels. The radionuclides present were effectively adsorbed by the barrier material. To ensure the localization of radionuclides in case of the radionuclide migration from the irradiated zirconium alloy into the barrier material, the sorption properties were determined of the barrier material used for creating the long-term storage point for the graphite stack from uranium-graphite reactors.

1. Introduction

The decommissioning of uranium-graphite reactors (UGR) presents a wide range of issues that demand the solutions both in the preparation phase and directly during the process of decommissioning. Among them, the problem of handling structural elements of zirconium alloys is defined by the combination of properties and characteristics inherent to the initial material and acquired by it in the process of the irradiation in the reactor core.

The alloys of zirconium with up to 2.5% by wt. of niobium are used for manufacturing pipes for technological channels (TC) in the uranium-graphite channel type RBMK reactors currently in operation. Besides, the TC pipes of zirconium alloy were used in the final stages of operation of some production uranium-graphite reactors (PUGR); the pipes were installed in certain zones of the graphite stack to maintain its integrity.

The primary issue of handling irradiated parts of zirconium alloy is associated with the long-lived ^{94}Nb (T$_{1/2}$=2.03×10^4 years) and ^{93}Zr (T$_{1/2}$=1.5×10^6 years) radionuclides contained in the material. The

decay of ^{94}Nb is accompanied by the emission of high energy gamma quanta (E_γ=703 keV, 100% yield and E_γ= 871 keV, 100% yield). So far as the activity of ^{94}Nb can reach values substantial to induce high gamma dose rate levels, serious restrictions are imposed on the access of personnel to the irradiated zirconium parts handling.

According to the attribution criteria stated in the Russian Government Regulation No.1069 of 10.19.2012, various options are considered for handling UGR radioactive waste (RW) of zirconium. If the zirconium waste is attributed to the disposable RW category, it is to be retrieved and conditioned; if it is attributed to the special RW category, it is not retrieved from the reactor (the burial option).

The aim of this study is to determine the nuclide composition and activity of the irradiated zirconium alloy, radionuclide leach rates, sorption properties of the clayey barrier material with respect to the radionuiclides in question. The study is performed to justify the economically feasible technique for zirconium RW handling.

2. Determination of the radionuclide composition and activity of irradiated zirconium samples

Samples of the material for the investigation were taken from four irradiated TC pipes of the E110 zirconium alloy. The operation period of the pipes in the reactor ranged from 2/5 to 10 years; the cooling time was ~20 years. Sampling was performed in several points along the height of the TC pipes as follows: at the half-height (C), at the distance of ~0.5-1 m from the top (T), and bottom (B) end.

Prior to the radiometric measurements the irradiated zirconium alloy sample was dissolved in the 10 g/L nitric acid solution in the presence of 5 g/L ammonium chloride. The content of γ-emitting radionuclides in the solution, including ^{93m}Nb and ^{94}Nb, was determined by the digital gamma spectrometric complex with the coaxial GEM30 and planar GLP-36360 detectors of ORTEC Company. The prepared solution was neutralized by ammonia with pH of 5-6 until a precipitate was formed. The precipitate was allowed to settle and filtered.

The precipitate of zirconium hydroxide was dissolved in 4 mole/L HCl solution. One part the solution was used to determine actinides, the other was analyzed for ^{93}Zr. Actinides were separated by the extraction-chromatographic technique on TRU resin. The actinides were successively eluted by solutions of different composition followed by the electrolytic deposition of an actinide on the metal support plate. The measurements were performed on the low-background semiconductor alpha-spectrometer equipped with BDEC-01 detector unit.

Zirconium was separated from the solution by the liquid extraction technique [1]. The samples were examined on the LC TRI-CARB 3170 TR/SL spectrometer by PerkinElmer. Recorded spectra were processed using the RadSpectraDec application program complex.

The radionuclides identified in the irradiated zirconium samples as a result of the spectrometric studies were the following: ^{93m}Nb, ^{94}Nb, ^{93}Zr, ^{60}Co, ^{137}Cs, ^{90}Sr, and certain actinides.

It was determined that the shape of ^{93m}Nb, ^{94}Nb, and ^{93}Zr activation product distribution is close to the distribution of the neutron flux during the reactor operation.

To date after ~20 year cooling the primary dose forming radionuclide (the activity of up to 1×10^6 Bq/kg) in the E110 zirconium alloy was the long-lived ^{94}Nb radionuclide with the half-life of 2.03×10^4 years. Despite the ^{93m}Nb radionuclide had the higher activity of up to 3×10^6 Bq/kg, its decay was accompanied by the low energy gamma emission, which for the practical purposes did not contribute into the external irradiation of the personnel. The long-lived ^{93}Zr radionuclide with the half-life of 1.5×10^6 years and the specific activity of ~3×10^4 Bq/kg was also present in the irradiated zirconium, but its decay was accompanied merely by the low energy beta-particles.

The contact with graphite and leaks of the cooling agent resulted in the contamination of the external TC pipe surface. Deposits formed on the internal walls contained ^{60}Co (up to 3×10^4 Bq/kg), ^{137}Cs (up to 2×10^3 Bq/kg), ^{90}Sr (up to 3×10^1 Bq/kg), and some actinides transferred by the coolant from the surface of the primary loop pipework.

The distribution of ^{90}Sr, ^{137}Cs radionuclides and actinides did not depend on the neutron flux distribution and was probably associated with the corrosion deposits on internal walls of the channels and with consequences of the local accidents in the course of the reactor operation.

The distribution of ^{60}Co along the channel height was defined by different sources of its formation. It came both from the activated cobalt impurities in the alloy itself and from cobalt incorporated in the corrosion deposits formed on the channel walls.

Thus, to date the primary dose forming radionuclide in the zirconium alloy was the ^{94}Nb radionuclide; its activity did not exceed 1×10^6 Bq/kg. Taking into account the distribution of the activity along the channel height, matching the shape of the neutron flux distribution, the average specific activity of ^{94}Nb was approximately 2 times as less, and amounted 5×10^5 Bq/kg.

Counting by the basic ^{94}Nb, ^{60}Co, and ^{93}Zr radionuclides, the maximum specific beta-activity of TC pipes was defined by ^{93}Zr and did not exceed 1×10^6 Bq/kg. Similarly to ^{94}Nb, the average specific activity of ^{93}Zr was 2 times as less of 5×10^5 Bq/kg.

The content of actinides did not exceed 1×10^2 Bq/kg. No isotopes of neptunium, americium, and curium were detected. The gross activity of irradiated zirconium channels in the graphite stack of PUGR at JSC "Pilot & Demonstration Center for Decommissioning of Uranium-Graphite Nuclear Reactors" (JSC "DNR Center") did not exceed 1% of the gross activity of the whole stack.

3. Determination of radionuclide leach rates from the irradiated zirconium samples

To determine a possible option for handling irradiated zirconium, the strength of radionuclide localization in the alloy was evaluated by determining leach rates of the radionuclides in question. Samples of the irradiated E110 zirconium alloy taken from two TC pipes were immersed into distilled water in glass beakers. The volume of distilled water in each beaker was 50 cm^3. Water in the beakers was replaced according to the technique defined in GOST P52126-2003. The samples were analyzed according to the technique described above.

The leach rate for an individual radionuclide R_n^i g/(cm^2·day) was determined according to the formula (1):

$$R_n^i = \frac{a_n^i}{A_o^i S t_n},\qquad(1)$$

where

a_n^i – denoted the activity of an individual nuclide leached for the given period of time, Bq;

A_0^i – the specific activity of the nuclide in the initial sample, Bq/g;

S – the square area of the open geometric surface of the sample, cm^2;

t_n – the duration of the nth leaching period, days.

Thus, the R was the ratio of the activity of a radionuclide transferred into the solution from 1 cm^2 of the zirconium alloy surface within 24 hours to the specific activity of the given radionuclide in the sample.

Results of the experimental determination of leach rates for the primary dose forming radionuclides from the irradiated zirconium were presented in Fig.1.
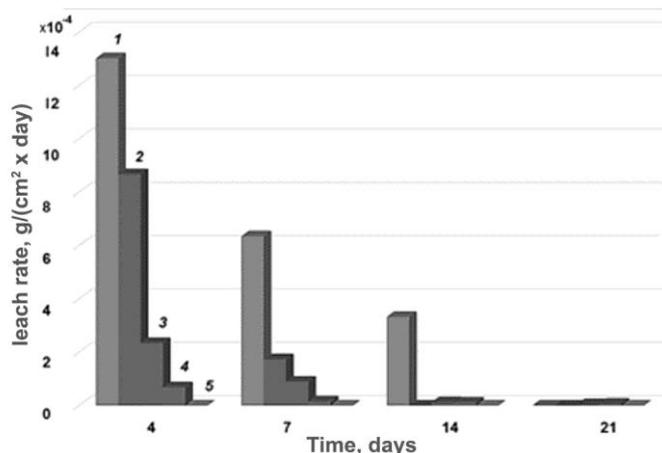
Figure 1. Radionuclide leach rates from the zirconium alloy: 1 – ^{90}Sr; 2 – actinides; 3 – ^{137}Cs; 4 – ^{60}Co; 5 – ^{94}Nb.

As it can be seen from Fig.1, ^{60}Co, ^{90}Sr, ^{137}Cs, and actinides were present in the liquid after leaching. The leach rate depended on the contamination of the deposits, radionuclide localization strength, and radionuclide speciation in the deposits.

It should be noted that the leach rates for all radionuclides were decreased with time. For the 35 day duration of the runs the statistically significant values were obtained for cobalt and cesium. The decrease in leach rates being detected merely in the final stage of monitoring. Leaching of strontium and actinides was discontinued much faster. Those radionuclides were not leached from all samples.

Not more than 2% of the activity of strontium, cesium, cobalt, and actinide radionuclides localized in the surface deposits was leached during the runs. By the end of the run the leach rates of all radionuclides were decreased by several orders of magnitude. As the contact time was increased, no further leaching was observed.

Leaching of ^{94}Nb was observed merely for the 1st day of the sample contact with water. This phenomenon can be explained either by the micro particles of the alloy remained on the sample surface during the sampling process, or by the presence of those isotopes in the irradiated graphite that was in contact with the zirconium pipe channels during the reactor operation, or both.

Results of the zirconium and niobium leaching studies were in good agreement with the data of the corrosion tests of the non-irradiated zirconium [2, 3, 4]. They proved the high corrosion resistance of the technological channels of the irradiated zirconium alloy. Obviously, the extended radiation and thermal impact on the zirconium alloy during the reactor operation did not result in any significant change in the corrosion stability of the material. It should be taken into account during the consideration of different options for handling parts of the irradiated zirconium alloy, particularly in long-term storage or burial.

4. Sorption properties of the clayey barrier material with respect to radionuclides contained in the irradiated zirconium alloys

The investigation of sorption properties of the barrier material with respect to the radionuclides present in the irradiated zirconium alloy was directly associated with the demand to justify the environmental and radiation safety of its long-term storage, disposal, or burial. The clay currently used for the engineered safety barriers was the effective sorption material, affordable by its low-cost and available resources. At the JSC "DNR Center" similar barrier was installed in the PUGR EI-2 uranium-graphite reactor vault and adjacent premises to create the long-term storage point for graphite stack and construction steelwork [5]. Results of the predictive modeling showed that the installed barrier confined the distribution of radionuclides in the geological medium and maintained their concentrations below the intervention level outside the boundaries of the created object.

Sorption experiments were conducted with the sample of the barrier material obtained by LLC "PIK", the City of Krasnoyarsk. Protective properties of the material were increased using a mix of several clays prepared by the preliminary grinding and mixing of components. To increase the

sorption and capacity characteristics of the material, the poly-mineral mixes contained different minerals, namely, montmorillonite, kaolinite, chlorite, vermiculite, micas and hydromicas, etc.

The water simulant composition was chosen close to the natural water at the location area of the PUGR of the JSC "JSC "DNR Center"". The simulated water contained, mg/L: $^{2+}Ca - 40.7$; $^{2+}Mg - 4.5$; $Na^+ - 6.9$; $\sum CO_3^{2-} + HCO_3^- - 20.6$; $SO_4^{2-} - 14.3$, and $Cl^- - 72.3$; pH 7.3. The S/L ratio was 1/20; the phases were separated by the centrifugation. Solutions for the sorption runs contained, mole/L (Bq/L): $^{90}Sr - 2.2 \times 10^{-10}$ (1.0×10^5); $^{137}Cs - 1.1 \times 10^{-9}$ (5.0×10^5); $^{233}U - 2.0 \times 10^{-7}$ (1.66×10^4); $^{238}Pu - 5.0 \times 10^{-10}$ (7.5×10^4); $^{60}Co - 4.0 \times 10^{-11}$ (1.0×10^5); $^{93}Zr - 5.0 \times 10^{-6}$ (4.4×10^4), and $^{94}Nb - 5.0 \times 10^{-8}$ (3.25×10^4).

Sorption processes with the different mechanisms were characterized by the cumulative index, namely, the interphase distribution coefficient. It was equal to the ratio of the amount of the radionuclide adsorbed in the solid phase to its equilibrium content in the liquid (2):

$$K_d = \frac{N}{C_f} = \frac{C_i - C_f}{C_f} \cdot \frac{V_l}{m_s}, \qquad (2)$$

where:

N - denoted the activity of the rock in the sample, Bq/kg;

C_i and C_f - the initial and final activity of the solution, Bq/L, mole/L;

V_l -volume of the solution, cm^3;

m_s -weight of the sample, g.

K_d - values were used in the radionuclide migration calculations. Retention properties of the sample were characterized by the effective porosity P_e and the retention factor R according to the formulas (3, 4):

$$P_e = \frac{N \cdot \rho + C_0 \cdot P_0}{C_0} = K_{id} + P_0, \qquad (3)$$

$$R = \frac{P_e}{P_0} = 1 + \frac{K_p}{P_0} = 1 + \frac{K_d \rho}{P_0}, \qquad (4)$$

where:

P_0 denoted the active or opened porosity of the rock;

$K_p = K_d \cdot \rho$ - the interphase distribution coefficient;

ρ - density of the sample, g/cm^3.

The retention factor R was one of the parameters defining the radionuclide behavior in the process of the interaction with rocks. It also characterized the ratio of the adsorbed radionuclide component velocity to the distribution velocity of the water flow.

For the irradiated zirconium alloy the most interest represented the behavior of long-lived zirconium and niobium isotopes during their interaction with the barrier material. In aqueous solutions zirconium and niobium were subjected to the hydrolysis and polymerization processes. Depending on the metal concentration, solution acidity, and temperature different zirconium species were formed, such as monomers $Zr(OH)_4^{(4-n)+}$, where n=0,1, 2, 3, and 4, or trimers and tetramers. The formation of species started in the solution with the concentration over $10^{-4} - 10^{-3}$ g-atom/L. The zirconyl ZrO^{+2} ion could also exist in the solution. The poly-nuclear nature of zirconium hydroxide remained even in high dilutions. It existed in the ionic form just below the pH of 2. Therefore in natural systems, in neutral and weak alkaline media as well as at the low zirconium and niobium concentrations those radionuclides would exist as the hydrolyzed ion species. Their behavior and speciation were similar to plutonium.

When the simulated water containing ^{93}Zr and ^{94}Nb was brought into contact with the barrier clayey material, the sorption equilibrium was attained rather quickly, in 1-2 days (see Fig.2).
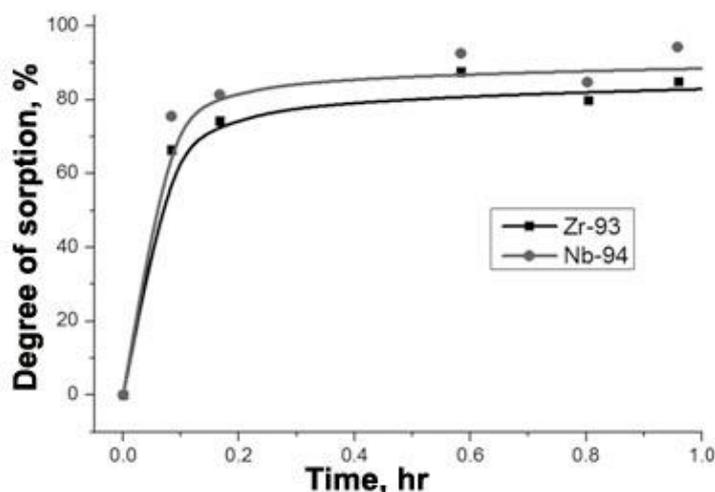
Figure 2. The sorption kinetics of ^{93}Zr and ^{94}Nb radionuclides on the barrier material.

After the equilibrium in the system was attained, the distribution coefficient K_d and retention factor R values were determined. The K_d and R values for the other radionuclides leached from the irradiated zirconium after 35 days of the interaction were presented in Table 1.

Table 1. The sorption characteristics (K_d, cm^3/g, R) of the LLC "PIK" clay sample with respect to radionuclides.

Parameter	^{93}Zr	^{94}Nb	^{90}Sr	^{137}Cs	^{233}U	^{239}Pu
K_d	0.4×10^3	0.8×10^3	1.3×10^2	0.6×10^3	2.3×10^2	2.0×10^3
R	1.3×10^3	2.6×10^3	2.6×10^2	2.1×10^3	5.4×10^2	0.6×10^4

The R value was determined with the sample of the bulk density of 0.8-1.0 g/cm^3 corresponding to the minimum packing of the rock and its porosity of 0.5. This supposed a minor packing of the barrier material during the construction stage. It was the barrier material which was used at the initial phase of backfilling the barrier for the EI-2 PUGR.

It should be noted that the distribution coefficient characterized not only the most common mechanism of the sorption process (the ion exchange) but the other mechanisms, too, Among the specific sorption mechanisms were: the chemisorption – the formation of a chemical compound on the phase boundary; the physical adsorption – the capture of organic molecules by the surface of the solid body; the molecular adsorption – the formation of ion pairs and complex associations on ion exchange materials [6]. Therefore, the technique used to determine the distribution coefficient was true when the separation of a radionuclide from the liquid phase occurred not only by ion exchange, but by means of the other specific processes, too.

The sorption capacity of clay was higher with respect to plutonium and cesium. The K_d values were lower for strontium and uranium, which were the active migration species in natural systems. The K_d values for zirconium and niobium were consistent with those for plutonium (actinides). When the material samples with adsorbed radionuclides were brought into contact with the simulated radionuclide-free layer water, not more than 15% of strontium, cesium, and uranium was desorbed, and less than 3% of niobium and zirconium.

The radionuclide distribution velocity at the minimum degree of the clay packing of 1.0 g/cm^3 would be 10^2–10^4 times slower than the velocity of the water distribution. As the degree of the clay packing was increased up to 1.5 g/cm^3, those values were increased by several orders of magnitude. The inspection of the clay packing in the EI-2 PUGR clay barrier showed that the latter value was exceeded. Under the circumstances the radionuclide distribution would occur merely by the diffusion

mechanism. As a result, not only radionuclides adsorbed on clays, but the non-adsorbed ones would be also captured in pores of the swelling montmorillonite, when water entered the interlayer space of montmorillonite decreasing the water permeability of the barrier material.

5. Conclusions
Thus, results of the accomplished studies allowed to certify the following:
1) The dynamics of leaching and the absolute leach rates values of ^{93m}Nb, ^{94}Nb, ^{93}Zr, ^{60}Co, ^{137}Cs, ^{90}Sr, and actinide radionuclides identified in the samples of the irradiated technological channels of the E110 zirconium alloy witnessed the high corrosion resistance of the irradiated structural elements and parts of the zirconium alloy. It should be mentioned that the extended radiation and thermal impact on the zirconium alloy during the reactor operation did not result in any significant change in the corrosion stability of the irradiated zirconium alloy.
2) When creating the long-term storage point for the graphite stack and construction steelwork from the PUGR the sorption properties of the barrier material of the mix of clays ensured the localization of radionuclides contained in the parts of the irradiated zirconium alloy. The gross activity of those parts was about 1%, which was less than in the irradiated graphite stack of the reactor.
3) Zirconium radwaste PUGR should be attributed to the special RW category and it is not necessary to retrieve it from the reactor. The burial option is more suitable to solve the zirconium RW PUGR problem.

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