

## SPECIATION OF RADIONUCLIDES IN BARRIER MATERIALS OF RADIOACTIVE WASTE STORAGE FACILITIES

Varlakova G. A.<sup>1</sup>, Barinov A. S.<sup>2</sup>

<sup>1</sup>JSC A.A. Bochvar High-technology Research Institute of Inorganic Materials», Moscow, Russia

<sup>2</sup>Nuclear Safety Research Institute of RAS, Moscow, Russia

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*The paper overviews the results of experiments performed to determine the speciation of cesium, cobalt and strontium in natural materials. Such materials are glaciolacustrine clay soils and sands considered as natural barriers in radioactive waste storage facilities. It was found that changes in radionuclide speciation occur as the result of their continuous interaction with the barrier materials. Over time, fixed forms of cesium, cobalt and strontium radionuclides become predominant in the studied barrier materials.*

**Keywords:** radioactive waste, radionuclides, speciation, barrier materials, interaction time, absorption.

Low- and intermediate-level waste are stored/disposed of in near-surface repositories that can be either located at the ground surface level or embedded into the ground. A multi-barrier safety system involving a combination of natural and engineered barriers helping to prevent the effects of ionizing radiation and the migration of radioactive substances into the environment is used to provide the safety of such structures at operational and post-operational stages [1, 2]. Host medium (bedrock) with the repository being located either inside or on its surface is considered as a natural barrier, whereas, the elements of engineered barriers include: buffer material, underlying and covering screens. Natural materials are often used in engineered barriers construction: sand, retrieved soils or their mixtures, since they provide good barrier properties impeding radionuclide migration and are readily available. Thus, material of the host medium can act as a buffer and be applied to construct underlying and covering screens,

which is indeed practiced quite often during the construction of such facilities. Barrier materials limit radionuclide migration but to provide this function these should have good sorption properties with respect to relevant radionuclides and retain the ability to firmly fix them during the time while the radioactive waste potentially remains hazardous. Migration of radionuclides outside the repository and their distribution in the environment depends on sorption properties of the barrier materials, which, in turn, affects radionuclide speciation, especially in a long-term perspective. Over time, after the radionuclides release into natural materials, their physical and chemical speciation changes [3] as the result of the interaction with the barrier materials providing radionuclide fixation on a solid phase and slowing down the migration. Similar to heavy metals, radionuclide speciation in rocks and soils can be conventionally divided into mobile and fixed [3, 4] with water-soluble, absorbed and exchangeable ones attributed to the

## Disposal of Radioactive Waste

mobile type and hardly soluble and residual being attributed to the latter.

It has been continuously noted that during RW repository operation radionuclides speciation in the barrier materials (host rock, buffer backfill) experiences some redistribution [5, 6], the ratios between the portion of radionuclides available in mobile and fixed forms change, affecting their migration capacity [7, 8].

The study is focused on the strength of radionuclide fixation in barrier materials during a long-term interaction with them.

### Experimental part

The experiments were carried out using samples of clay loam mantle taken from a RW repository site and sand of a lake-glacial genesis applied as barrier materials in a near-surface RW repository. Chemical and mineralogical compositions of loams and sand are provided in [9–11]. Clay loam mantle contained quartz, feldspars and clay minerals of kaolinite, illite, vermiculite, montmorillonite groups and hydromica present in the admixtures. Sand mainly consists of quartz with clay minerals, feldspars, glauconite, hydromica, iron compounds being present in some small amounts. In the experiments, fractions of materials with a particle size of less than 2 mm were applied.

The experiment was based on successive treatment of samples with reagent solutions of various compositions after relevant sample material interaction with radioactive solutions for 2 weeks, 1, 2, 4 and 6 months.

The experiments were performed in a following way. At the first stage, sorption experiments were performed suggesting that the studied samples of materials were brought into contact with model deionized water-based solutions containing  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$  and  $^{60}\text{Co}$ . Interaction of soil samples with model solutions took place under static conditions with a 1:2 ratio of solid and liquid phases and a temperature of 22 °C. Individual samples of the two material types corresponded to each contact time and each radionuclide. After a specified time, solid and liquid phases were separated by centrifuge treatment. Activity in the liquid phase was measured by radio- and spectrometric methods. Based on the measurements, the specific activity of a radionuclide in the solid phase ( $A_{s.ph.}$ , Bq/g) was calculated using the following equation:

$$A_{s.ph.} = \frac{(A_0 - A_{l.ph.}) \cdot V}{m},$$

where  $A_0$  is the specific activity of the initial model solution, Bq/ml;

$A_{l.ph.}$  is the specific activity of the model solution after a contact time, Bq/ml;

$V$  is the volume of the model solution interacting with the solid phase, ml;

$m$  is the mass of the solid phase, g.

This method was used to obtain model samples of barrier materials containing radionuclides of cesium, cobalt and strontium.

The second stage involved selective desorption of radionuclides from the solid phase enabling to identify their speciation in the material samples. The method suggested consecutive treatment of samples with solutions involving various reagents [3, 7, 12] enabling the extraction of solid phase radionuclides with different speciation. Table 1 presents the reagents used, the identified radionuclide speciation and the experimental conditions. The samples were treated with reagents in the indicated sequence with a 1:10 ratio of solid and liquid phase stirring. Each stage was completed by solid phase separation from the liquid one using centrifuge treatment. radiometric and spectrometric methods were used to measure the total activity of desorbed radionuclide in the separated liquid phase.

**Table 1. Desorption experiment setup**

Speciation	Stage	Reagents	Experimental conditions
Water soluble	(I)	H <sub>2</sub> O	S:L = 1:10; 22 °C; treatment time 15 min
Exchangeable, readily soluble	(II)	1M·CH <sub>3</sub> COONH <sub>4</sub>	S:L = 1:10; 22 °C; treatment time 60 min
Acid soluble	(III)	6M·HCl	S:L = 1:10; 22 °C; treatment time 60 min
Residual	(IV)	7,5·M HNO <sub>3</sub>	S:L = 1:10; 85 °C; treatment time 60 min

### Results and discussion

Experiments focused on the identifying sorption capabilities with respect to radionuclides [13, 14] gave an idea about their total content in the solid phase (barrier materials), whereas the data on the desorption of radionuclides from the solid phase gave an answer about their speciation allowing to conclude on their bonding strength with the barrier materials and to predict their behavior.

Experiments have shown that the speciation and content ratios for radioactive cesium, strontium and cobalt differ for the studied barrier materials. Radionuclide speciation in these materials changes over time, as evidenced by the data presented in Figures 1–3.

A decreasing fraction of mobile forms (I–III desorption stages) with an increase in the interaction

time with the materials is believed to be characteristic for all radionuclides. At the same time, an increasing fraction of strongly bonded forms of radionuclides extracted at the fourth stage and not being removed from the solid phase is observed. Notably, processes associated with the changing speciation of radionuclides in the materials occur with different speed due to the mechanism of radionuclide absorption by the solid phase: clay minerals entering the crystal lattice, ion exchange, chemical coprecipitation, etc. [15].

Since the first weeks of such interaction with the materials, a significant portion of cesium undergoes into a fixed state (Figures 1a, b). In the soil, cesium is firmly fixed at the level of 95–98% (with the experiment lasting from 4 to 6 months), in sand – at the level of 89–96% and, over time, the portion of fixed cesium increases rapidly. This phenomenon is explained by the fact that cesium enters the crystal lattice of potassium minerals (mica and feldspars, etc.) mainly due to isovalent isomorphism [16], as well as by the presence of iron films (oxides, hydroxides) on the surface of particles significantly contributing to sorption processes.

Over time, a largest portion of mobile forms of strontium present in soil and sand (29% and 25%, respectively) will account for exchangeable and readily soluble forms of radionuclides (Figures 2a, b).

Within the studied timeframe, the content of strontium being available in fixed forms increases by about 2–3 times, but the duration of radionuclide interaction with materials noticeably does not affect its transition to a fixed state.

It has been demonstrated [10, 17] that the content of exchange strontium appears to be practically independent of its interaction time with the soil. As is commonly known, strontium is absorbed by clay minerals via an ion exchange mechanism acting in the interlayer space, gradually replacing exchange cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) until the equilibrium is reached [18], which probably explains the fact that the sorption capacity remains almost unchanged in the subsequent period.

A significant part of cobalt radionuclides changes over from a water-soluble and exchange form into a fixed one as the result of their prolonged interaction with barrier materials (Figures 3a, b).

As noted in [19], cobalt is actively absorbed by clay minerals and oxygen compounds of iron contained in the considered barrier materials. The behavior of cobalt during sorption and its subsequent migration depends on its speciation (available either as an ion or complex) [13, 20] in the soil solution. Under the discussed sorption experiments, cobalt in the model solutions had a cation speciation.

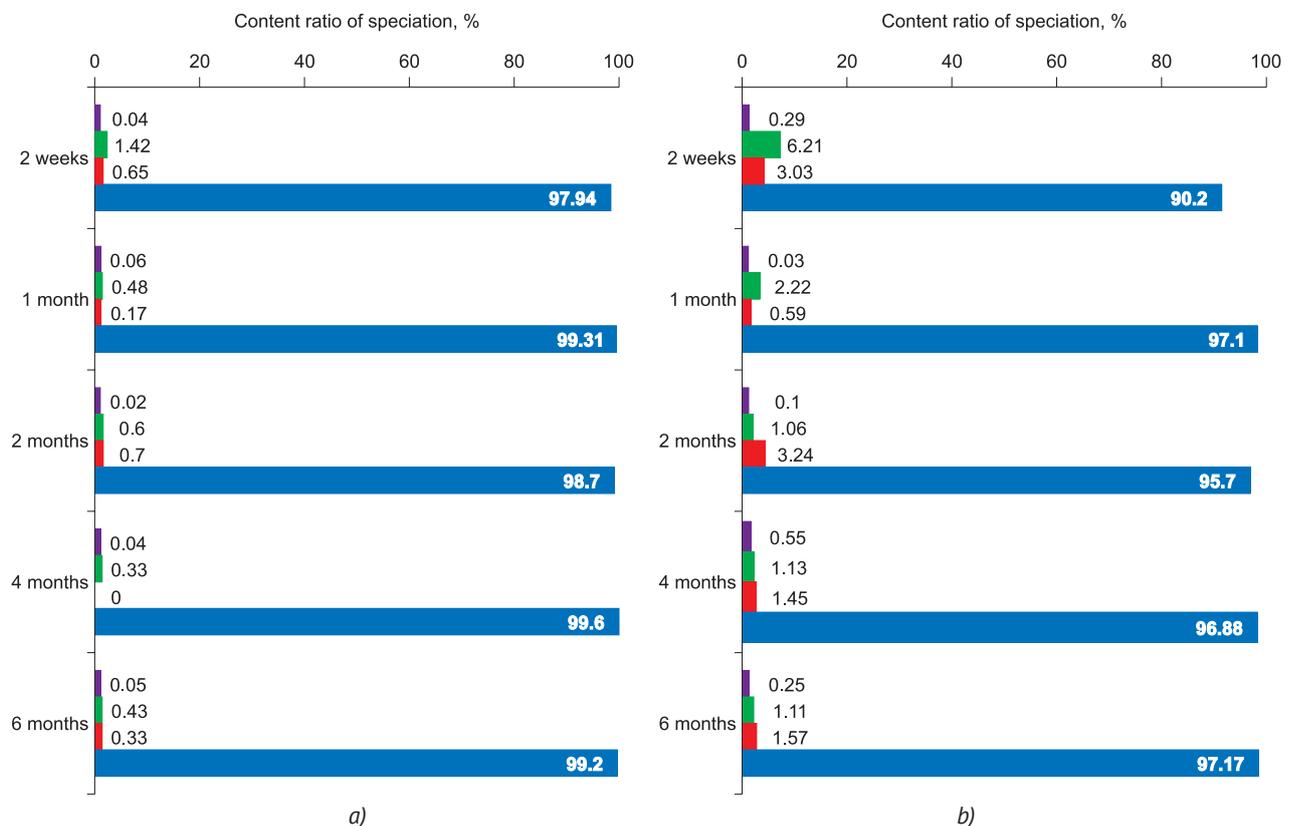


Figure 1.  $^{137}\text{Cs}$  speciation depending on the interaction time with clay soil (a) and sand (b):  
■ – water soluble, ■ – exchange, ■ – acid soluble, ■ – residual

## Disposal of Radioactive Waste

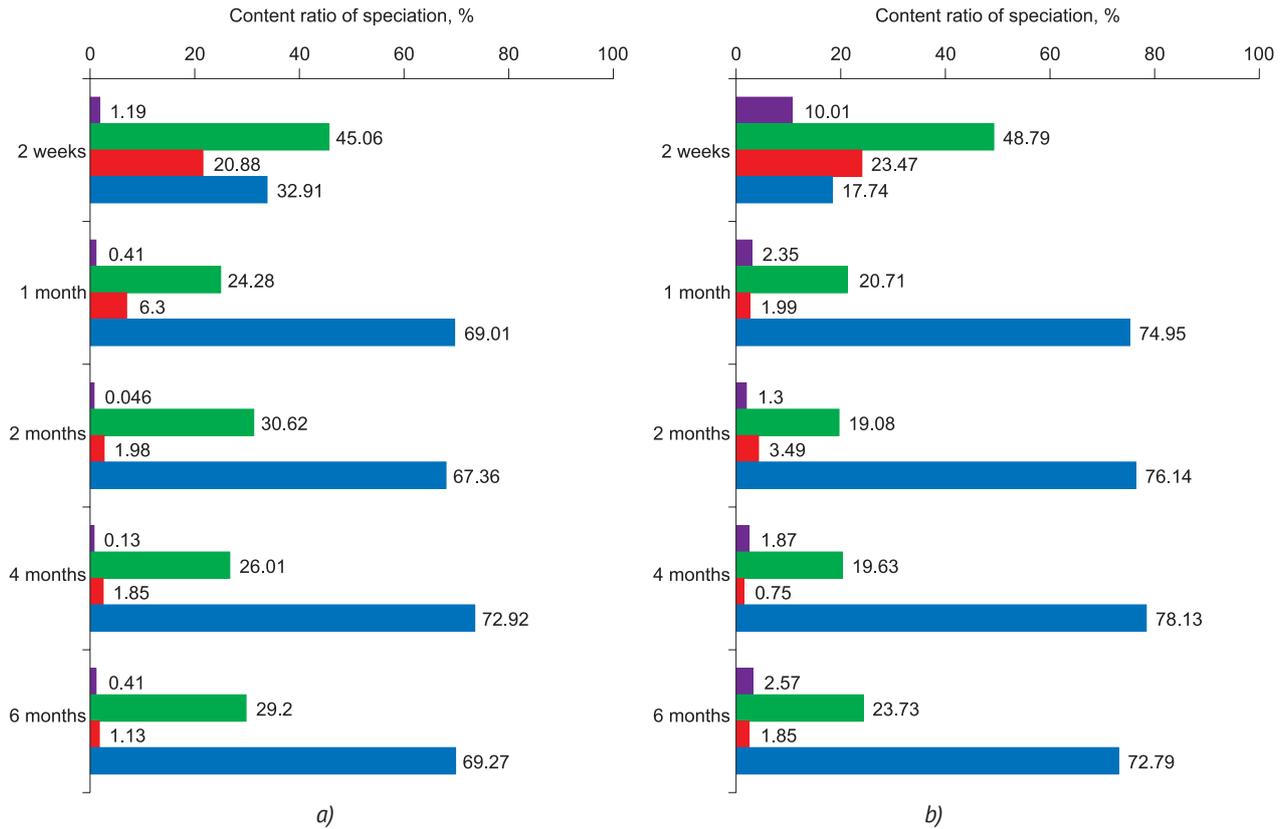


Figure 2.  $^{90}\text{Sr}$  speciation depending on the interaction time with clay soil (a) and sand (b):  
 purple – water soluble, green – exchange, red – acid soluble, blue – residual

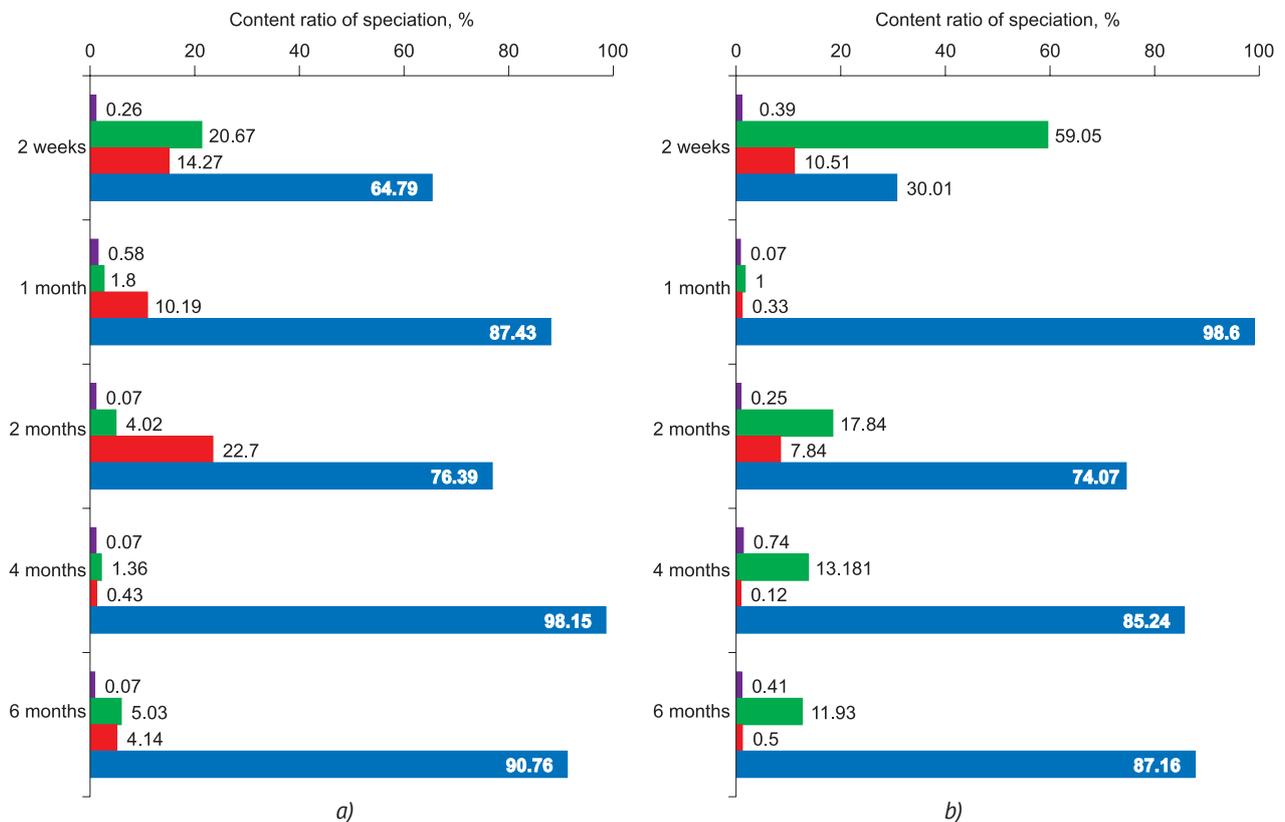


Figure 3.  $^{60}\text{Co}$  speciation depending on the interaction time with clay soil (a) and sand (b):  
 purple – water soluble, green – exchange, red – acid soluble, blue – residual

Identification of radionuclides having various speciation in the materials used for engineered barrier construction evidences that the strength of their bonding to the solid phase, and, consequently, the rate of their migration beyond the repository and into the environment differs. Evaluation of the experiments conducted showed that strontium radionuclides, in comparison with cesium and cobalt being present in a cationic form, are characterized with higher mobility, whereas their transition into fixed forms occurs gradually throughout the experiment. Redistribution of the considered radionuclide speciation in clay soil occurs faster than in sand. In this case, the redistribution rate and the fraction of fixed forms increases over time in the following order  $Sr < Co < Cs$ .

Thus, fixed forms of cesium, cobalt and strontium prevail in the considered materials, which indicates the availability of strong bonds between the radionuclides and the mineral components of clay soil and sand. Over time, the strength of radionuclide fixation by materials increases contributing to their containment within the barriers, whereas radionuclide migration decreases, which was previously confirmed by calculations for strontium and cesium [21].

To conclude it seems worth noting that the findings of the current and other studies on radionuclide behavior in natural environments should be expediently considered and taken into account, for example, in the design development of safety barriers for RW repositories and in assessing long-term safety of RW disposal facilities.

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### Information about the authors

*Varlakova Galina Andreevna*, PhD, Main specialist, JCS "VNIINM" (5a, Rogova St., Moscow, 123098, Russia), e-mail: [varlakova@inbox.ru](mailto:varlakova@inbox.ru).

*Barinov Aleksandr Sergeevich*, PhD, Senior Researcher, Nuclear Safety Institute of RAS (52, Bolshaya Tulkaya, Moscow, 115191, Russia), e-mail: [barinov@ibrae.ac.ru](mailto:barinov@ibrae.ac.ru).

### Bibliographic description

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