LITERATURE CITED

1. V. M. Zaletin, I. N. Nozhkina, V. I. Fomin, et al., "Mercuric iodide crystals for gamma radiation detectors," At. Energ., 48, No. 3, 169 (1980).
2. V. M. Zaletin, V. A. Kochevanov, I. N. Nozhkina, et al., "Detectors on the basis of mercuric iodide crystals for x rays and gamma radiation," At. Energ., 52, No. 3, 193 (1982).
3. M. Slapa, G. Huth, W. Scibt, et al., "Capabilities of mercuric iodide as a room temperature x-ray detector," IEEE Trans. Nucl. Sci., NS 23, No. 1, 102 (1976).
4. E. Sakai, "Present status of room temperature semiconductor detectors," Nucl. Instrum. Methods, 196, No. 1, 121 (1982).
5. A. Dabrowski and G. Huth, "Toward the energy resolution limit of mercuric iodide in room temperature low energy x-ray spectrometry," IEEE Trans. Nucl. Sci., NS-25, No. 1, 205 (1978).
6. V. S. Goreev, V. A. Kozhemyakin, O. A. Matveev, et al., "Application of detectors on the basis of cadmium telluride in the dosimetry of gamma radiation," Prib. Tekh. Eksp., No. 1, 60 (1981).

ASSESSMENT OF PROCESSES OF LEACHING OF SOLIDIFIED RADIOACTIVE WASTE IN THE PRESENCE OF THE WATER OF BARRIER MATERIALS

V. D. Balukova and M. K. Savushkina

UDC 621.039.743

The storage of solidified radioactive waste in geological formations of any type requires an assessment of the possible long-term consequences with due account for the specifics of the radiation effect, which manifests itself both within the medium of the waste itself and in the materials surrounding it. According to available data [1], not one of the matrices proposed at present for the solidification of waste products can be considered to ensure total isolation of radionuclides from the ambient medium. In order to enhance the reliability of the isolation of wastes, additional barriers must be set up when waste materials are buried in geological formations.

The choice of barrier materials should be made with due account for their stability under the possible action of the geological medium and the solidified waste materials.

Determining how long the waste materials must be isolated (hundreds of years) and assessing natural materials from the standpoint of their capability for concentrating radionuclides and confining them under conditions of a thermal and aqueous regime, we can conclude that clay rock is a suitable barrier material. Possessing high sorption properties with respect to radionuclides leached from the waste materials, such rock has low filtration characteristics, which will substantially limit the zone of water exchange around the storage site. Any clay rock, however, contains a considerable amount of water (up to 12 mass %), which under conditions of elevated temperature that is characteristic of storage sites of radioactive waste materials will be released into a separate phase and will appear as a leaching agent. Thus, the creation of clay barriers in storage sites will entail leaching processes for any variant of utilization, including relatively dry conditions.

In this paper we give the results of a study of the physicochemical state of the system: vitrified, on the basis of alumophosphate compositions, waste materials and desorbed water in the temperature range 293-473°K. The model adopted for the interaction process was:

— contact of the water with the waste materials begins immediately after the storage site is loaded as a result of thermal migration of water from bentonite clay, and the protective barrier is mostened;

— as a result of the contact of the water with the waste materials macrocomponents as well as radionuclides are leached out of the waste;

Translated from Atomnaya Énergiya, Vol. 63, No. 4, pp. 277-279, October, 1987. Original article submitted January 12, 1987.

0038-531X/87/6304-0801$12.50

TABLE 1. Leaching Rate of Elements of Aluminophosphate Compositions at Different Temperatures, $V \cdot 10^6$, $g \cdot cm^{-2} \cdot day^{-1}$

Temp., °K	V_P	V_{Al}	$V_{Na, K, Sr, Fe, Cr, Ca}$	V_{Cs}
293	1,12	0,2	2,61	26,1
368	5,66	0,6	11,18	111,8
393	16,65	1,7	22,40	224,0
473	86,40	9,0	126,60	1266,0

TABLE 2. Distribution of Stable Elements in the Studied Systems at Different Temperatures, °K*

Charateristic	Series No.													
	3	4	5			6			7			8		
	293	293	293	368	473	293	368	473	293	368	473	293	368	473
Element in solid phase, %														
Fe	—	21	45	35	38,0	91	93,5	94	97,5	98	99	94,5	97,5	98,5
Al	51	71	91	93	92,8		~ 99			~ 99			~ 99,9	
Cr	—	—	—	—	—		~ 70			~ 84			~ 93,0	
Ca	—	—	—	—	—		~ 45			~ 87			~ 90,0	
Amount of solid phase:														
vol. %	—	—	—	—	—	6,5	1,5	1,0	12,0	3,5	2,5	38,0	12,4	9,0
mass % of initial salt content	—	—	1,84	—	—	9,3	9,45	8,34	9,16	11,92	10,2	16,0	18,0	16,6

*The sensitivity of the methods of analysis used allowed the aluminum determination to be started from series No. 3, that of Fe from series No. 4, and that of Cr and Ca from series No. 7.

— the low filtration parameters of clay rock allow us to disregard the processes of water exchange in the barriers over a period of several years.

In accordance with the model adopted, the physicochemical parameters of the system formed in particular periods of interaction will depend on the leaching rate of components of the waste materials under the particular conditions of the storage site, i.e., under the conditions of the radiation-thermal loads and with a low ratio V/S = 0.3-0.5 cm, on interaction time, as well as on amount of desorbed water, which depends on the thickness of the bentonite barrier.

Experiments designed to ascertain the effect of the temperature (up to 673°K), irradiation (range of absorbed dose 10^5-10^9 Gy), and leaching agents of various quantitative and qualitative composition on the elution rate of components of alumophosphate composition (P_2O_5:Me_2O:ΣMe_nO_m = 5:3:2) showed that the leaching temperature is the main parameter that determines their stability; under conditions when the temperature is above 373°K the process of fracturing of the matrix is intensified substantially while at 473°K the leaching rate of modifer-elements (Na, K, Cs, Sr, etc.) becomes equal to the leaching rate of the vitrifier-element, phosphorus (Table 1).

The experimental values obtained for the leaching rate of components of alumophosphate compositions under conditions when V/S = 0.5 cm in the temperature range 368-473°K enable us to calculate the parameters of solutions formed during the interaction of desorbed water with solidfied wastes. For our experimental study we chose a wide range, comprising eight series, in which the concentration of elements increases by a factor of five from series to series (pH = 9.93):

TABLE 3. Radionuclide Distribution in the Studied Systems at Different Temperatures, °K

Precipitate, %	Series No.													
	1–3	4	5			6			7			8		
	293–473	293–473	293	368	473	293	368	473	293	368	473	293	368	473
^{90}Sr	0	5,6—5,8	59	79,8	91,3	56	89	93,3	87,2	93	95,2	98,2	98,9	99,2
^{137}Cs	0	0	0	0	0	0,07	1,31	10,2	6,13	4,1	8	5,5	1,4	8,2

Element	Conc., g-ion·liter
P	$1 \cdot 10^{-4}$—$2{,}55 \cdot 10^{-1}$
Na	$2{,}4 \cdot 10^{-4}$—$4 \cdot 10^{-1}$
K	$1 \cdot 10^{-5}$—$5 \cdot 10^{-2}$
Al	$6{,}8 \cdot 10^{-6}$—$1{,}9 \cdot 10^{-2}$
Fe	$1{,}8 \cdot 10^{-7}$—$5 \cdot 10^{-3}$
Cr	$8 \cdot 10^{-8}$—$3{,}2 \cdot 10^{-4}$
Ca	$1 \cdot 10^{-7}$—$3{,}8 \cdot 10^{-4}$
^{90}Sr, Bq·liter^{-1}	$2{,}2 \cdot 10^{7}$—$1{,}1 \cdot 10^{11}$
^{137}Cs, Bq·liter^{-1}	$1{,}5 \cdot 10^{8}$—$3{,}7 \cdot 10^{11}$

The systems were modeled by means of nitrate salts. Phosphorus was introduced in the form of disubstituted phosphate, which corresponds to the form in which phosphorus exists in leached solutions at pH = 9-9.3. The cations were analyzed by the atomic-absorption method (Perkin-Elmer 503), phosphorus was analyzed calorimetrically on the basis of phosphorus—molybdenum blue, and ^{90}Sr and ^{137}Cs on the basis of the β and γ count, respectively. Besides monitoring the phase state and the behavior of the radionuclides in the individual phases, we also studied the effect of the temperature on the indicated processes.

The data given in Table 2 on the state of the stable elements in the studied series attest to a homogeneous instability of the systems, which begins to manifest itself even in the initial series, i.e., in the initial stages of the leaching process. Variation of the temperature in the range 293-473°K has little effect on the distribution of the elements, while the second-phase precipitate that is formed becomes substantially denser with rising temperature.

Table 3 gives data on the radionuclide distribution under the conditions of the formation of solid phases: we seen that the bulk of the eluted ^{90}Sr and part of the ^{137}Cs are introduced into the solid phase, and as the temperature rises the amount of ^{90}Sr introduced into the second-phase precipitate increases. The behavior of the leached ^{137}Cs is interesting. During the formation of a considerable amount of solid phase, some of the radionuclides are removed from the solution and the temperature dependence of the cesium content in the precipitate passes through a minimum at 368°K while at 473°K it exceeds the analogous value determined at 293°K.

The experimental data permit the conclusion that in a comprehensive consideration of the problem of leaching of solidified radioactive waste materials, when elution of macrocomponents is taken into account along with elution of radionuclides, the leaching process is accompanied by the formation of second solid phases, which substantially affect the behavior of the radionuclides. Of the ^{90}Sr leached out 99% is once again fixed in the solid phase, while all of the ^{137}Cs remains in the active form. An increase in the temperature in the range 293-473°K promotes the introduction of radionuclides into the solid phase.

Since any geological rock formation contains sorption water, that water will act as the first leaching agent.

The data reported here attest to the necessity of making certain corrections to the calculations of the migration of radionuclides beyond the boundaries of the storage site.

LITERATURE CITED

1. Characteristics of Solidified High-Level Waste Products, Technical Rep., Ser. No. 187, IAEA, Vienna (1979), pp. 1-113.