

Influence of Phosphate Glass Recrystallization on the Stability of a Waste Matrix to Leaching

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Abstract—In Russia, highly radioactive liquid wastes from recycling of spent fuel of nuclear reactors are solidified into Na–Al–P glass for underground storage. The properties of the matrix including the radionuclide fixation will change with time due to crystallization. This is supported by the results of study of the interaction between glassy matrices, products of their crystallization, and water. The concentration of Cs in a solution at the contact of a recrystallized sample increased by three orders of magnitude in comparison with an experiment with glass. This difference is nearly one order of magnitude for Sr, Ce, and Nd (simulators of actinides) and U due to their incorporation into phases with low solubility in water. Based on data on the compositional change of solutions after passing through filters of various diameters, it is concluded that Cs occurs in the dissolved state in runs with a glass and recrystallized matrix. At the same time, Sr, lanthanides, and U occur in the dissolved state and in the composition of colloids in runs with glass, and mostly in colloid particles after contact with the recrystallized sample. These results should be regarded for substantiation of safety for geological waste storage.

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Solidified highly radioactive wastes (HRWs) from recycling of spent nuclear fuel (SNF) should be isolated from the biosphere in geological storage for many hundreds of thousands of years [1]. A system of engineering barriers with a form (or matrix) for wastes is a key element for localization of HRW. Among the other elements are a metallic container, sorption bentonitic buffer, filling of crushed rocks, and concrete lining of the storage container.

Aluminophosphate glasses are applied as a matrix for HRW on an industrial scale in Russia, and borosilicate glasses are used in other countries [1]. From 1987 to 2010, 28 600 m³ of liquid HRWs were vitrified at the Mayak plant and 6200 t of phosphate glass with a total activity of 640×10^9 Ci or 2.4×10^{19} Bq was obtained [2]. By the year 2020, solidification of the existing 18 000 m³ of liquid wastes will additionally produce ~6000 t of glass, which should be placed in underground storage.

The safety of such storage is mostly determined by the ability of the matrix to hold radionuclides. The properties of Na–Al–P glasses, including their behavior in water, were previously studied in the range of 20–250°C [1, 3–9]. An increase in their solubility with temperature [1–5] and after crystallization [3, 5–9], as well as enhancement of corrosive stability upon introduction of iron and boron, were observed. The glass will recrystallize with time, which is stimulated by heating resulting from radionuclide decay. This will lead to an increase in matrix solubility in water after corrosion of the container. Thus, the rates of Na and Cs leaching in experiments with a duration of several days increase by one or even two orders of magnitude [5–8], whereas recrystallization of glass does not have a significant influence on the behavior of Sr.

It is considered [10] that, after closure, the storage of vitrified HRWs will be characterized by a high temperature and atmosphere of unsaturated vapor. The temperature will change from 90 to 140°C, and the relative humidity will not exceed 80% during the first 50 years, and will reach 100% only after 100 years due to water penetration from host rocks. Corrosion of the container at this stage will cause recrystallization of the aluminophosphate glassy matrix under the influence of heated water vapor and change in its isolation properties.

We studied the influence of glass crystallization with waste simulators on its behavior in water. The

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Table 1. Compositions (wt %) of initial and hydrated glass and phases in the recrystallized glass sample. The atomic contents of elements in conventional formulas calculated for 10 cations are given

Oxide/At. content	Glass		Na–Al-phosphate-I	Na–Al-phosphate-II	Sr–Ln–U-phosphate	Cs–U-phosphate
	starting	hydrated				
Na ₂ O	17.3	8.6 ¹ (10.3) ²	22.9	14.2	–	1.9 ¹ (2.2) ²
Al ₂ O ₃	14.0	12.7 (15.3)	19.2	14.4	2.0*	1.5 (1.8)*
P ₂ O ₅	51.1	45.5 (54.4)	53.1	50.4	32.1	15.9 (18.8)
Fe ₂ O ₃	5.5	5.7 (6.8)	4.8	10.1	–	1.1 (1.3)*
NiO	1.1	1.1 (1.3)	–	7.0	–	–
SrO	2.1	1.9 (2.2)	–	2.8	11.5	–
Cs ₂ O	2.5	2.3 (2.7)	–	1.1	–	13.3 (15.7)
Ce ₂ O ₃	2.1	1.9 (2.3)	–	–	20.6	–
Nd ₂ O ₃	2.0	1.7 (2.0)	–	–	17.9	–
UO ₂	–	–	–	–	15.9	–
UO ₃	2.3	2.1 (2.7)	–	–	–	51.0 (60.2)
Σ	100.0	83.5 (100.0)	100.0	100.0	100.0	84.8 (100.0)
Na ⁺	3.27	2.11	3.84	2.69	–	1.00
Al ³⁺	1.61	1.89	1.96	1.66	0.44*	0.50*
P ⁵⁺	4.22	4.86	3.89	4.15	5.06	3.73
Fe ³⁺	0.40	0.54	0.31	0.74	–	0.23*
Ni ²⁺	0.09	0.11	–	0.55	–	–
Sr ²⁺	0.12	0.14	–	0.16	1.24	–
Cs ⁺	0.10	0.12	–	0.05	–	1.57
Ce ³⁺	0.07	0.09	–	–	1.41	–
Nd ³⁺	0.07	0.08	–	–	1.19	–
U ⁴⁺	–	–	–	–	0.66	–
U ⁶⁺	0.05	0.06	–	–	–	2.97
O ²⁻	15.76	17.53	15.05	16.08	19.77	20.62

¹ Real analysis; ² analysis normalized to a total of 100 wt %; * capture of other phases during the analysis. It is assumed that U occurs as U(VI) in glass and Cs–U phosphate and as U(IV) in the phase with the monazite-type structure. The data for the initial glass and hydrated glass from the run with water are given. The dash means that the concentration is below the detection limits (0.3–0.5 wt %). The accuracy of analysis is 3–5 rel %.

procedure of rapid glass alteration (vapor hydration test) was worked out in the United States [11, 12]. Massive samples with a small content of water (a relative humidity of 70–95%) are loaded into an autoclave at 90–300°C for a period from a few days to several hundred. Such investigations are aimed at estimation of the behavior of glass in water-unsaturated media (e.g., in tuff [11]) or on rapid testing of the properties of various matrices. One more task is to model alterations of the glassy matrix at the early stage, prior to inflow of water into the storage area from host rocks [12].

To study the influence of recrystallization on the properties of glass, we prepared a model sample with waste simulators (Table 1). In contrast to the regulated

composition, some aluminum (~25%) was replaced with iron in its composition. This is explained by the fact that iron occurs in wastes, as well as by the revealed high stability of iron–phosphate matrices [9] in relation to the aluminophosphate compositions. A glass sample with a surface area of 3 cm² and 1 ml of water was loaded into a titanium autoclave with a volume of 33 cm³ and kept for one day at 300°C. Such a content of water provided a water vapor pressure of 75% from the value of saturation. There was no free liquid in the experiment, which prevented leaching of elements from the sample and change in its bulk composition. After the run, the sample of modified glass was studied on a scanning electron microscope (SEM/EDS) and by the X-ray phase analysis (XRPA).

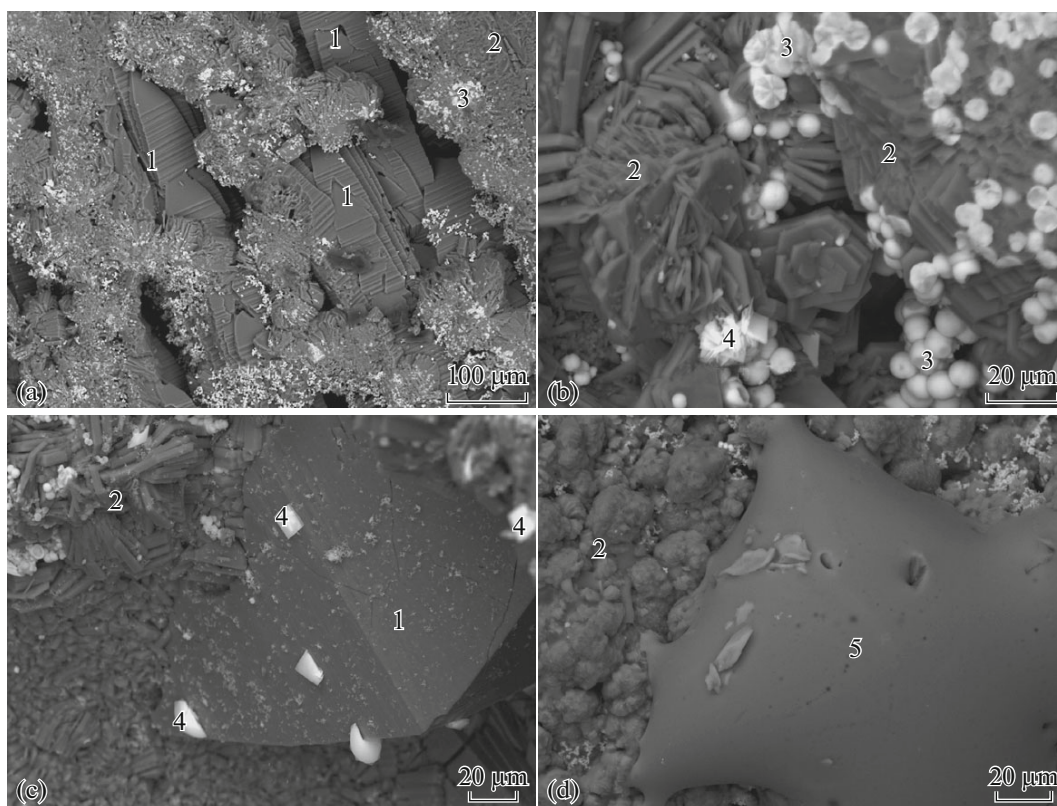


Fig. 1. SEM image of a recrystallized sample. Numerals indicate phosphate-I (1), phosphate-II (2), monazite (3), Cs-U phosphate (4), and amorphous material (5).

SEM/EDS study of the sample section treated with vapor showed that the sample was fully composed of an aggregate of newly formed phases (Fig. 1). The major phases among them are two types of Na–Al–Fe phosphates with different grain morphologies and compositions (Table 1). Phase I forms prismatic crystals with pyramidal edges and without impurities in the composition. Phase II has a flattened hexagonal grain morphology and a more complex composition with impurities of Ni, Sr, and Cs. Small spheres of white color are registered as Sr–Ln–U phosphate with a monazite structure; another phase is the Cs–U phosphate forming flattened crystals of a square shape. There are amorphous segregations with a size of a few hundreds of microns (Fig. 1d). The low total of elements in analysis and effervescence in an electron beam allow us to assume the presence of water. Excluding water, their composition is characterized by the following ranges (wt %): 18.6–22.9 Na, 0.6–1.0 Al, 24.4–26.7 P, 10.6–11.9 Cs, 41.1–42.2 O. One analysis is recalculated for oxides (wt %): 30.7 Na₂O, 1.4 Al₂O₃, 58.6 P₂O₅, 9.3 Cs₂O, which corresponds to the conventional formula (Na_{5.18}Cs_{0.35}Al_{0.15}P_{4.32})O_{13.79}.

To study the influence of crystallization on the behavior of the matrix in water, glass or the product of its crystallization together with 26 ml of water were loaded into autoclaves for 44 days at 90°C. After runs,

they were studied by the SEM/EDS methods, and the composition of the solution was analyzed by the method of ICP-MS. The solution was passed through filters with a pore diameter of 450–25 nm and then was analyzed by ICP-MS in order to study speciation of elements in the solution.

The compositions of the phases were recalculated for nominal (integral) formulas like Na₄(Al,Fe)₂P₄O₁₅ for phosphate-I, (Na,Sr,Cs)₃(Al,Fe,Ni)₃(PO₄)₄ for phosphate-II, (Ce,Nd,Sr,U)PO₄ for monazite, and (Cs,Na)UPO₆. A more exact formula of the latter phase is Cs₂[(UO₂)(PO₄)₂(H₂O)₅], and, according to the structural peculiarities, it corresponds to the meta-autunite group [13]. The low total of the element concentrations (Table 1) provides evidence for the presence of water in it. The occurrence of phosphate with a monazite structure in the sample is supported by XRPA. Note that the first of the phases (phosphate-I) mentioned was found in the products of crystallization of phosphate glasses under dry conditions [7]. Additional studies will be carried out on a transmitted electron microscope. The presence of water-soluble phases (Cs–U phosphate and amorphous material) in the recrystallized sample shows that the free phase was actually absent in this run.

Table 2. The compositions of solutions (ppb) from runs with glass (g) and the crystalline sample (c). Numerals indicate initial solution (1) and its aliquots after filtration through the pores of 450 (2), 200 (3), 100 (4), and 25 (5) nm.

No.	Na	Al	P	Ni	Sr	Cs	Ce	Nd	U
g-1	11116	2976	5292	84	148	384	13	9	124
g-2	10572	2568	2100	44	140	416	9	5	28
g-3	11648	2676	2120	28	164	532	10	5	18
g-4	11940	2456	2420	60	140	472	8	4	10
g-5	11096	2320	1536	56	140	440	7	4	2
c-1	763268	5604	954592	96	864	339444	180	136	1852
c-2	770480	2944	937804	38	252	343184	16	12	224
c-3	748252	2396	921252	44	184	335300	11	7	140
c-4	742568	2556	924708	72	164	333144	9	5	88
c-5	729596	2332	894920	56	144	331280	8	4	64

The detection limit is 1–10 ppb for light elements (including Ni) and 0.01 ppb for heavier elements. The accuracy of analysis of these elements is 3–10 and 1 rel %, respectively.

The compositions of the initial solutions in runs with glass and the recrystallized sample and their filtrates are given in Table 2. Significant changes in the composition of the solution in the run with glass are observed for P and U. Their concentrations decrease by factors of 2.5 and 4.5 after the largest filter (450 nm), whereas this decrease is less significant for Al and REEs. Passing through pores of smaller size results in a continuous decrease in the concentrations of Ce, Nd, and especially U in the solution. The last filtrate (25 nm) contains almost half of the starting Ce and Nd concentrations and only a few percent of the uranium. The concentrations of other elements remain on the same level (Na, Cs, and Sr) or change irregularly (Ni). Such a feature is most likely explained by difficulty in analysis of the low concentrations of Ni. We should also emphasize the decrease in the concentration of phosphorus in the solution after the finest filter.

The concentrations of Na, Cs, and P increase sharply (by factors of 70–900) in the solution with the recrystallized sample and almost do not change after filtering. The concentrations of Al, Sr, Ce, Nd, and U increase to a lower degree (by factors of 2–15) (Table 2). Filtering through pores with a size of 450 nm results in a decrease in the concentrations of Al, Ni, and Sr in the solution by a factor of 2–3, but then their concentrations in filtrates change slightly. At the same time, Ce, Nd, and especially U demonstrate a remarkable decrease in their concentrations in the solution after passing through filters with decreasing pore size. This shows that the colloid form is significantly important for these elements; the role of this form increases from Al, Ni, and Sr to Ce, Nd, and U. It is expected that the three last elements will occur as colloid particles of various sizes.

We may suggest with a high degree of confidence that a sharp increase in the concentrations of Na, Cs, and P in the solution from the run with recrystallized

glass results from dissolution of amorphous material. This is evident from the similar proportions Na : Cs : P in this material and the solution after the run (Tables 1, 2), which are ~2 : 2.5 : 1. The high concentration of U in this solution is most likely explained by dissolution of Cs–U phosphate, and then U is mostly sorbed on colloid particles. Due to dissolution, amorphous material and Cs–U phosphate were not registered after the contact between the recrystallized sample and water.

We should point out the low concentration of Sr and REEs in solutions from the runs with the crystalline sample, which is explained by their fixation in phosphate with the monazite-type structure. This phosphate is characterized by a high uranium content, which prevents its leaching. In contrast to Cs–U phosphate with U⁶⁺, monazite most likely contains U⁴⁺. This explains incorporation of Sr in monazite by the reaction $2(\text{Nd}, \text{Ce})^{3+} = \text{Sr}^{2+} + \text{U}^{4+}$. The atomic portion of Sr²⁺ is almost two times higher than U⁴⁺, and preservation of a zero charge of the crystalline cell requires the occurrence of some cerium as Ce⁴⁺. Therefore, the formula of this phase may be written as $(\text{Nd}_{0.25}^{3+}\text{Ce}_{0.15}^{3+}\text{Sr}_{0.3}^{2+}\text{Ce}_{0.15}^{4+}\text{U}_{0.15}^{4+})\text{PO}_4$.

The data on the compositions of unfiltered solutions are applied for calculation of the normalized rate of leaching of elements from glass by the formula

$$J_{el} = \frac{C_{el}\rho V}{St},$$

where C_{el} is the weight concentration of an element in the solution; ρ is the density of the solution; V is the volume of the solution; t is the period of leaching; and S is the sample surface. The values obtained are the following ($\text{g m}^{-2} \text{day}^{-1}$): 0.11 (Na), 0.05 (Al), 0.03 (P), 0.02 (Cs), 0.01 (Ni), 0.01 (Sr), 0.008 (U), 0.0009 (Ce), 0.0006 (Nd). We should emphasize the lower value for Cs than that for Na. Waste simulators, especially

REEs and U, are characterized by low rates of leaching comparable with those of crystalline matrices worked out for their immobilization [1]. A thin (20 μm) zone with a low concentration of sodium and total of all elements (Table 1) is formed on the sample surface after the contact with water, which indicates the presence of water in it. Its appearance is explained by the reactions of ion exchange between glass and solution and by diffusion of water into the matrix. Such zones are typical of hydrothermally altered borosilicate glasses [1, 12]. Their formation impedes the transition of elements from the glassy matrix to the solution. The rate of leaching was not calculated for the recrystallized sample due to the high porosity and complexity in estimation of its surface area.

We can see the significant influence of glass recrystallization on the concentration of Cs in the solution and the less significant influence on other waste simulators (Ni, Sr, Ce, Nd, and U). Intensification of leaching after vapor hydration was registered for borosilicate matrices as well [11, 12]. Glasses used for immobilization of wastes in the plants of the Savannah River (SRL glass) and West Valley (WV glass) and containing U, Th, Np, Pu, Am, and Tc were hydrated by vapor at 90°C (30–180 days), 150°C (30–143 days), and 200°C (10–44 days). The size of alteration increases with the temperature and duration of treatment, but does not exceed 70 μm . The following phases were registered on the surface of the samples: potassic feldspar KAlSi_3O_8 , zeolites, namely analcite ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$) and gyrolite ($\text{NaCa}_{16}(\text{Si}_{23}\text{Al})\text{O}_{60}(\text{OH})_8 \cdot 14\text{H}_2\text{O}$), as well as phosphates of Ca (apatite), Na–Ca–Fe (wicksite), and LiPO_4 . This provides evidence for the much higher stability of borosilicate glass to recrystallization in comparison with aluminophosphate glass. There was no liquid phase in runs; therefore, actinides were not removed from the samples and they preserved their composition. After vapor hydration, the samples were subjected to leaching with distilled or mineralized water at 90°C for 28 days. The proportion between the sample surface and solution volume varied from 0.1 to 0.3 cm^{-1} . The concentration of actinides in water from runs with altered glass SRL increased by factors of 10 (for Np) and 300–500 (for Pu and Am) in comparison with unaltered glass. Their concentrations in unaltered glass WV [11] increased by factors of 3 for Np and 4–10 for Pu and Am. Leaching of Cs after vapor hydration of glass increased by a factor of 5–20, which differentiates borosilicate matrices from the aluminophosphate composition studied.

The change in the concentrations of elements in the solution after vapor hydration of glass is determined by the properties of newly formed phases. If crystallization of glass results in the formation of poorly soluble phases of radionuclides, their concentration in the solution at the contact with the matrix will be low. The newly formed phase may be repre-

sented by REE silicate of the britolite type and phosphates for borosilicate matrices or monazite for phosphate glassy matrices. The relatively slight increase in the degree of Cs leaching from borosilicate glass after vapor hydration is explained by the formation of silicate phases (tobermorite, zeolites), which bond Cs tightly in the crystal structure [11, 12].

The results obtained allow us to conclude that Cs in the products of leaching occurs in dissolved form in runs with glass and the recrystallized matrix. Sr and Ni in water from the experiment with glass occur in the dissolved state as well, whereas REEs and especially U are characterized by a significant role of the colloid form in the contact solution. The significance of colloid particles increases upon glass recrystallization: most REEs and U occur as colloid particles of various sizes in the solution. In addition, in contrast to the run with glass, a remarkable portion of elements such as Ni and Sr (from 50 to 80%) occurs in the colloid particles in the solution after contact with recrystallized sample.

Behavior similar to that of REEs and U should be expected from actinides with the stable tri- (Am, Cm) and tetra (Np, Pu) states under conditions of the HRW storage [14]. The most dangerous are colloid form [15] of these elements, as well as long-living radiogenic isotopes ^{14}C , ^{36}Cl , ^{79}Se , ^{99}Tc , and ^{129}I , which migrate in anionic state. Their fixation is provided by the bentonitic buffer, and small portion released from the waste storage will be diluted up to a safe level with pure underground waters.

Thus, rapid crystallization of aluminophosphate glass proceeds under the influence of heated water vapor. The intensity of alteration of this composition is much higher than that of borosilicate glasses. After crystallization, the concentrations of Na, P, and Cs in the contact solution increase sharply (by factors of 70–900), whereas the concentrations of other elements increase by less than a factor of 15. This is explained by their fixation in different phosphate phases with a low solubility in water.

Considering the state of waste imitators, we should note that Ni, Sr, and Cs are dissolved in water in the run with glass. Other elements, such as Ce, Nd, and U are in the dissolved state and form colloid particles of different sizes as well. The portion of the colloid form is 45–55% for REEs and 98% for U. After recrystallization of glass, the colloid form still predominates strongly for U and increases up to 95–97% for lanthanides. The same behavior may be expected for radionuclides with similar properties (Np, Pu, Am, and Cm). Some Ni and Sr occur in colloid particles in the solution from the run with recrystallized glass as well, whereas Cs occurs only in the dissolved state. These results should be considered for the long-term prediction of the behavior of vitrified HRWs in the storage and for creation of an optimal system of safety barriers in it. In particular, the presence of a waterproof and

sorption capacious bentonitic buffer will be a reliable barrier against migration of HRWs in the dissolved (Cs) and colloid forms.

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