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It was found that under heating the influence of porosity on deformation and thermophysical properties of rocks enhances. Thus, at higher temperatures the pattern of their changes will be similar to the changes of porosity one. However, to establish more accurate correlations calls the further studies.

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Mineral matrix materials for fixation of radionuclides.

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Abstract. For immobilization of radwaste elements in the Earth crust we for the first time enunciate the principle of phase and chemical accordance in the system matrix – enclosing rock. This principle allows producing motivated synthesis of specific mineral matrixes. Mineral matrixes for immobilization of alkaline, alkaline-earth and rare earth elements – radionuclides were experimental synthesized. Besides that the methods of fixation and separation of noble metals (radwaste components) and halogenides (Br and I) were developed and tested. The problem of processing of glass matrixes (borosilicate and aluminophosphate glasses) to the stable crystalline mineral materials is considered. Methods of radwaste elements fixation from glasses to mineral solid solutions have been developed.

Keywords: experiment, radioactive waste, mineral matrix, borosilicate and aluminophosphate glasses

During more than semicentennial period of exploitation of nuclear piles through to recent time a lot of radwaste is accumulated. Existent methods of radwaste immobilization into glasses are not in accord with specification of defensive keeping of matrix materials because glasses are metastable phases.

In this paper two main problems of radwaste immobilization are considered:

1. synthesis of mineral matrix materials for radwaste fixation (based on the solid solutions of rock-forming and accessories minerals);
2. remaking of glass matrixes into stable mineral matrixes.

Determination of first problem provides for formation of matrix materials stable in conditions of long-time keeping in rocks of Earth crust. For development of mineral matrixes principle of phase and chemical correspondence in the system matrix – country rock which allow producing of task oriented synthesis of determine mineral matrixes has been represented.

Following specifications to matrix materials have been developed:

1. capacity to join and refrain as solid solutions most number of radionuclides and products of their disintegration during a long time (for geological scale);
2. to be stable materials in relation to the processes of physics-chemistry weathering in conditions of dumping (longtime keeping);
3. to have a complex of physics-chemistry properties which any matrix material must have: mechanical resistance, high thermal conductivity, small coefficients of heat expansion, stable to radiation damage;
4. technological scheme of their producing must be maximum simple;
5. matrix material in terms of quantity must satisfy to conception of phase and chemical correspondence in the system matrix – solution – country rock.

Table 1. Compositions of radwaste (after 5 years exposition in the pools-settling sumps)

Z[1)]	Elements	mass.%[2)]	Z	Elements	mass.%	Z	Elements	mass.%
11	Na	19.94	32	Ge	0.00091	50	Sn	0.05
12	Mg	0.56	33	As	0.00037	51	Sb	0.03
13	Al	4.54	34	Se	0.13	52	Te	0.07
14	Si	0.84	35	Br	0.06	53	I	0.29
15	P	0.01	37	Rb	1.29	55	Cs	7.10
19	K	6.74	38	Sr	1.75	56	Ba	2.66
20	Ca	0.85	39	Y	2.02	57	La	1.46
24	Cr	0.09	40	Zr	9.70	58	Ce	6.64
25	Mn	1.12	41	Nb	0.02	59	Pr	2.03
26	Fe	4.47	42	Mo	6.17	60	Nd	7.10
28	Ni	0.83	43	Tc	1.63	62	Sm	1.28
	Sum	39.99	44	Ru	3.77	63	Eu	0.38
			45	Rh	1.00	64	Gd	0.06
			46	Pd	1.29	65	Tb	0.003
			47	Ag	0.03	66	Dy	0.00009
			48	Cd	0.03		Sum	58.52
			49	In	0.03			
						92	U	0.66
						93	Np	0.02
						94	Pu	0.03
						95	Am	0.57
						96	Cm	0.02
							Sum	1.30

1) Z – element number; elements Z= 11÷28 – constructional and technological; Z= 32÷66 – fission-produced; Z= 92÷96 actinides.

2) Element contents calculated on the dry balance.

In our work we decided to apply method of so called “wet” process which allows producing control fixation of radionuclides on the mineral sorbents at normal conditions and allows to distinct decrease PT-parameters of matrix materials synthesis.

Total scheme of process can be presented by following way: water solution of radwaste elements → separation into element group → sorption from water solutions, precipitation and substitution reactions → phase transformation → mineral matrix for location in the rocks of Earth crust.

We suppose original methods of synthesis of mineral matrix materials based on the sorption reactions, metasomatic substitution reactions and reactions of precipitation from water solution which produce at room temperature and pressure. Follow phase transformation transverses these materials into high stable mineral matrix materials geochemically compliant with rocks of assumed fields of location and dumping of matrixes with radionuclides. Compositions of radwaste are presented in Table 1.

More dangerous radionuclide groups are: (1) alkaline and alkaline-earth elements (Rb, Cs, Sr, Ba); (2) rare earth and transuranium elements (La…Dy; U...Am); (3) halogenides (Br, I); (4) precious metals (Ru, Rh, Pd, Ag).

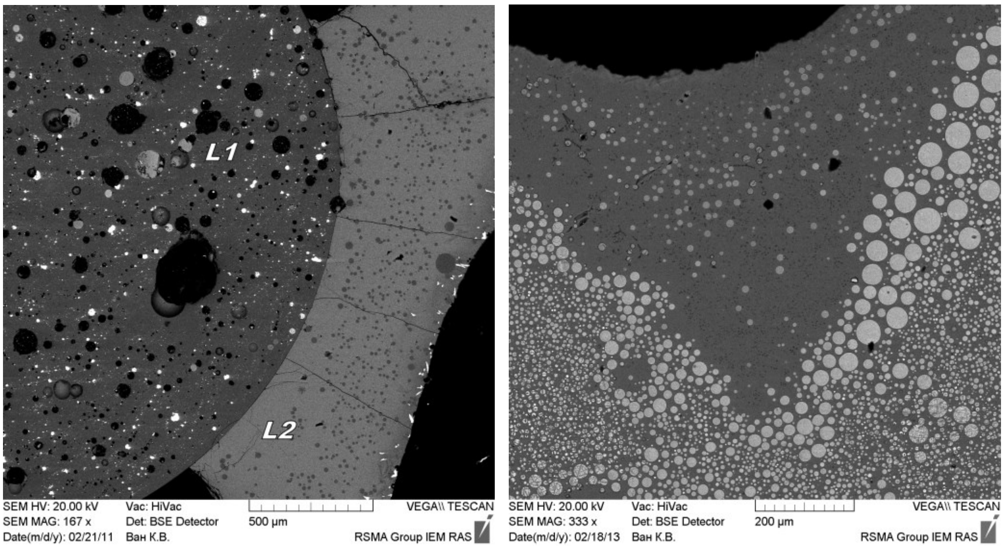
Mineral matrixes have been experimentally synthesized for immobilization of alkaline, alkaline-earth and rare earth elements – radionuclides. Methods of fixation and segregation of precious metals (radwaste components) and halogenides (Br, I) have been developed and tested, too. Examinations carried out showed high stability of synthesized materials to hydrolytic dissolution.

Problems of glass matrixes (borosilicate and aluminophosphate glasses) remaking into stable crystalline mineral materials are considered.

This study is based on the selective extraction of elements by melts of different compositions during the process of liquid immiscibility arise in them. As melts – concentrator phosphate and aluminofluoride phases are used.

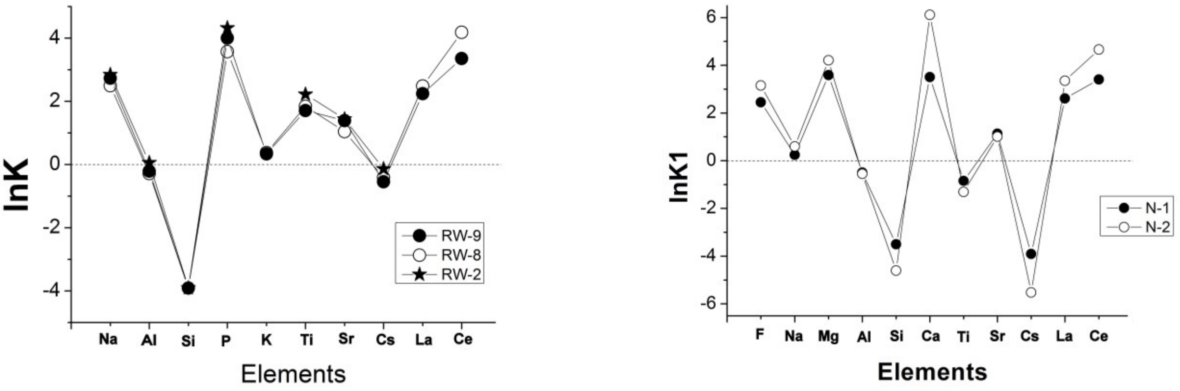
In the run of experiments liquid immiscibility between borosilicate and phosphate (or aluminofluoride) melts and between silicate and aluminophosphate melts appeared (fig. 1). Herewith partition of elements between phases took place. Among elements – radwaste imitators Sr, La and Ce enrich phosphate (or aluminofluoride) phase and Cs concentrates in borosilicate glass (fig. 2). In water-bearing borosilicate-phosphate system and in the system aluminophosphate glass – SiO_2 REE concentrate in monazite phase which is high stable in natural processes (fig. 3).

Methods of fixation radwaste elements from glasses to solid solutions of minerals have been experimentally developed. We supposed and tested two methods of remaking of borosilicate glass matrixes: method of salting out and liquation method. It has been shown that used method of salting out melt crystallization with formation of Nb-bearing rutile and euxenite can be obtained. As salting out agent aluminium oxide was used (fig. 4).



a b

Fig. 1. Liquid immiscibility between borosilicate and phosphate (a) melts (L1 – borosilicate melt, L2 –phosphate melt) at T=1200°C, P=1 kbar and between borosilicate (dark) and aluminofluoride (light) melts (b) at T=800°C, P=1.5 kbar.



a b

Fig. 2. Partition coefficients K=C_{L2}/C_{L1} of elements (lnK) between borosilicate glass (L1) and phosphate phase (L2) in dry system (a) and partition coefficients of elements between borosilicate glass and aluminofluoride phase (lnK1) in dry (N-1) and water-bearing (N-2) system (b).

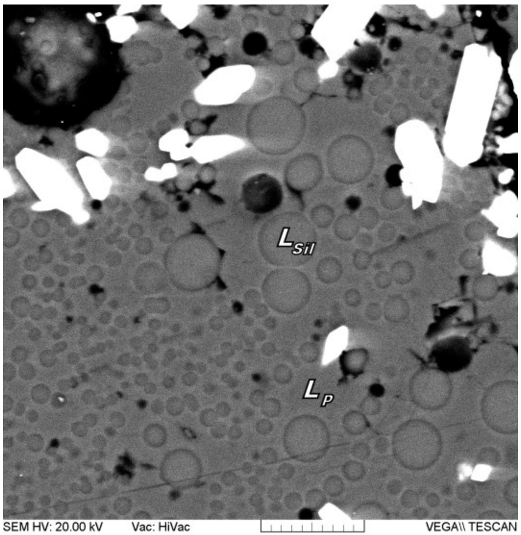


Fig. 3. Formation of monazite crystals in the system aluminophosphate glass – SiO_2 at 1200°C, P=2 kbar in dry conditions. L_P – phosphate melt, L_{Sil} – silicate melt. BSE-image.

Liquation method of element partition is that as a result of liquation borosilicate melt depleted in SiO_2 from which loparite, sodium titanate and silicate of cesium crystallize is formed (fig. 5).

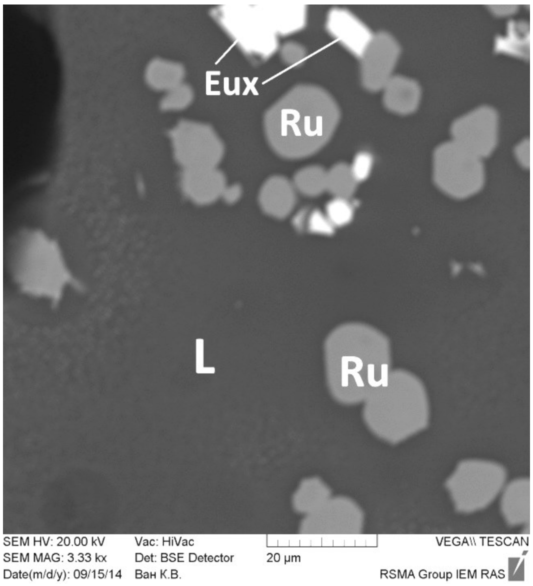


Fig. 4. Experimental products obtained used method of salting out at 2 kbar ane 1100°C. Ru – Nb-bearing rutile, Eux – euxenite, L – glass. BSE-image.

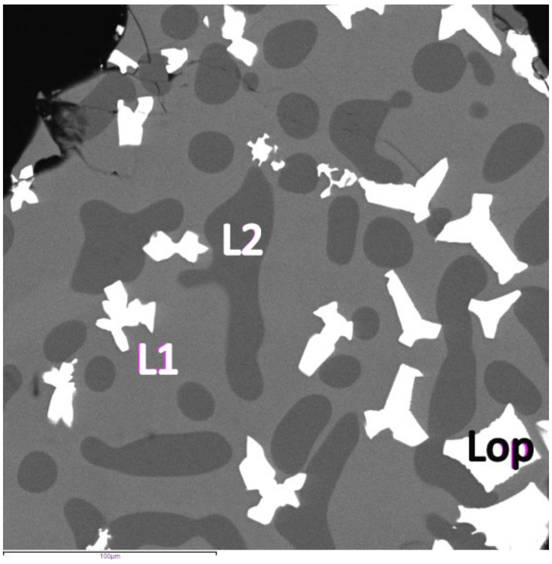


Fig. 5. Experimental products obtained used liquation method (1300°C → 850°C). Lop – loparite, L1, L2 – glasses of liquating melts. BSE-image.