

## PHYSICOCHEMICAL PROPERTIES OF SOME MATRIXES FOR IMMOBILIZATION OF RADIOACTIVE WASTE

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### ABSTRACT

The materials used for the immobilization of the radioactive waste, should have radiation, thermal and chemical stability and the high mechanical strength. In the technology of the processing of waste their fractionation is envisaged with separation of long-lived actinides from other radionuclides. The subsequent immobilization of the radioactive waste fractions in glassy, mineral-like and other solid matrixes should guarantee their safe storage.

In recent work the data on the investigation of the boron-basalt matrix for including of radioactive waste are presented.

### EXPERIMENTAL

At simulation of the radiation-chemical processes occurring at highly active waste storage, it was guessed that the highest possible temperatures and absorbed doses of  $\gamma$ -irradiation would not exceed 600-700°C and 105 kGy correspondingly [1].

For simulation of the radiation - thermal diffusion conditions we have used the Kokroft-Walton accelerator with electrons energy 1 MeV (dose rate is  $1.5 \cdot 10^4$  kGy/h). The maximum absorbed dose for all kinds of samples was 100 MGy. The thermal diffusion of glasses was investigated at irradiation in the specially modernized vertical irradiation furnace SNOL1.62.51/P-42 at 600 and 750° C during 15-120 day.

Diffusion profile of glass components on the interface glass - container material arisen as a result of thermo- and radiation diffusion have been studied by the method of X-ray microprobe on the instrument «CAMEBAX» MVX 100, CAMECA, France. The magnetic susceptibility was determined on the device «Kappametr»; model K-T5 in terms of SI. Magnetic susceptibility and volumetric weight were determined on the one sample before heat treatment and irradiation by accelerated electrons with energy 1 MeV, the determination of the ferric oxides was conducted on several samples of the same group.

Registration of ESR spectra of powdery rock casting samples was conducted on the device «Radiopan SE/X» 2544 with frequency of the alternating field 9.2 GHz and modulation frequency 100 kHz at 77K.

Mössbauer spectroscopy is the modern precision method of the ferrous ions valence state determination and their nearest-neighbor environment, which registers transitions conditioned by  $\gamma$ -rays absorption by atomic nuclei. These transitions are characterized by change of the nuclear

spin quantum number. The conditions of the absorption depend on electronic density around the nucleus, and the number of observed lines is connected with the symmetry of the nearest-neighbor environment and presence of the magnetic moment.

For registration of the Mössbauer spectrum the source is displaced relatively sample and the running speed of the source, corresponding to the maximum of  $\gamma$ -ray absorption is determined. The position of lines depending on chemical environment is characterized by values of the running speed of the source in mm/s and this is called as isomeric shifts.

The experiments were conducted on the device «Mössbauer lab», Hungary.

It is not possible to study the influence of the high level  $\alpha$ -radiation. Apparently, high temperatures condition plays the determining role in the composite process of the glasses crystallization. Therefore the influence of the thermal annealing on chemical stability of the boron-silicate systems (influence of the crystallization) was investigated rather thoroughly. For this purpose samples of boron basalt matrixes inclusive oxides of elements - components of radioactive waste (SrO, Cs<sub>2</sub>O, Nd<sub>2</sub>O<sub>3</sub>, Ce<sub>2</sub>O<sub>3</sub>), were kept at given temperature (accuracy is  $\pm 1^\circ\text{C}$ ) in the furnace «Nabertherm» during 100 hours. After that the rate of their dissolution in water was measured during 20 day, at 20°C.

The composition of the solid radioactive waste (SRW) is listed in Table I (below this waste is designated as waste № 1).

Table I Composition of SRW

SRW component	Contents, % wt.	SRW component	Contents, % wt.
Oxides: magnesium	26.4	oxides: nickel	2.8
ferrous	15.1	silicon	6.7
aluminum	11.7	lead	1.0
barium	10.0	titanium	0.8
calcium	16.2	sodium	1.6
chromium	4.9	plutonium	0.8
manganese	2.8		

The compositions of high-level liquid radioactive waste (HLRW) (below there are waste № 2-5) of «MAYAK» Enterprise before and after fractionation are listed in Table II, including the fraction of transplutonium elements (TPE) and rare earth elements (REE).

Table II Composition of HLRW

Element, g/l	Solution 2. Raffinate of the cycle 1	Solution 3. Sr+Cs fraction	Solution 4. TPE+REE fraction	Solution 5. Raffinate of the cycle 6
Al	0.1	0.0024	0	0.013
Fe	0.4	0.0040	0	0.053
Ni	0.1	0.0024	0	0.013
Cr	0.1	0.0024	0	0.013
Ca	0.1	0.124	0	0
Mo	0.2	0	0	0.027
Ba	0.1	0.124	0	0
Zr	0.4	0	0.27	0
REE	1.2	0.0014	0.8	0.00024
HNO <sub>3</sub>	200	250	pH=1-2	50
U	≤ 0.01	0	≤ 0.01	≤ 0.00001
Pu	≤ 0.005	0	≤ 0.005	≤ 0.00005
<sup>241</sup> Am	0.01	1.2×10 <sup>-5</sup>	0.00670	2×10 <sup>-6</sup>
<sup>244</sup> Cm	0.01	1.2×10 <sup>-6</sup>	0.00067	2×10 <sup>-7</sup>
<sup>237</sup> Np	0.06	0	0.04000	0
β, Bk/l	1.2×10 <sup>12</sup>	1.1×10 <sup>12</sup>	7.7×10 <sup>10</sup>	1.2×10 <sup>7</sup>
α, Bk/л	6×10 <sup>12</sup>	<1.6×10 <sup>7</sup>	3.2×10 <sup>10</sup>	5.4×10 <sup>6</sup>
Sr	0.08	0.1	2.7×10 <sup>-6</sup>	1.5×10 <sup>-5</sup>
<sup>137</sup> Cs	0.22	0.27	7.5×10 <sup>-6</sup>	0
<sup>134</sup> Cs	0.00042	0.005	0	0
Ce	0.00066	0	0.00044	2.4×10 <sup>-5</sup>
<sup>125</sup> Sb	0.0018	0	0	7.6×10 <sup>-5</sup>
<sup>106</sup> Ru	0.00057	0	0	0
<sup>154</sup> Eu	0.002	0	0.013	0
V, m <sup>3</sup> /t U	6.2	5	9.3	46.3

## RESULTS AND DISCUSSION

In the studied materials thermo- and radiation-stimulated processes will be connected first of all with the change of the valence states of the metal ions due to oxidation-reduction processes that can result in disturbance of multicomponent systems structure and change their physicochemical characteristics.

For the investigation of irradiation and temperature influencing on the structure and properties of the stone casting, the samples relating to different kinds of the cationic diagram were selected.

The 1m sample concerns to the magnetite kind of the cationic diagram and is obtained from the mixture consisting of pyroxene porphyrite (70 %), gabbrodiabase (30 %), and chromite (3 %). The 2m sample concerns to the kind of pyroxene primary crystallization. It consists of pyroxene porphyrite and 1-1.5 % chromite. The 3m sample represents the stone casting and glass from halleflinta with the addition of marble, magnesite and chromite.

In the Table III the data of chemical analysis of FeO and Fe<sub>2</sub>O<sub>3</sub>, and also the values of volumetric weight of monolithic samples are given.

Table III Properties of materials for the immobilization

Sample №	Characteristics	Volumetric weight, kg/m <sup>3</sup>		FeO/Fe <sub>2</sub> O <sub>3</sub>	
		before irradiation	after irradiation, (dose, kGy)	before irradiation	after irradiation
1m	Tablet, monolithic sample	2980	2980 (2.6×10 <sup>5</sup> )		
1m	Tablet, powder	-	-	0.88	0.95
2m	Stone casting	2990	2990 (2.6×10 <sup>5</sup> )	-	-
2 m	Glassceramic	2930	2930 (1.6×10 <sup>4</sup> )	-	-
3 m	Glass	2700	2700 (7×10 <sup>4</sup> )		

The data of the Table III demonstrate, that the volumetric weight of samples after irradiation is not changed practically, and the ratio of FeO/Fe<sub>2</sub>O<sub>3</sub> is changed insignificantly. The volumetric weight of monolithic samples is increased after heating, and magnetic susceptibility and oxidation level of iron is not changed practically. The content of Fe<sub>2</sub>O<sub>3</sub> in 2m sample (glassceramics powder) is essentially increased after heating. In the 3m sample casting with a little iron contents, obtained in oxidizing conditions, the oxidation level is not changed at heating.

The obtained data have shown that the oxidation of FeO in studied materials takes place only on the sample surface. It causes the minor decrease of the magnetic susceptibility. Some increase of the volumetric weight (by  $40 \text{ kg/m}^3$ ) in 1m and 2m samples is connected, apparently, both with crystallization of the residual glass, and with oxidation of the sample surface. The least change of volumetric weight ( $20 \text{ kg/m}^3$ ) takes place in the 3m casting with a small iron contents, in which oxidation of iron is observed neither in a volume, nor on a surface of sample.

Different methods are used for determination of the valence state of Fe ions in studied materials [2,3]. The contents of  $\text{Fe}^{+2}$  ions in the stone casting were determined by the method of the electron spin resonance (ESR). It allows determining the absolute concentrations of paramagnetic ions ( $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$  ions). The ESR spectra of the 3m casting from porphyrite represent the broad singlets with  $g \approx 2.01$  and  $\Delta H_{1/2} = 70.0 \text{ mT}$ . Such large width of  $\text{Fe}^{+3}$  ions signals, is observed usually in glasses and is connected with the non-uniformity of polyhedrons of the nearest neighbor of  $\text{Fe}^{+3}$  environment. For large  $\text{Fe}^{+3}$  ion concentrations, the widening of the line is possible owing to the spin-spin interaction that can influence on accuracy of the determination of true spins concentration. In the casting from halleflinta, the  $\text{Fe}^{+3}$  ion concentration is unchanged neither at irradiation, nor at heating (intensity of signals are practically the same). In the casting from porphyrite the  $\text{Fe}^{+3}$  ions concentration in the initial and irradiated samples is practically identical, and in heat-treated samples ( $750^\circ\text{C}$ , 105 day) it increases by two orders. The ESR spectra of the initial and irradiated 1m casting represent the nonresonance absorption, i.e. the  $\text{Fe}_3\text{O}_4$  ferromagnetic phase is present.

In ESR spectra of the heat-treated samples the signals of  $\text{Fe}^{+3}$  ions are observed and the  $\gamma$ -irradiation does not influence on their contents practically. The essential changes in the oxidation level of Fe ions are not observed for monolithic samples after heating. The oxidation of ferrous minerals takes place only on surface of samples. Thus, the  $\text{Fe}^{+3}$  ion concentration both in octahedral (pyroxene), and in tetrahedral (oxides) coordination is increased. In the casting from halleflinta with small iron content, in which almost all iron is present in  $+3$  valence state, the change of the ferrous valence state is not observed.

For the determination of the oxidation level of iron in studied samples, the Mössbauer spectra of the standard samples with known valence state were recorded. The values of the isomeric shifts in spectra of the stone casting and rocks were compared with spectra of the measurement standards. The Fe ions in the divalent state predominate in initial rocks (porphyrite, diabase). Besides, in the porphyrite (silicates) composition  $\text{Fe}^{3+}$  in octahedral environment is also observed, and in diabase -  $\text{Fe}_2\text{O}_3$ . After heating of powdery samples at  $750^\circ\text{C}$ , the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  takes place, and in diabase the concentration of  $\text{Fe}_2\text{O}_3$  increases. The irradiation does not result in visible changes of Mössbauer spectra of sample. In spectra of the 1m casting mainly the  $\text{Fe}^{2+}$  ions,  $\text{Fe}_3\text{O}_4$ , and also small concentration of  $\text{Fe}^{3+}$  ions in octahedral coordination are detected. In the spectra of the irradiated samples there are no new isomeric shifts indicating change of the ferrous valence state.

Formation of  $\text{Fe}^{3+}$  in the octahedron and  $\text{Fe}_2\text{O}_3$  takes place at keeping of samples at  $750^\circ\text{C}$ . The comparison of the Mössbauer spectra of the initial samples of the casting from porphyrite, glassceramic and glass allows concluding that the degree of material crystallinity influences on oxidation level a little. The isomeric shifts indicate the presence of  $\text{Fe}^{2+}$  ions and small amount of

Fe<sup>3+</sup> ions. However the half-width of the absorption line describing the symmetry of the nearest neighbor environment of the ferrous ion, is less for glassceramics, than for the casting and glass from porphyrite.

In spectra of all heat-treated samples the isomeric shifts, characteristic for Fe<sup>3+</sup> in octahedral environment, are observed. The irradiation practically does not change the Mössbauer spectra. Heat treatment of 3m samples at 750°C and irradiation up to doses  $3.2 \cdot 10^4$  kGy do not result in change of the ferrous ions valence state.

For choice of the containing rocks, and also container materials, it is necessary to study not only the changes of their properties under irradiation, but also investigate chemical interaction of the radioactive components of glasses with materials. Therefore the processes of Sr, Ce and Cs diffusion into rocks and stone casting from fused on their surface glasses, modeling the radioactive waste, and also the influence of heating and irradiation on this process were studied.

It was shown, that at fusing of the glass with the Cs ions addition on the interface glass – sample, some increase of Cs contents is observed as contrasted to remaining volume of glass. Probably, there is the formation of Cs compounds with silicate on the surface that results in the slowdown of diffusion. The diffusion profile of Sr ions increases with increase of thermodiffusion time, however maximum of its contents on the interface keeps. The diffusion profiles of all studied ions have unusual nature. The concentrations of these ions increase not only on interface, but also in the bulk of the material. The nonuniform distribution, probably, is the consequence of the different interaction with separate phases in the material. The calculation of diffusion coefficients on such profiles is not possible.

On the basis of the obtained experimental data one can conclude that the depth of isotopes - simulators penetration remains low even under heats and irradiation.

The data of the investigation of the boron-basalt materials composition obtained after including of the wastes 1-5 in them are shown in the Table IV.

Table IV shows that homogeneous glassy or stone-like melts are obtained at the contents of all investigated waste in boron-basalt matrix up to 40 %. The increase of amount of waste up to 60 % in the case of 4 and 5 waste results in obtaining of cakes. It is explained by the presence in the mixture of zirconium and chromium, which are badly included in the glass matrix.

1 and 2 wastes contain approximately same components, as stone casting used in the present activity for obtaining of boron-basalt matrixes. Therefore the glass is obtained when this waste contents amount to 60 %. It considerably exceeds the possible contents in the matrix of the individual SRW or LHRW components determined in the previous researches.

Table IV Boron-basalt matrixes composition with included waste. \*)

Waste, №	Variety	Content, % wt.	B <sub>2</sub> O <sub>3</sub> , % wt.			
			0	8	12	20
1	SRW	20	cm	cm	gm	glass
		40	cake	cm	cm	glass
		60	cake	cm	cm	glass
2	HLRW	20		gm	gm	glass
		40		gm with impurities	gm with impurities	gm
		60		gm with impurities	gm with impurities	cm
3	HLRW	20		glass	glass	glass
		40		glass	glass	glass
		60		glass	glass	glass
4	HLRW	20		glass	glass	glass
		40		glass	gm	glass
		60		flowed cake	flowed cake	cm
5	HLRW	20		cm	cm	glass
		40		cm	cm	cm.
		60		flowed cake	flowed cake	flowed cake

\*) Basalt is the remainder.

cm – crystalline melt

gm – glass melt

Results of investigation of leaching in twice distillate water (the measurement was conducted by a conductometry method) are listed in Table V.

Table V Leaching rate of boron-basalt materials in water

Waste, №	Waste, % wt.	B <sub>2</sub> O <sub>3</sub> , % wt.			
		0	8	12	20
		Leaching rate, $k \times 10^{-7} \text{g/cm}^2 \text{day}$			
1	20	3.5	1.0	1.0	1.0
	40	10	5	5	10
2	20		1.0	1.0	1.0
	40		1.0	1.0	1.0
3	20		1.0	1.0	1.0
	40		1.5	1.0	1.0
4	20		0.7	1.0	1.0
	40		0.5	1.0	1.0
5	20		2.0	3.0	1.5
	40		2.0	3.0	3.0

From the data, given in the Table V, it is possible to conclude that obtained boron-basalt materials have high chemical stability and can be considered as perspective materials for the SRW and LHRW immobilization.

The phase transformations in high radioactive materials can take place under influencing of different kinds of radiation and heating caused by them. The composition of the investigated samples and obtained data are listed in Table VI.

The analysis of diffractograms, obtained after annealing of the samples at 800°C (annealing time 100 hours), allows to make following conclusions: (1) all given in the Table VI compositions of boron-basalt matrixes are crystallized to a variable extent; (2) matrixes with REE are crystallized to a less degree; (3) presence and the nature of oxide determine the process of the boron-basalt matrixes crystallization. Thus, the structure and composition of the crystalline phases depend mainly on nature of vitrifying component. The analysis of diffractograms allows to suppose that the crystalline phases contains such compounds as Fe<sub>2</sub>O<sub>3</sub>, MgSiO<sub>3</sub> or isomorphous with them.

From the data, given in the Table VI follows, that the annealing at the temperature above 600°C results in some decrease of the chemical stability of materials inclusive thorium oxide, irrespective of their composition. The alteration of dissolution rate does not exceed error limits of these values at measurement by conductometric method, i.e. it is possible to suppose that the temperature of annealing above 600°C does not influence essentially on samples properties. It is



quite explainable, since this composition with thorium oxide was obtained as stone-like melt and in this case their recrystallization is possible.

Table VI Leaching rate of boron-basalt matrixes in water

№	Oxide	Mixture composition, % wt.			Annealing temperature, °C						
		Stone casting	B <sub>2</sub> O <sub>3</sub>	Oxide	Without annealing	400	500	600	700	800	
					Leaching rate, k×10 <sup>-7</sup> g/cm <sup>2</sup> day						
19	ThO <sub>2</sub>	75.2	7.5	17.3	>0.5	>0.5	>0.5	2.5	4.0	1.6	
20		71.4	7.2	21.4	-"-	-"-	-"-	2.5	4.0	1.6	
21		72.4	10.9	16.7	-"-	-"-	-"-	0.7	2.0	1.0	
22		69.0	10.3	20.7	-"-	-"-	-"-	2.5	0.5	1.0	
23	SrO	76.9	7.7	15.4	2.5	1.0	2.5	5.0	30	70	
24		71.4	7.2	21.4	5.0	2.5	3.0	5.0	30	80	
25		66.7	6.7	26.2	10.0	3.5	3.0	4.0	30	80	
26		74.1	11.1	14.8	1.5	2.0	2.5	5.0	30	70	
27		69.0	10.3	20.7	4.0	2.5	2.5	4.0	10.0	60	
28		64.5	9.7	25.8	10.0	8.0	5.0	7.0	25	70	
29	Cs <sub>2</sub> O	76.9	7.7	15.4	0.5	0.5	2.0	5.0	25	8	
30		71.4	7.2	21.4	0.5	1.0	2.0	8.0	20	13	
31	CeO <sub>2</sub>	82.0	10.0	8.0	2.0	>0.5	0.5	2.5	22	2.0	
32		78.0	10.0	12.0	2.0	-"-	0.5	1.0	4.0	1.5	
33		76.0	9.0	15.0	2.0	-"-	0.5	1.0	6.0	1.5	
34		82	10.0	8.0	2.0	0.5	>0.5	3.5	11	3.0	
35		Nd <sub>2</sub> O <sub>3</sub>	78	10.0	12.0	2.0	>0.5	-"-	3.0	11	2.5
36			76	9.0	15.0	2.0	-"-	-"-	1.5	8.0	2.5
37	-	90.0	10.0	-	3.0	>0.5	1.0	5.0	6.0	4,0	

The considerable decrease of the stability to leaching in water for the boron-basalt samples containing strontium and cesium oxides (samples № 23-28 and 29, 30) takes place at annealing temperature above 500°C. The higher is annealing temperature, the higher is leaching rate. It is explained by the much lower chemical stability of the material in the crystalline state than in glassy state. However at annealing temperature <600°C the leaching rate changes a little.

Distinctive feature of boron-basalt matrix and matrixes inclusive lanthanide's oxides (samples № 31-33, 34-36) is the increase of stability to leaching in water at annealing in the temperature

range 400-500°C. Therefore the annealing at indicated temperature could be recommended as preliminary operation of the LHRW immobilization in boron-basalt matrix. The crystallization of matrixes at higher temperature does not result in a considerable decrease of their chemical stability relative to samples, not subjected to the annealing. It can be because of these materials are subjected to crystallization to a less degree, as it was already mentioned above. Their full crystallization requires either much greater time, or more heats.

Thus, the effect of the thermal annealing on the leaching rate of boron-basalt matrixes in water depends mainly on nature of HLRW component included in matrix and practically does not depend on the composition of the vitrified mixture, i.e. on the oxide and boric anhydride contents in it. For this reason it is possible to forecast the behavior of matrixes at joint presence of the indicated components in them.

The conducted consideration allows one to conclude that the boron-basalt materials are perspective matrixes for the immobilization of the radioactive waste. They are very stable against thermal, chemical and radiation action. Stone casting itself can be utilized as material for production of various facilities and items (for instance, for manufacture of containers for long-term storage of radioactive components of wastes).

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