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COMPARISON OF THE IMMOBILIZING PROPERTIES OF RUSSIAN PHOSPHATE AND BOROSILICATE GLASSES ENSURING THE SAFE OPTIONS FOR LONG TERM UNDERGROUND STORAGE AND FINAL DISPOSAL OF WEAPON PLUTONIUM PRODUCTION WASTE

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ABSTRACT

The paper presents the results of the studies on physical and chemical properties of phosphate and borosilicate glasses produced at the Krasnoyarsk Mining & Chemical Combine (MCC) for immobilization of medium-level radioactive waste of weapon plutonium production. Actual waste is composed of long-life radionuclides – uranium and plutonium. Tests on mechanical stability of phosphate and borosilicate glass matrices and lab-scale tests on chemical stability to the impact of the model ground water of various salt composition, at the temperatures compared to those of the deep geological formations, were carried out.

The methodological issues of application of the experimental results for comparison of matrix materials as the elements of a multi-barrier system for the long-term storage of plutonium-containing waste are examined.

Nowadays, the intensive works on radioactive sludges extraction from the storage tanks of the MCC, development of the technology of radioactive sludge solidification in phosphate and borosilicate glass matrices, and the studies on plutonium and other nuclides leaching from vitrified waste when contacting with waters of various salt composition are carried out with the involvement of the American specialists and financial support of the U.S. Department of Energy.

The experimental production of phosphate and borosilicate glass has been launched at the MCC. For this purpose, the SHF-heating installation has been created in the "hot" chamber of the MCC Central Plant Laboratory. The studies on physical and chemical properties of the produced glasses under conditions simulating a long term storage and final disposal of the immobilized plutonium-containing waste are carried out under methodological leadership of VNIPIpromtechnologii (Moscow).

Three types of MCC phosphate and borosilicate glass samples were utilized for the experiments to study the chemical stability and mechanical solidity of the glass, and plutonium and uranium sorption-desorption on the rocks: with actual sludge imitator, actual sludge, sludge imitator and plutonium dioxide with plutonium mass contents of 0.5% (Tab.1).

Table 1. Composition Of Borosilicate And Phosphate Glass With Sludge Imitator And Plutonium

Component	Contents in glass, mass %	
	Borosilicate (BG)	Phosphate (PhG)
PuO_2	0.5	0.5
UO_3	8.4	6.5
MnO_2	5.8	4.4
Al_2O_3	3.1	1.1
NiO	1.0	0.9
Fe_2O_3	14.4	5.5
Cr_2O_3	1.9	6.5
Na_2O	14.8	23.4
Li_2O	7.0	-
SiO_2	36.1	0.4
B_2O_3	7.0	-
P_2O_5	-	56.4

Major directions and stages of the works are shown in Figs. 1, 2.

All the glass samples were preliminary kept aside for 40 days at a temperature of 90°C, with no water contact.

Then, the samples with pulp imitator were put into interaction with the distilled water at a temperature of 25°C and 90°C, and pressure of 0.1 MPa. In the process, the glass dissolution rates and velocities of the main elements' release from the matrix were assessed: from phosphate glass – uranium, phosphorus, sodium, chrome, silicon, iron, aluminum, nickel, manganese; from borosilicate glass – uranium, boron, sodium, chrome, silicon, iron, aluminum, manganese.

The analysis of possible conditions at the prospective location depths for an intermediate storage and a repository for immobilized radioactive sludges from weapon plutonium production – 250-350 m and 1500-2000 m – was carried out.

The composition of two types of water for the lab-scale experiments was determined based on the ground water chemical analysis data for the depths of the MCC underground facilities (hydrocarbonaceous calcium-sodium-magnesium water, mineralized - 0.4 g/l, and pH=7.5-8.5), and the previously summarized data on drilling the deep and super-deep boreholes in the former USSR, and abroad (neutral chloride sodium-calcium-magnesium water, mineralized - 50 g/l). For the above conditions, the following temperature and pressure values were accepted for the experiments: T=80°C, p=0.1 MPa and 15 MPa, accordingly. Hereinafter, the above water types will be referred to as the model water of 1^{st} and 2^{nd} types.

The phosphate and borosilicate glass samples with the actual MCC sludges were interacting with the 1^{st} type model water (0.4 g/l) at a temperature of 90°C, and pressure of 0.1 MPa. Under these conditions, the plutonium and uranium leaching rates from borosilicate glass will be of the order of 10^{-2} to that from phosphate glass for the test glass samples. Mass losses in sample phosphate glass will be higher to a factor of 350.

Experimental studies on changing of the plutonium and uranium leaching rates from the glass in interaction with the 2^{nd} type model water (50 g/l), at a temperature of $80^{o}C$ and pressure of 15 MPa, were carried out. Under these conditions, there is practically no visible difference in plutonium and uranium leaching rates from phosphate and borosilicate glass samples. However, in 40 days, the plutonium leaching rate were of the order of 10^{-2} than that of uranium, for both types of glass. Mass loss in borosilicate glass samples was lower than that in phosphate glass to a factor of five.

The mechanical solidity experiments for phosphate and borosilicate glass samples were conducted; the samples' limits of solidity for compression and strain were defined. The samples of 30 mm diameter and 30 mm height were utilized for the tests. It resulted from the experiments that the solidity of borosilicate sample glass was higher than that of phosphate glass to a factor of two. In contact with the model waters, the phosphate glass destroys and has a higher mass loss in sample.

Preliminary results of the studies on sample glasses physical and chemical properties are shown in Table 2.

Table 2. Preliminary Properties Of The Kmcc Phosphate And Borosilicate Glass With Plutonium-Containing And Radioactive Waste Of Weapon Plutonium Production

Indicators	Units	Experimental conditions for studies on the glass physical and chemical properties	
		p=0.1 Mpa, T=90°C, salt contents in water - 0.4 g/l, glass with actual sludge	P=15 MPa, T=80°C, salt contents in water - 50 g/l, glass with imitator and PuO_2
Dissolution rates for main glass components	g/cm^2 x day		
1.1. Phosphate glass			
Phosphorus		$2.5\cdot10^{-3}$	$8.4\cdot10^{-4}$
1.2. Borosilicate glass			
Boron		$1.5\cdot10^{-4}$	$5.0\cdot10^{-5}$
Silicon		$1.0\cdot10^{-5}$	$1.0\cdot10^{-5}$
2. Radionuclides leaching rates	g/cm^2 x day		
2.1. Phosphate glass		$1.0\cdot10^{-5}$	$3.0\cdot10^{-8}$
Plutonium		$1.5\cdot10^{-5}$	$8.0\cdot10^{-6}$
Uranium			
2.2. Borosilicate glass			
Plutonium		$5.0\cdot10^{-8}$	$1.0\cdot10^{-7}$
Uranium		$5.0\cdot10^{-7}$	$1.0\cdot10^{-5}$
3. Solidity limits of samples, for compression and strain	Mpa		
3.1. Phosphate glass			
compression		11-14	
strain		2-8	
3.2. Borosilicate glass			
compression		15-25	
strain		5-17	
4. Thermoconductivity of Phosphate and Borosilicate glass	W/m·°K	1.2	

The laboratory experiments for investigation on plutonium sorption on the rocks and glass and steel destruction products were carried out: with the 1st type model water at T=90°C and p=0.1 MPa, and the 2nd type model water at T=80°C and p=15 MPa. The experimental results show that plutonium is strongly sorbed on the rocks under conditions of those similar to the low depths, i.e. at a pressure of 15 MPa and the model water of high salt composition.

A safety evaluation and a feasibility financial study on corresponding options of the multi-barrier systems for intermediate storage and geological disposal of waste will be have a necessity in carrying out, to substantiate the priorities of utilizing the glass produced for immobilization and further underground disposal of the MCC radiochemical production waste. The results of the studies on matrix materials properties should be considered in this matter, and a comparison of the above options according to a comprehensive "risk-benefit" criteria shall be carried out.

For the multi-barrier systems developed for radioactive waste (RW) storage in underground workings, the main potential way for the radionuclides release outside the storage facilities will be their migrations with contaminated waters. Considering the substantiation of a possible RW storage facility development within the limits of a specific rock mass area, the assessment of mining and ecological safety in respect of any potential abnormal situations, which can result in the radionuclides release into the environment, will be carried out.

The isolation performance of the multibarrier system for long-term storage of RW is considered to be reliable, if the risk when at least one radionuclide (plutonium, for instance) exceeded the admissible concentration in water (admissible activity level, AAL) outside the control area of radius L to a value lower than a rather minor pre-determined value E, both for the normal storage operation, and for all potential abnormal situations:

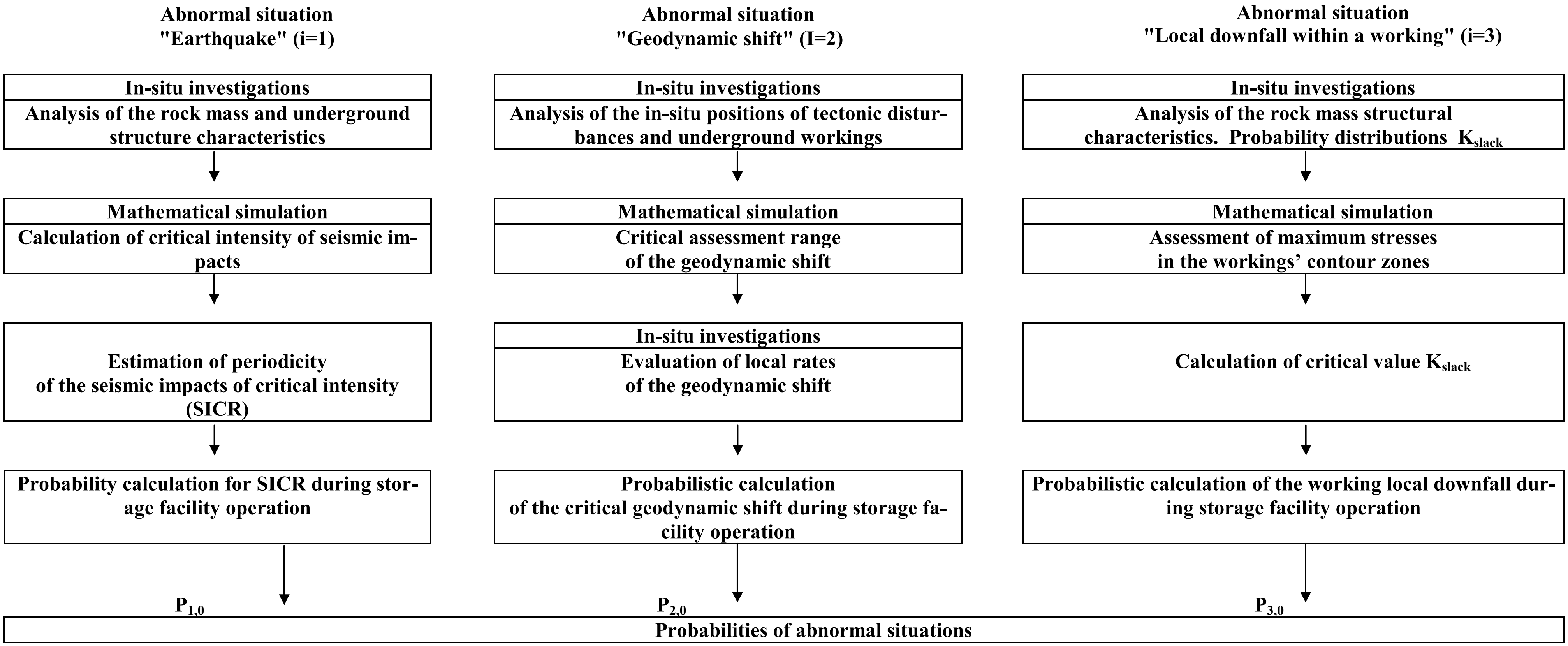
$$\mathbf{r\ (\ell = L;\ T_{st};\ N_o;\ T_{1/2};\ R;\ V;\ A;\ X;\ Y;\ Z) \leq E} \qquad \textbf{(Eq. 1)}$$

where:

- **r** - risk of plutonium release (with $AAL_{b)}$ into the waters of the active flow exchange zone, 1/year;
- **A** - characteristics of the on-site natural conditions;
- **Z** - characteristics of the rock mass considering the impact of storage facility thereon;
- **X, Y** - set of the RW and engineered barriers characteristics;
- $\mathbf{N_o}$ - relative plutonium activity in contaminated waters when released from the storage, AAL units;
- **R** - plutonium retention factor in the rocks considering the destruction of engineered barrier;
- **V** - velocity of the contaminated water spread over the zone of enhanced fracturing in the rock mass, m/year;
- $\mathbf{T_{st}}$ - period of the storage facility operation, years;
- **L** - minimum length of the possible plutonium migration pathway in the rock mass, from the storage facility to the active flow exchange zone, m;
- **E** - maximum admissible risk value, 1/year (= 1 x 10^{-6} 1/year).

The initiating events for abnormal situations and normal conditions of operation constitute a complete closed system which is dependant of both factors.
Probabilities of the abnormal situation occurrence and conventional probabilities of the events included into the respective accident-related sequences are defined by analyzing and prediction of the natural area conditions, the on-site rock mass structure and characteristics for the storage; the underground structures' strength; the engineered barrier characteristics for the studied rock mass; hydrogeological and physical and chemical characteristics considering the RW composition. The mathematical modeling of the rock mass stress-strained state at the contour zone is carried out, and the strength characteristics for the "rock mass - lining" system are calculated considering a possible dynamic impacts of various intensities, and the results of the in-situ rock mass and lining measurements for the underground workings. The assessment scheme for probable initial events of the abnormal situations at the underground storage for solidified radioactive materials is shown in Tab. 3.

Table 3. Assessment Scheme For Probabilistic Occurrence Of Abnormal Situation, Applied For The Solidified Radioactive Materials Storage



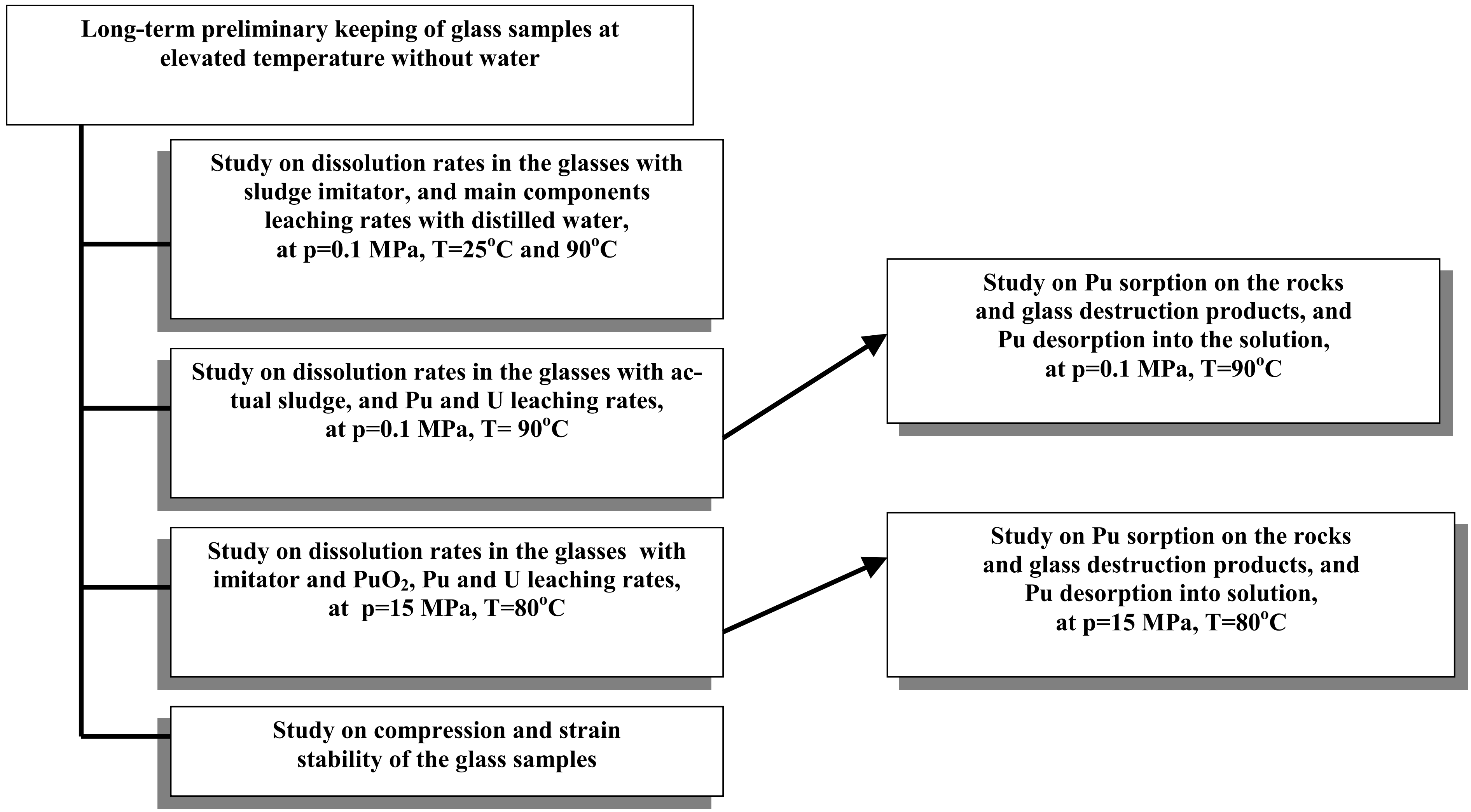
CONCLUSION

1. To immobilize the plutonium sludges in the MCC "hot" chamber, the Combine has created an SHF-heating solidifying installation.
2. Phosphate and borosilicate glasses containing the sludge imitator, sludge imitator with Pu of 0,5% mass contents, and sludge imitator with actual sludge addition were produced.
3. Major physical and chemical properties of phosphate and borosilicate glass were investigated. Chemical stability of the glass samples with borosilicate matrix is higher than that of the glass with phosphate matrix: both in tests with the distilled water ($25^{o}C$ and $90^{o}C$, 0.1 MPa), and the initial water under conditions of intermediate storage of the glasses ($90^{o}C$, 0.1 MPa), and in the deep ground water imitator for the disposal conditions ($80^{o}C$, 15 MPa). In most cases, the rates for uranium and plutonium leaching from borosilicate glass are significantly lower than of those from phosphate glass.
4. The final evaluation of prioritized application of an individual matrix type shall be performed based on the safety assessments for the multi-barrier system as a whole, in terms of a long–term storage and disposal of the MCC solidified radioactive sludges.

Fig. 1 Laboratory scale tests support for studies on KMCC phosphate and borosilicate glass properties during immobilization of weapon plutonium production wastes

- **Production of K-26 phosphate and borosilicate glass samples of three types**
  - with sludge imitator
    - phosphate (PhG-I)
    - borosilicate (BS-I)
  - with actual sludge
    - phosphate (PhG-S)
    - borosilicate (BS-S)
  - with imitator and PuO_2
    - phosphate (PhG-Pu)
    - borosilicate (BS-Pu)
- **Determination of laboratory testing conditions for leaching and sorption-desorption experiments under normal and high pressure**
  - model water 1, p=0.1 MPa, T=90^{o}C
  - model water 2, p=15 MPa, T=80^{o}C
- **Development of test techniques for radionuclide leaching from glasses**
  - for 0.1 MPa pressure
  - for high pressure
- **Assembly and launch into operation of the KMCC laboratory installation for leaching from glasses under normal and high pressures, and temperatures**
  - for 0.1 MPa pressure
  - for high pressure

Fig. 2 Laboratory scale tests to study on KMCC phosphate and borosilicate glass properties in respect of the storage and geological disposal of immobilized weapon plutonium production wastes



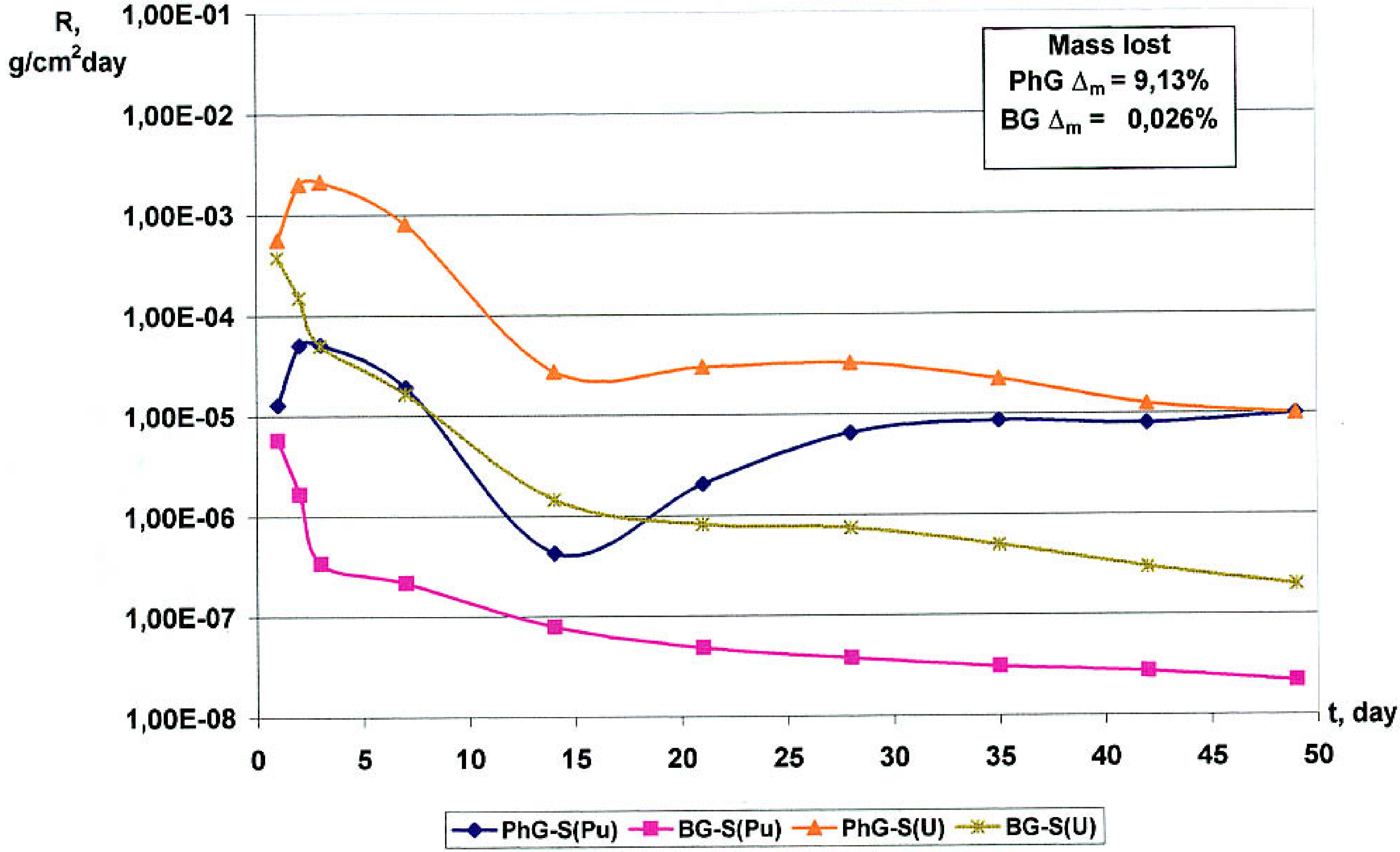


Fig. 3. Pu, U leaching rates for glasses containing MCC actual radioactive sludges at T=90C, P=0,1 Mpa; PhG-S- phosphate, borosilicate glasses containing MCC actual radioactive sludges

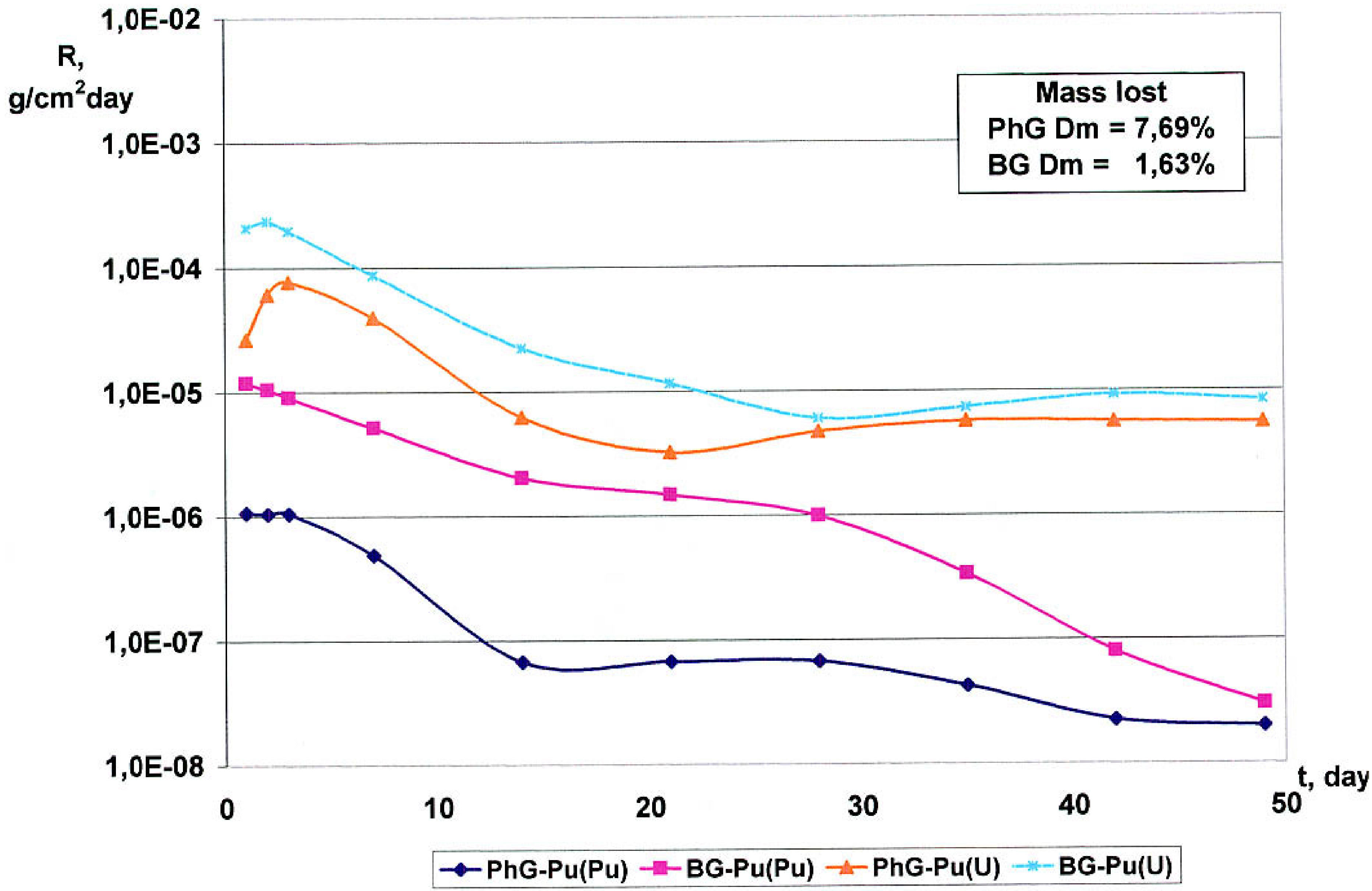


Fig. 4. Pu, U leaching rates for glasses containing PuO_2 at T=80C, P=15 Mpa. PhG-Pu, BG-Pu phosphate, borosilicate glasses containing imitator of radioactive sludges and plutonium dioxide