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Leaching of actinides and other radionuclides from matrices of Chernobyl "lava" as analogues of vitrified HLW

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ABSTRACT

The paper commemorates the 30th anniversary of the severe nuclear accident at the Fourth Unit of the Chernobyl Nuclear Power Plant. Results of the investigation of radioactive glassy lava-like materials formed as a result of the accident are presented. Leaching of Pu, Am and Cs in distilled water and sodium carbonate solution at 25 °C from matrices of black and brown Chernobyl "lava" is comparable, however, leaching of Cs from black "lava" in seawater at 25 and 90 °C is almost 2 times higher than that for brown "lava". Chemical alteration of black and brown "lava" in seawater is much more intensive that in distilled water and sodium carbonate solution. Comparison of leaching behavior of Chernobyl "lava" and aged samples of nuclear glass is not clear so far because of the lack of data. Further study of Chernobyl "lava" as analogues of vitrified high level waste (HLW) and possibly, Fukushima's corium is needed.

1. Introduction

The severe nuclear accident at the Fourth Unit of the Chernobyl Nuclear Power Plant (ChNPP) on 26 April 1986 was accompanied by full destruction of the reactor core. Interaction between hot destroyed fuel cladding and silicate materials of reactor (concrete, sand, serpentinite) caused formation of a lava-like highly radioactive melt, which penetrated into different premises below the reactor basement and solidified, forming the so called Chernobyl "lava" or fuel-containing masses [1–14]. Some direct measurements of "lava" volume gave at least 192 m^3 [4], although there is still uncertainty related to precise evaluation of total volume of fuel-containing masses and amount of fuel (calculated on UO_2) remaining inside the "Shelter" (the enclosure built around the ruined reactor) [4,13].

Scientists of the V.G. Khlopin Radium Institute (KRI) took part in the study of the scenario and consequences of the Chernobyl accident as early as May 1986. However most samples of Chernobyl "lava" from the KRI archive were manually collected and transported to Leningrad (now St. Petersburg) only in 1990 (Fig. 1). It is assumed that the KRI collection of Chernobyl "lava" is the only one in the world still available for further research. There are two main types of these "lava" samples, having black and brown color (Fig. 2). Brown color appears to be caused by numerous tiny inclusions of uranium oxide phases containing up to several wt% zirconium [10]. Black "lava" contains fewer inclusions and its color can be related to uranium dissolved in the glass matrix and to radiation defects. In some samples the glass matrix of black "lava" contains iron up to 6–7 wt% but usually the content of Fe in black glass matrix does not exceed 1 wt% [6,10]. Thus the color is not an obvious indicator of oxidation state or other physicochemical conditions of formation.

Bulk chemical composition of Chernobyl "lava", results of electron-probe microanalyses of glass-like "lava" matrices (avoiding inclusions of different crystalline phases) and content of main radionuclides in "lava" are summarized in Tables 1–3.

In 1990 some newly formed material of yellow color was observed on the surface of Chernobyl "lava" in different places [4]. Study of this material at KRI [11] confirmed that it consists of different uranyl phases such as $UO_4{\cdot}4H_2O$ (analogue of natural studtite); $UO_3{\cdot}2H_2O$ (analogue of epiianthinite); $UO_2 \times CO_3$ (analogue of rutherfordine) and $Na_4(UO_2)(CO_3)_3$. Also the sodium carbonate phases $Na_3H(CO_3)_2{\cdot}2H_2O$ and $Na_2CO_3{\cdot}H_2O$ were identified among the secondary uranium minerals [11]. This observation proved that active chemical alteration of Chernobyl "lava" is going on at the present time inside the "Shelter". Analysis of chemical composition of water existing inside the "Shelter" [12] confirmed that such solutions are alkaline (pH = 8.5–10) with high content of carbonate and bicarbonate ions (up to 2 g/l and 8 g/l, respectively). Chemical alteration supports radionuclide migration from "lava" matrices into groundwater which should be kept under permanent monitoring. Moreover, possible formation of secondary

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Fig. 1. Large fragment of Chernobyl "lava" prepared for packing and delivery to Leningrad. Photo had been taken by B. Burakov inside "Shelter" in 1990.

uranium minerals on the surface of some "lava" samples kept at KRI under laboratory conditions has been observed in 2011, when part of KRI Chernobyl collection was repacked (Fig. 3).

Although Chernobyl "lava" contain inclusions of some crystalline phases including different solid solutions "UO_2–ZrO_2", high-uranium zircon, $(Zr_{1-x}U_x)SiO_4$, etc. [5,8], their matrices are characterized by relatively homogeneous distribution of radionuclides [14]. Therefore the glass-like matrix of the "lava" might be considered as an analogue of aged (30 years old) vitrified high level radioactive waste (HLW). A study of radionuclide leaching from Chernobyl "lava" provides very important information to be used for both thermodynamic and kinetic modeling of long-term behavior of vitrified HLW. Some results obtained from the study of Chernobyl "lava" can be used to predict physico-chemical properties of the "corium" formed at the Fukushima nuclear power plant.

This paper summarizes current and earlier data on chemical durability of Chernobyl "lava" in distilled water, simulated sea water and aqueous solution of sodium-carbonate.

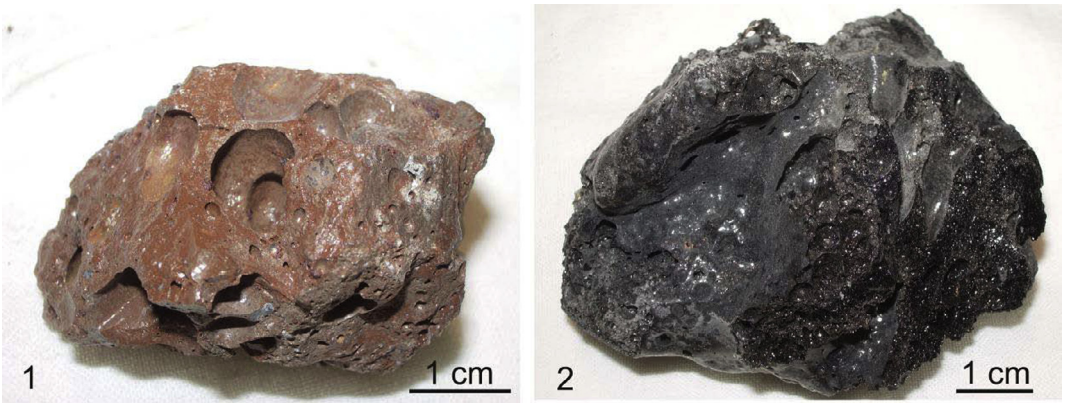

Fig. 2. Some samples of Chernobyl "lava" from KRI collection: (1) brown "lava" from steam-discharge corridor and (2) black "lava" from Elephant Foot" (room 217). Photos had been taken by B. Burakov and V. Zirlin in 2011.

Table 1
Simplified bulk chemical composition of Chernobyl "lava" [6,7].

Type of "lava"	Chemical composition, wt%							
	U	Zr	Na	Fe	Mg	Ca	Si	Al
Black	4–5	2–6	2–10	0.3–6	1–5	3–13	19–36	3–8
Brown	8–7	5–6	4	1–2	4	5	31–33	4

Table 2
Results of electron-probe microanalyses of glass-like silicate matrix of Chernobyl "lava" avoiding inclusions of crystalline phases [6,10].

Type of "lava"	Chemical composition, wt%								
	U	Zr	K	Na	Fe	Mg	Ca	Si	Al
Black	2.7–4.0	3.1–3.7	1.4–2.7	0.4	0.3–6.7	1.2–3.2	5.1–7.2	28–37	2.7–4.4
Brown	2.0–2.4	2.4–2.9	1.2–2.3	0.6	0.2–0.4	3.5–4.4	4.5–8.2	37	2.8–4.0

Table 3
Content of main radionuclides in Chernobyl "lava" on 06.2013 [15] and recalculated for 26.04.1986 [1,7].

Type of "lava"	Radionuclides, Bq/g						
	^{137}Cs	^{144}Ce	^{154}Eu	^{244}Cm	^{241}Am	$^{239,240}Pu$	^{238}Pu
Black	$2{\cdot}10^7$ ($2.3{\cdot}10^7$)	($2{\cdot}10^9$)	$5{\cdot}10^5$ ($1.3{\cdot}10^6$)	$5{\cdot}10^4$ ($1.2{\cdot}10^7$)	$1.2{\cdot}10^6$ ($3.5{\cdot}10^7$)	$8.2{\cdot}10^5$ ($7.3{\cdot}10^7$)	$4.3{\cdot}10^7$ ($3.8{\cdot}10^7$)
Brown	$4.1{\cdot}10^7$	($2.1{\cdot}10^9$)	$1.2{\cdot}10^6$	$1.1{\cdot}10^5$	$2.8{\cdot}10^6$	$1.8{\cdot}10^6$	$9.2{\cdot}10^5$