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Physico-chemical properties of Chernobyl lava and their destruction products

Andrey A. Shiryaev [a, b, c, *], Irina E. Vlasova [b], Boris E. Burakov [d], Boris I. Ogorodnikov [e], Vasily O. Yapaskurt [f], Alexey A. Averin [a], Alexey V. Pakhnevich [g], Yan V. Zubavichus [h]

[a] Institute of Physical Chemistry and Electrochemistry RAS, Leninsky pr., 31 korp. 4, Moscow 119071, Russia
[b] Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory 1 bld. 3, Moscow 119991, Russia
[c] Institute of Ore Geology, Petrography, Mineralogy and Geochemistry RAS, Staromonetny per, 35, Moscow 119017, Russia
[d] V.G. Khlopin Radium Institute, 2nd Murinsky av. 28, St.Petersburg 194021, Russia
[e] Karpov Physical Chemistry Institute, Vorontsovo Pole str. 10, Moscow 105064, Russia
[f] Department of Geology, Moscow State University, Moscow 119991, Russia
[g] Paleontological Institute RAS, Profsoyuznaya str. 123, Moscow 117997, Russia
[h] NRC "Kurchatov Institute", Akademika Kurchatova Sq. 1, Moscow 123098, Russia

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ABSTRACT

The paper commemorates 30th anniversary of severe nuclear accident at the 4th Unit of Chernobyl NPP. Results of the investigation of radioactive glassy lava-like materials formed as a result of the accident at their current state are presented. Complementary analytical methods: vibrational spectroscopy, XAFS, SEM, EBSD, X-ray tomography, provide new information about structure of the Chernobyl lava matrix and inclusions. Most of these techniques are applied to the lava samples for the first time and allow to derive consistent model of the lava and to resolve some of existing controversies. The glassy matrix of the lava is an anhydrous depolimerised metaluminous glass with signs of devitrification. Principal inclusions are $(U,Zr)O_{2-x}$ and $(Zr,U)O_{2-x}$ solid solutions with tetragonal and monoclinic structures, UO_2 and U-rich zircon. Cracks around large inclusions are observed; some of them could be caused by volume expansion during tetragonal to monoclinic transition in zirconia. The lava accumulations are characterized by different stability against spontaneous destruction, with the pumice-like lava being the least stable, generating radioactive aerosols and particles with sizes up to 250 μm.

1. Introduction

The accident at the 4th Unit of Chernobyl Nuclear Power Plant (ChNPP) on 26 April 1986 led to destruction of the reactor core and release of an enormous amount of solid and gaseous radioactive products to the environment due to explosion and subsequent fire. Independent approaches based on ^{137}Cs and ^{90}Sr fractionation and structural peculiarities of dispersed fuel and corium particles showed that transient (few seconds or less) temperatures immediately prior to the explosion event reached at least 2200–2600 °C leading to reactions between the UO_2 fuel and zircaloy cladding (Burakov et al., 1997a, 2003; Kashparov et al., 1996; Kashparov et al., 1997). The explosion epicenter was presumably localized in a relatively small volume of the reactor core (Abagyan et al., 1991; Adamov et al., 1988; Kashparov et al., 1997). Though the estimates vary, the amount of fuel dispersed to dust (both inside and outside the reactor building) and expelled from the reactor shaft is estimated as ~4–6% from the total amount of 190 metric tons of uranium (Arutyunyan et al., 2010; Information …, 1986; Lebedev et al., 1992).

In the RBMK reactors the reactor basement plate is a cylinder 14.5 m in diameter and 2 m in height, filled with serpentinite with bottom and top steel lids interconnected by stiffening ribs and water tubes. During the explosion a 100–110° sector of the basement plate was pushed approx. 4 m down, merging the reactor shaft with a former sub-reactor room 305/2 (e.g., Arutyunyan et al., 2010). The amount of nuclear fuel in the room 305/2 is estimated at 65–80 tons of UO_2 (Borovoi et al., 1998). Before and shortly after the explosion the fuel reacted with zircaloy and later with construction materials (sand, concrete, serpentinite, steel), leading to the

* Corresponding author. Institute of Physical Chemistry and Electrochemistry RAS, Leninsky pr., 31 korp. 4, Moscow 119071, Russia.
E-mail address: shiryaev@phyche.ac.ru (A.A. Shiryaev).

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formation of so-called lava-like fuel-containing materials (LFCM) or Chernobyl "lava" (Burakov et al., 1994, 1997a,b; Ushakov et al., 1997). Several days after the accident considerable fraction of the initial lava pool spread into other rooms of the reactor building (Burakov et al., 1997a), forming vertical and horizontal flows which solidified into a highly radioactive glassy material with inclusions of high-uranium zircon crystals $(Zr_{1-x}U_x)SiO_4$, particles of molten stainless steel, uranium oxide dendrites and grains, and particles of Zr-U-O phases (solid solutions in the system of UO_2-ZrO_2). Several varieties of the lava are known (e.g., Anderson et al., 1993; Borovoi et al., 1990, 1991a, 1991b; Burakov et al., 1994, 1997a,b; Pazukhin, 1994; Pazukhin et al., 2006; Savonenkov et al., 1991; Trotabas et al., 1993): 1) brown lava; 2) black lava, and 3) much less abundant and less studied polychromatic lava. On the lower levels of the reactor building the flow of brown lava entered water in the bubbler tank forming pumice-like material (Borovoi et al., 1991a; Trotabas et al., 1993). Controversy still exists about the total amount of uranium in all "lava" streams in comparison with initial fuel inventory. Estimates vary from 9–13% (Kiselev and Checherov, 2001) to >80% (Arutyunyan et al., 2010) of total amount of the ChNPP fuel; the rest is believed to remain in inaccessible premises of the reactor, possibly as fuel rods fragments.

Although the microstructure and other properties of the Chernobyl "lava" were extensively studied in the past, in particular, in 1990–1997 (Anderson et al., 1993; Arutyunyan et al., 2010, Borovoy et al., 1990, 1991a, 1991b; Burakov et al., 1994, 1997a,b; Pazukhin, 1994; Pazukhin et al., 2006; Savonenkov et al., 1991; Trotabas et al., 1993), some important features relevant for prediction of their long-term behavior remains poorly studied. The main obstacle is high radioactivity of the samples. We report here new results on present (as of 2014–2015) state of lava samples and aerosols collected inside the "Shelter" building, complementing our recent investigation of radioactivity distribution in the lava samples (Vlasova et al., 2015). Most of the analytical techniques employed by us are applied to the lava samples for the first time and obtained results are important to derive consistent model of the lava and to resolve some of existing controversies.

2. Samples and methods

All samples described in the paper were collected inside the confinement building "Shelter" of ChNPP.

2.1. Bulk lava samples

Bulk lava samples were manually detached under harsh conditions in 1990 by MrVladimir Zirlin of the V.G. Khlopin Radium Institute (St. Petersburg, Russia) from two different types of lava. Small samples described in the current paper represent pieces of much larger specimens (several tens cm^3): the fragments of black lava (Sample I, approx. 3 × 1.5 × 1.5 mm in size, Fig. 1A, B, and Sample II ca. 4.5 × 2 × 2 mm in size, Fig. 1C, D) were collected from the lava stream "Elephant foot", level +6.0 m (Borovoi et al., 1991a; Burakov et al., 1997a); and the fragment of brown lava (Sample III, 3 × 2 mm, Fig. 1E, F) was collected from the steam-discharge corridor at level +6.0 m (Borovoi et al., 1991b; Pazukhin et al., 2003). The fragments were mounted in 1991 into acrylic resin and manually polished in a glove box. For the polishing SiC powder with grain sizes (decreasing during the process) 28/14, 10/5 and 3/1 μm were used; final polishing was performed on dense paper with diamond paste (1/0). After the polishing the samples were stored at laboratory till 2015. This process provided mirror-like finish with virtual absence of a damaged layer as confirmed by successful EBSD analyses of steel droplets (see below). Despite pronounced radiation damage of the resin at the contact with the lava after 24 years of storage, the surface of LFCM remains mirror-like.

2.2. Aerosol particles

Aerosol particles were collected in 2010–2014 at the distance of 20–30 cm from the lava heap in room 012/7 (level 0.0 m, the first floor of the Bubbler tank (Borovoi et al., 1991a)) using a pack of three Petryanov filters with different particulate retention sizes mounted on the nose of the air blower H810 RadeCo operating for 2 h at a pump rate 100 dm^3/min. Daily variations of the air temperature in this room are negligible, annual variations are within 4°C (+9°C in winter and +13°C in summer). Chemical and radionuclide (e.g., $^{137}Cs/^{241}Am$) composition of the particles collected is consistent with composition of the heap (Pazukhin et al., 2003; Ogorodnikov et al., 2013).

2.3. Spontaneously detached individual sub-millimeter particles

These chips were collected in 2013–2014 on the planar cuvette placed for 6 months on the floor 0.50 m in front of a lava heap in room 012/7 (see chapter 2.2). These particles are of particular interest, since their detachment from the lava accumulation appears to be spontaneous. The particular lava agglomeration is mechanically heterogeneous: the internal part is highly porous (pumice-like or granulated, see Fig. 1G, H) since it was formed when hot brown lava stream entered in contact with water in the Bubbler tank, whereas the outer shell is glassy due to rapid quenching (Borovoi et al., 1991a; Pazukhin et al., 2003). The glassy shell was partly broken by researchers. The exact origin of the studied particles – the heaps' shell or interior or even destruction of eventual pieces of pumice observed in this room – is unclear.

2.4. Experimental details

Several analytical methods revealing different chemical and structural features of the samples were employed. Note that spectroscopic data for the "lavas" were not available before. Quantitative SEM-EDX analyses of the polished samples (described in chapter 2.1) was performed using JEOL JSM-6480LV equipped by Oxford X-Max^n 50 spectrometer and Oxford Nordlys Max2 EBSD detector. Analytical conditions were as following: 30 nm carbon coating, accelerating voltage – 20 kV, electron beam current – 10 nA, working distance – 10 mm. Quantification of detected elements was achieved using the following reference materials: albite, FeS_2, $Ca_3Si_3O_9$, TiO_2, Cr_2O_3, Mn, Zr, UO_2, and Di-117733, Hbl-143965, Hyp-746, Kfs-143966, Hyp-746 from (Corrections, 1980). XPP-correction was applied. The data are given in mass% to facilitate comparison with literature data, which were mostly obtained using Emission analysis. Semi-quantitative SEM-EDX investigation of loose unpolished aerosol and sub-mm particles (described in chapters 2.2 and 2.3) study was performed using JEOL JSM-6380 LA with JED 2300 analyser. Raman spectra in quasi-backscattering geometry were acquired with Senterra (Bruker) spectrometer with an Olympus BX-51 microscope with long working distance objectives. Excitation wavelengths of 532 and 785 nm were employed. The laser power was kept sufficiently low to prevent sample modification; the spot size was 2–5 μm depending on magnification used. IR reflectance spectra were acquired using SpectrumOne FTIR spectrometer with AutoImage microscope (Perkin Elmer). To assess homogeneity mapping of the whole sample with a 100 μm aperture was performed. In addition, spectra of representative points and of selected inclusions were acquired with up to 256 scans with spectral resolution of 4 cm^{-1}. X-ray microtomography (X-ray micro-CT) of aerosol filters and of