Article

Long-Term Aging of Chernobyl Fuel Debris: Corium and “Lava”

Bella Zubekhina 1,2, *, Boris Burakov 1,3, Ekaterina Silanteva 1,3, Yuri Petrov 1, Vasilii Yapaskurt 4 and Dmitry Danilovich 5

Abstract: Samples of Chernobyl fuel debris, including massive corium and “lava” were collected inside the Chernobyl “Sarcophagus” or “Shelter” in 1990, transported to Leningrad (St. Petersburg) and stored under laboratory conditions for many years. In 2011 aged samples were visually re-examined and it was confirmed that most of them remained intact, although some evidence of self-destruction and chemical alteration were clearly observed. Selected samples of corium and “lava” were affected by static leaching at temperatures of 25, 90 and 150 °C in distilled water. A normalized Pu mass loss (NL Pu) from corium samples after 140 days was noted to be 0.5 g/m² at 25 °C and 1.1 g/m² at 90 °C. For “lava” samples NL Pu was 2.2–2.3 g/m² at 90 °C for 140 days. The formation of secondary uranyl phases on the surface of corium and “lava” samples altered at 150 °C was confirmed. The results obtained are considered as an important basis for the simulation of fuel debris aging at Fukushima Daiichi nuclear power plant (NPP).

Keywords: leaching; chemical alteration; Chernobyl “lava”, corium; fuel debris; Fukushima Daiichi NPP; plutonium

1. Introduction

The severe nuclear accident in the 4th Unit of the Chernobyl nuclear power plant (NPP)—presently in the territory of Ukraine—occurred on 26 April 1986 [1,2]. During a planned test, unit 4 of the RBMK (High-power channel-type reactor) reactor was unintentionally drawn in a potentially unstable (with positive reactivity) condition, which was followed by a combination of unexpected events that caused an uncontrolled nuclear chain reaction to occur within its extended core, resulting in a large amount of energy suddenly being released. In some local parts of the reactor core, very high temperatures were reached as a result of prompt supercriticality. This vaporized the superheated cooling water and ruptured the reactor core in a highly destructive steam explosion, followed by an open-air reactor core fire that released a considerable amount of airborne radioactive contamination [3,4]. Chernobyl corium was formed before the explosion as a result of the short time high-temperature (≥2400–2600 °C) interaction between the nuclear fuel and the zirconium cladding in the local part of the reactor core [5–7]. Basically, solidified corium consists of solid solutions “ZrO₂–UO₂”, but it may also include molten steel or steel oxidation products.

After the explosion, an interaction between fuel fragments, solidified corium and silicate materials (concrete, serpentinite, sand) at an initial temperature of 1500–1600 °C
occurred, causing the formation of a highly radioactive silicate melt—so-called Chernobyl “lava” or “lava-like fuel containing masses”—below the reactor shaft (mainly in room #305/2). Later, “lava” melt penetrated into different premises and solidified, forming brown and black colored streams. Only a small amount of massive corium survived in room #305/2, on the surface of steel pipes [6,7].

Samples of Chernobyl massive corium and “lava” were collected inside the “Shelter” in 1990 by scientists of the V.G. Khlopin Radium Institute (KRI) [5–7]. For many years these samples were stored at KRI under laboratory conditions at temperatures of around 20–25 °C in air without humidity control. In 2011, these samples were visually re-examined and it was confirmed that most samples remained intact. Only a couple of samples of black “lava” demonstrated mechanical self-destruction into small fragments. The formation of secondary uranyl phases were also observed in local areas of some corium and “lava” pieces [7]. Although no information has been reported so far about uranyl phases formed on the surface of Chernobyl “hot” particles, some evidence of higher leach rates of $^{90}\text{Sr}$ have been published [8,9] for fuel particles in contaminated soils, comparing them to ones from the Chernobyl cooling pond, where U-oxide particles are less affected by oxygen.

A study of Chernobyl sample aging is important not only for the optimal retrieval of highly radioactive materials located inside the Chernobyl “Shelter”, but also for the evaluation of fuel debris’ chemical behavior at Fukushima Daiichi NPP. Another important task is to conclude the role of self-irradiation on aging phenomena in corium and similar solids containing high amounts of radionuclides [10]. For this reason, experiments on the chemical alteration of Chernobyl corium and “lava” were recently carried out at KRI.

2. Materials and Methods

The following Chernobyl samples were used for leaching and alteration experiments:

1. A total of 3 fragments of corium from room 305/2—for leaching experiments at 25 and 90 °C and for alteration experiments at 150 °C in distilled water. Chemically, Chernobyl massive corium is very inhomogeneous [11]. The plutonium ($^{238,239,240}\text{Pu}$) content in massive corium samples used for leaching tests varies from 1.4 to 5.6 MBq/g.

2. Two fragments of black “lava” and Two fragments of brown “lava”—for leaching at 90 °C and alteration at 150 °C in distilled water. Distribution of U and other alpha-emitters in matrices of Chernobyl “lava” (both black and brown) is relatively homogeneous [12]. Bulk content of plutonium ($^{238,239,240}\text{Pu}$) in “lava” matrices is 1.5 and 3 MBq/g for black and brown “lava”, respectively [6,7,13,14].

Before the leaching experiments, all samples have been weighted and analyzed by non-destructive analytical methods (gamma-spectrometry, X-ray fluorescence analysis, optical microscopy). The weights of corium fragments used in this research varied from 0.15 to 0.18 g; the weights of “lava” fragments were 0.3 and 0.7 g for black and brown samples, respectively.

Conditions of static leach tests, including the calculation of normalized mass loss, were the same as in our previous work [11]. Leaching experiments were performed at temperatures of 25 and 90 °C in distilled water. For accelerated chemical degradation, long-term alteration experiments were performed at a temperature of 150 °C in distilled water.

For measurements of Pu in leachates, a Canberra 7401 alpha-spectrometer was used.

For studying the corium phase composition various techniques were used including, XRD, Raman Spectroscopy and SEM-EDX methods. Two polished samples with carbon coating were prepared for SEM-EDX analysis (Figure 1) using Tescan Vega 3 SBH equipped with an INCA X-Act EDS detector and a JEOL JSM-6480LV Scanning Electron Microscope equipped with a W thermal emission cathode and an Oxford X-Maxn 50 detector (active area 50 mm$^2$). The XPP correction was applied using Oxford Instruments INCA software. The accelerating voltage was 20 kV; electron beam current—10 nA, working distance—10 mm.
Figure 1. SEM-BSE microphotographs of two polished samples of Chernobyl massive corium.

Summarizing the EDX analysis results, we conclude that the main phases of Chernobyl corium are:

- Matrix consists of an iron oxide phase doped with Al and Cr (from 1 to 13 wt. % of Al and from 1 to 15 wt. % of Cr). This phase was identified by Raman spectroscopy and XRD analysis as \( \text{Fe}_3\text{O}_4 \) (PDF #011111). Different contents of Cr in the iron oxide phase affects the different levels of contrast in the BSE pictures.

- Minor phases of solid solutions “\( \text{UO}_2\)-\( \text{ZrO}_2 \)” (Figure 2) with the following compositions:
  1. Zr-U-O with 50–60 wt. % of Zr and 13–20 wt. % of U;
  2. mainly U-oxide phase with admixtures of Zr (1–2 wt. %) and Fe (1–3 wt. %);
  3. mainly Zr-oxide phase with admixtures of U (1.5–3 wt. %) and Fe (3–10 wt. %).

Figure 2. SEM-BSE microphotographs of corium sample with different phases of (U,Zr)O\(_2\) solid solutions. Content of U varies from 1.5 to 82 wt. %; Zr—from 1 to 67 wt. %. For “\( \text{UO}_2\)-\( \text{ZrO}_2 \)” phase the U and Zr contents are comparable (50–60 wt. % of Zr and 13–20 wt. % of U).

In addition, an certain amount of the Si-Fe-bearing phase and metallic inclusions with Fe, Ni and Cu were found.

The simplified chemical and radionuclide composition of Chernobyl corium and “lava” are presented in Tables 1 and 2.
Table 1. Bulk contents of the chemical elements (except oxygen) in matrices of Chernobyl “lava” and massive corium [7,13].

| Material            | U  | Zr | Fe  | Na  | Mg  | Ca  | Si  | Al  |
|---------------------|----|----|-----|-----|-----|-----|-----|-----|
| Black “lava”        | 4–5| 2–6| 0.3–6| 2–10| 1–5 | 3–13| 19–36| 3–8 |
| Brown “lava”        | 7–10| 5–6| 1–2 | 4   | 4   | 5   | 31–33| 4   |
| Massive corium      | 1–40| 0.2–20| 40–95|     |     |     |     | No data |

Table 2. Contents of main radionuclides in matrices of Chernobyl “lava” and massive corium [7,11].

| Material      | $^{137}$Cs | $^{154}$Eu | $^{155}$Eu | $^{244}$Cm | $^{241}$Am | $^{239,240}$Pu | $^{238}$Pu |
|---------------|------------|------------|------------|------------|------------|---------------|------------|
| Black “lava”  | 20–40      | 1–3        | 2          | 0.1        | 1          | 0.03          | 1          | 0.5        |
| Brown “lava”  | 50–60      | 3–4        | 5          | 0.2–0.3    | 3          | 0.06          | 2          | 1          |
| Massive corium| 0.1–30     | 0.2–5      | 0.1–1      | 0.03–0.07  | 0.1–1      | 0.01–0.04     | 1–4        | 0.4–1.6    |

3. Results

The normalized mass losses of Pu for Chernobyl black and brown “lava” are shown in Table 3 and Figure 3. Black and brown “lava” did not demonstrate essential differences in Pu mass loss. The total NL$_{Pu}$ (distilled water, 90 °C, 140 days) was 2.2 and 2.3 g/m$^2$ for black and brown “lava”, respectively. The normalized mass losses of Pu from corium matrix are shown in Table 3 and Figure 4.

Table 3. The normalized mass losses of Pu from different materials in distilled water.

| Sample                   | Conditions of Leaching | Total Pu Normalized Mass Loss in Distilled Water, g/m$^2$ |
|--------------------------|------------------------|----------------------------------------------------------|
| black “lava”             | 25 °C for 7 days       | 0.3 [13]                                                  |
|                          | 25 °C for 270 days     | 5.7 [13]                                                  |
|                          | 90 °C for 140 days     | 2.2 ± 0.2                                                 |
| brown “lava”             | 25 °C for 8 days,      | 0.4 [15] $^1$                                             |
|                          | 25 °C for 7 days       | 0.1 [13]                                                  |
|                          | 25 °C for 270 days     | 4.7 [13]                                                  |
|                          | 90 °C for 140 days     | 2.3 ± 0.2                                                 |
| Corium                   | 25 °C for 140 days     | 0.5 ± 0.08                                                |
|                          | 90 °C for 140 days     | 1.1 ± 0.12                                                |
| PuO$_2$ single crystals   | 90 °C for 28 days      | from 2 × 10$^{-4}$ to 9 × 10$^{-3}$ [16]                  |
| $^{239}$PuO$_2$ ceramic pellet | 25 °C for 28 days     | 4.6 × 10$^{-4}$ [16]                                      |
| LWR (Light-water reactor) spent U-oxide fuel, (burnup 54.5 MWd/kgU) | 25 °C for about 150 days | 3 × 10$^{-3}$ [17]                                       |

$^1$ performed in 1991.

Chemical alteration of Chernobyl “lava” has been observed inside the “Shelter” after several years after the accident. Some new-formed phases identified are UO$_3$ × 2H$_2$O (an analog of epianthinite), UO$_4$ × 4H$_2$O (an analog of studtite), UO$_2$CO$_3$ (an analog of rutherfordine), Na$_4$(UO$_2$)(CO$_3$)$_3$ and sodium carbonates [7,18]. During the dry storage of Chernobyl samples (corium and “lava”) in laboratory conditions, chemical alteration and formation of secondary uranyl minerals (“yellow phases”) were clearly observed for most of them. Fluorescence of secondary phases in UV-light confirms that uranium in these phases partially oxidized from U (IV) to U (VI) (Figure 5).
After 1 year of contact with distilled water at a temperature 150 °C, samples of “lava” and corium were significantly altered. On the surface of Chernobyl corium, secondary uranyl minerals of two forms were observed (Figure 6, right). One of them, with needle-shaped crystals, was not observed in alteration experiments at a lower temperature (90 °C). For “lava”, sample chemical degradation was clearly observed (Figure 6, left), in contrast with the “fresh” sample (Figure 7b). Different alteration processes took place dependent on the phase: formation of “gel” on the surface of the sample, corrosion of metallic inclusions in the “lava” matrix and oxidation of uranium in U-bearing phases with the formation of secondary uranyl minerals (Figure 6, left).

Figure 3. The differential normalized mass loss of Pu for black and brown “lava” in distilled water at temperature 90 °C. NL(Pu) in logarithmic scale. “Days” in figure does not refer to duration of leaching experiment, but time from the beginning of leaching experiments. Expanded uncertainty for all data is less than 20% of the value.

Figure 4. The differential normalized mass loss of Pu for corium samples in distilled water at temperature 25 and 90 °C. NL(Pu) in logarithmic scale. “Days” in figure does not mean duration of leaching experiment, but time from the beginning of leaching experiments. Expanded uncertainty for all data is less than 20% of the value.
After 1 year of contact with distilled water at a temperature 150 °C, samples of “lava” and corium were significantly altered. On the surface of Chernobyl corium, secondary uranyl minerals of two forms were observed (Figure 6, right). One of them, with needle-shaped crystals, was not observed in alteration experiments at a lower temperature (90 °C). For “lava”, sample chemical degradation was clearly observed (Figure 6, left), in contrast with the “fresh” sample (Figure 7b). Different alteration processes took place dependent on the phase: formation of “gel” on the surface of the sample, corrosion of metallic inclusions in the “lava” matrix and oxidation of uranium in U-bearing phases with the formation of secondary uranyl minerals (Figure 6, left).

Figure 5. Alteration of the surface of Chernobyl corium from room 217/2 with formation of secondary uranyl minerals in the light (left) and UV luminescence of alteration products (the same sample) (right).

Figure 6. Formation of secondary phases on the surface of Chernobyl brown “lava” (left) and corium (right) after 1 year contact with distilled water at 150 °C.
Figure 7. Chernobyl samples before leaching experiments: black “lava” from room 217/2 (a), brown “lava” from steam discharge corridor used for alteration experiment (b) and fragments of corium from room 305/2 (c).

4. Discussion

As assumed, the mechanism of plutonium release into water is mainly related to the dissolution of the silicate glass-like “lava” matrices and not the dissolution of the chemically stable crystalline inclusions of zircon (Zr,U)SiO$_4$ and solid solutions (Zr,U)O$_2$-(U,Zr)O$_2$. It is necessary to mention that the NL$_{Pu}$ from black and brown “lava” during short time leaching tests performed in 1991 [15] and 25 years later [13], are comparable. This indicates the relative chemical stability of “lava” matrices over long periods of time, although the effects of mechanical self-destruction of the black “lava” of the “Elephant foot” inside the “Shelter” and during storage under laboratory conditions were reported [7,11,19].

Plutonium release from the corium samples is less than one from “lava”. It is important to note that in contrast to the glass-like Chernobyl “lava”, the geometric surface area of which is considered as very realistic, the corium surface area could not be evaluated properly using formal geometrical measurements of the samples because of its high porosity. Therefore, the NL of Pu from corium, calculated for the real surface area, is expected to be less than that from “lava”. At the same time, release of Pu from corium was much higher in comparison with spent U-oxide fuel, which is surprisingly comparable with pure PuO$_2$ (Table 1). It is assumed that Pu in matrix of corium exists not only in stable forms such as an admixture in the crystalline structure of the solid solutions “ZrO$_2$-UO$_2$”, but also in chemically unstable species, such as nano-sized Pu-oxide particles, formed as a result of the high temperature melting in the system of “Zr$_{cladding}$—UO$_2$—steel—oxygen”.

It is important to note that at lower temperatures (25 and 90 °C), the dissolution of the “lava” matrix was not accompanied with “gel” formation. Such behavior of the “glassy” matrix of “lava” is controversial to nuclear waste glasses [20]. The material study of the secondary phases, formed as a result of chemical alterations, is a subject of future research.

The results obtained require further clarification from the precise study of the corium chemical and phase compositions using EMPA and XRD methods. However, it is possible to make the following conclusions:

1. Pu release into distilled water from matrices of black and brown Chernobyl “lava” is comparable. The total normalized Pu mass loss at 90 °C is 2.2–2.3 g/m$^2$ for 140 days.
2. Pu release from matrix of Chernobyl corium is less than that from “lava”. The total normalized Pu mass loss for 140 days is 0.5 and 1.1 g/m$^2$ at a temperature of 25 °C and 90 °C, respectively.
3. In comparison with the irradiated U-oxide LWR fuel, Chernobyl corium demonstrates, essentially, a lower level of chemical durability. Normalized Pu mass loss in distilled water at 25 °C for spent fuel and even $^{239}$PuO$_2$ is two orders of magnitude less than...
that for corium. It is assumed that at least part of the uranium and plutonium in the matrix of Chernobyl corium exist in chemically unstable forms.

4. The chemical alteration of Chernobyl corium and “lava” causes the formation of new formed phases with essentially different chemical and mechanical levels of durability. This has consequential effects on the long-term behavior of fuel debris.

**Author Contributions:** Conceptualization and methodology, B.Z. and B.B.; investigation, all authors; analytical support, E.S., Y.P., V.Y., D.D.; writing—original draft preparation, B.Z., B.B.; writing—review and editing. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by Russian Foundation for Basic Research (RFBR) grant #18-33-01182.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data presented in this study are available on request from the corresponding author. The data are not publicly available because original data owns to authors.

**Acknowledgments:** The authors are very grateful to V. Zirlin and L. Nikolaeva (Khlopin Radium Institute) for the treatment of the highly radioactive Chernobyl samples.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Information on the accident at the Chernobyl nuclear power plant and its consequences. *Sov. At. Energy* 1986, 61, 845–868. [CrossRef]

2. Rippon, S.; Blake, E.M.; Payne, J. Chernobyl: The Soviet Report. *Nucl. News* 1986, 29, 59–66.

3. International Atomic Energy Agency. *INSAG-7: The Chernobyl Accident: Updating of INSAG-1; Safety Series No. 75-INSAG-7; IAEA: Vienna, Austria, 1992.*

4. Poml, P.; Burakov, B. Study of a “hot” particle with a matrix of U-bearing metallic Zr: Clue to supercriticality during the Chernobyl nuclear accident. *J. Nucl. Mater.* 2017, 488, 314–318. [CrossRef]

5. Burakov, B.E.; Anderson, E.B.; Galkin, B.Y.; Pazukhin, E.M.; Shabalev, S.I. Study of Chernobyl “hot” particles and fuel containing masses: Implications for reconstruction the initial phase of the accident. *Radiochim. Acta* 1994, 65, 199–202. [CrossRef]

6. Burakov, B.E.; Anderson, E.B.; Shabalev, S.I.; Strykanova, E.E.; Ushakov, S.V.; Trotabas, M.; Blanc, J.-Y.; Winter, P.; Duco, J. The Behaviour of Nuclear Fuel in First Days of the Chernobyl Accident. *MRS Online Proc. Libr.* 1997, 465, 1297–1308. [CrossRef]

7. Burakov, B.E. Lava-like materials formed and solidified during Chernobyl accident. In *Comprehensive Nuclear Materials*, 2nd ed.; Konings, R., Stoller, R.E., Eds.; Elsevier: Amsterdam, The Netherlands, 2019.

8. Konoplev, A.V.; Bulgakov, A.A. Kinetics of $^{90}$Sr leaching from fuel particles in soils of the Chernobyl exclusion zone. *At. Energy* 1999, 86, 136–141. [CrossRef]

9. Bulgakov, A.; Konoplev, A.; Smith, J.; Laptev, G.; Voitsekhovich, O. Fuel particles in the Chernobyl cooling pond: Current state and prediction for remediation options. *Environ. Radioact.* 2009, 100, 329–332. [CrossRef]

10. Malkovskiy, V.I.; Yudintsev, S.V.; Ojovan, M.I.; Petrov, V.A. The Influence of Radiation on Confinement Properties of Nuclear Waste Glasses. *Sci. Technol. Nucl. Install.* 2020, 3, 1–14. [CrossRef]

11. Zubekhina, B.Y.; Burakov, B.E.; Bogdanova, O.G.; Petrov, Y.Y. Leaching of $^{137}$Cs from Chernobyl fuel debris: Corium and “lava”. *Radiochim. Acta* 2019, 107, 1155–1161. [CrossRef]

12. Vlasova, I.; Shiryaev, A.; Ogorodnikov, B.; Burakov, B.; Dolopolova, E.; Senin, R.; Averin, A.; Zubavichus, Y.; Kalmykov, S. Radioactivity distribution in fuel-containing materials (Chernobyl “lava”) and aerosols from the Chernobyl “Shelter”. *Radiat. Meas.* 2015, 83, 20–25. [CrossRef]

13. Zubekhina, B.Y.; Burakov, B.E. Leaching of actinides and other radionuclides from matrices of Chernobyl “lava” as analogues of vitrified HLW. *J. Chem. Thermodyn.* 2017, 114, 25–29. [CrossRef]

14. Nasirow, R.; Poeml, P. Gamma-Ray Spectrometry of Chernobyl Ceramic Samples; JRC Institute of Transuranium Elements: Karlsruhe, Germany, 2013.

15. Rogozin, Y.M.; Smirnova, E.A.; Savonenkov, V.G.; Krivokhatsky, A.S.; Avdeev, V.A.; Sagaidachenko, E.Y. Leaching of radionuclides from some newly formed products, extracted from reactor zone of 4th unit of Chernobyl NPP. *Radiochemistry* 1991, 33, 160–167.

16. Zubekhina, B.; Burakov, B. Plutonium leaching from polycrystalline and monocrystalline PuO$_2$. *Radiochim. Acta* 2018, 106, 119–123. [CrossRef]

17. Katayama, Y.B.; Bradley, D.J. Long-Term Leaching of Irradiated Spent Fuel. In *Scientific Basis for Nuclear Waste Management*; Northrup, C.J.M., Ed.; Advances in Nuclear Science & Technology: Springer: Boston, MA, USA, 1980.

18. Burakov, B.E.; Anderson, E.B.; Strykanova, E.E. Secondary Uranium Minerals on the Surface of Chernobyl “Lava”. *MRS Online Proc. Libr.* 1997, 465, 1309–1311. [CrossRef]
19. Borovoy, A.A. *Inside and Outside “Sarcophagus”*; CE IAE: Chernobyl, Ukraine, 1990. (In Russian)

20. Ojovan, M.I.; Pankov, A.S.; Lee, W.E. The ion exchange phase in corrosion of nuclear waste glasses. *J. Nucl. Mater.* **2006,** 358, 57–68. [CrossRef]