
Article:
Barlow, S.T., Bailey, D.J., Fisher, A.J. et al. (3 more authors) (2016) Synthesis of simulant 'lava-like' fuel containing materials (LFCM) from the Chernobyl reactor Unit 4 meltdown. MRS Advances, 2. pp. 1-6. ISSN 2059-8521

https://doi.org/10.1557/adv.2016.642

Synthesis of simulant 'lava-like' fuel containing materials (LFCM) from the Chernobyl reactor Unit 4 meltdown

Sean T. Barlow, Daniel J. Bailey, Adam J. Fisher, Martin C. Stennett, Claire L. Corkhill and Neil C. Hyatt
Department of Materials Science and Engineering, The University of Sheffield, S1 3JD, UK.

ABSTRACT

A preliminary investigation of the synthesis and characterization of simulant 'lava-like' fuel containing materials (LFCM), as low activity analogues of LFCM produced by the melt down of Chernobyl Unit 4. Simulant materials were synthesized by melting batched reagents in a tube furnace at 1500 °C, under reducing atmosphere with controlled cooling to room temperature, to simulate conditions of lava formation. Characterization using XRD and SEM-EDX identified several crystalline phases including ZrO_2, UO_x and solid solutions with spherical metal particles encapsulated by a glassy matrix. The UO_X and ZrO_2 phase morphology was very diverse comprising of fused crystals to dendritic crystallites from the crystallization of uranium initially dissolved in the glass phase. This project aims to develop simulant LFCM to assess the durability of Chernobyl lavas and to determine the rate of dissolution, behavior and evolution of these materials under shelter conditions.

INTRODUCTION

On the 26th of April 1986, an accident during an experimental power failure test destroyed Unit 4 of the Chernobyl Nuclear Power Plant, Ukraine. During the accident, temperatures reached in excess of 1600 °C resulting in melting of the nuclear fuel and zirconium cladding [1]. Interaction of the molten fuel mass with the structural materials of the reactor resulted in the formation of several lava-like flows. These lava-like flows formed glassy materials upon cooling in the basement levels beneath the ruined reactor [2]. These so called lava-like fuel containing materials (LFCM) are essentially glass-ceramic composite materials [3]. Accumulations of LFCM are located in numerous sub-reactor rooms beneath Unit 4, amounting to approximately 1250 tons [1]. LFCM masses are primarily brown or black and contain considerable porosity and compositional heterogeneity. However, granulated and pumice-like materials have also been observed. Solidified metallic spheres of varying diameter have been found in brown and black type lavas. Granulated and pumice-like materials are hypothesized to be the result of lava flows interacting with cold water, causing instant foaming and the formation of highly porous material [3].

Following the accident, an interim shelter was constructed to contain the ruined reactor and protect its contents. Although designed to last 30 years, degradation of the shelter structure has led to the ingress of substantial volumes of water. Interaction of water with LFCM within the shelter has caused weathering of substantial portions of the LFCM and formation of numerous secondary uranium compounds, studtite ($UO_4.H_2O$), rutherfordine (UO_2CO_3), schoepite ($(UO_2)_8O_2(OH)_{12}.12H_2O$) and paulscherrerite ($UO_2(OH)_2$). Constant wetting and drying of LFCM materials and associated secondary uranium mineral phases leads to the formation of fine radioactive aerosol particles; a significant respirable hazard within the shelter and a possible

source of airborne contamination [4], [5]. The study of the alteration of LFCM under shelter conditions is vital to understanding the long term behaviour of these materials, the hazard LFCM presents and the eventual remediation of the site. Due to the large amounts of spent nuclear fuel contained within LFCM, study of actual LFCM is hazardous and not without considerable challenge. Study of low activity simulant LFCM, derived from actual lava compositions, is needed to understand the durability of LFCM materials and to determine the alteration behaviour of these materials. This study was therefore conceived to design and synthesize representative simulant LFCM to allow the behaviour of LFCM to be studied without the additional complications of high radioactivity. The findings of this project could also assist in the development of glass wasteforms in engineered repositories.

REVIEW OF LFCM AND COMPOSITIONS AS SYNTHETIC TARGETS

Brown LFCM contains metallic iron in the form of spherical droplets within the glass matrix and ~11 wt% uranium. Black LFCM do not contain metallic iron and incorporate less uranium, ~6 wt% [1]. Analysis of LFCM by the Khloplin Radium Institute revealed several crystalline inclusions including non-stoichiometric UO_2, ZrO_2, from the fuel cladding materials, and a high uranium zircon phase termed Chernobylite. Dendrite-like inclusions of UO_x + Zr were reported, representing recrystallization of LFCM after cooling, along with phases of a fused morphology from the interaction between droplets of UO_x and Zirconium alloy cladding [6]. Compositions of brown and black LFCM have been reported in numerous publications, but each differ with regards to major glass components [1], [3], [7]–[9]. Consequently, averaged compositions were determined and used to produce the simulant materials in this study. Synthesized simulant compositions are shown in Table 1.

Table 1. Synthesized LFCM compositions

Component	Brown LFCM (mol%)	Black LFCM (mol%)
SiO_2	65.6	67.9
CaO	7.3	8.2
ZrO_2	3.3	3.0
Na_2O	5.3	5.8
BaO	0.1	0.1
Al_2O_3	4.2	5.1
MnO	0.5	0.4
Fe_2O_3	0.5	-
MgO	10.7	8.4
UO_2	2.5	1.2

EXPERIMENTAL PROCEDURE

Stoichiometric amounts of SiO_2 (Lochaline Quartz Sand 99.6%), $CaCO_3$ (Fisher 98%), ZrO_2 (Aldrich 99%), Na_2CO_3 (Alfa Aesar 98%), $BaCO_3$ (Alfa Aesar 99%), $Al(OH)_3$ (Acros 95%), Mn_2O_3 (Aldrich 99%), $Fe/Cr_{18}/Ni_{10}/Mo_3$ (Goodfellow), $Mg(OH)_2$ (Sigma-Aldrich 99.9%)

and UO_2 (British Drug Houses) were batched accordingly to produce both black and brown compositions. Batched compositions were carefully mixed prior to melting in an Elite Thermal Systems TSH 15/50/450 tube furnace under flowing H_2/N_2. Reducing conditions were utilized to simulate formation conditions during the accident. Samples were melted at 1500 °C and cooled to room temperature at a controlled rate. Initial samples were prone to spontaneous fracturing and an intermediate annealing step was successfully applied to reduce the residual stresses within the glass and obtain monolithic samples.

X-ray powder diffraction (XRD) was performed to determine the crystalline phases present within synthesized materials. Measurements were conducted using a Bruker D2 X-ray diffractometer in reflectance mode over the range $10° < 2\theta < 60°$ with Cu Kα radiation (30 kV, 10 mA). Subsequent data was processed using the Bruker DiffracEva 3.0 software package and the PDF-2 database used for peak identification.

Representative cross-sections of synthesized LFCM were produced by sectioning melted glasses using a Buehler Isomet Low Speed Saw. Crystalline phase assemblage of the cross-sections was studied by scanning electron microscopy (SEM) using a Hitachi TM3030 SEM. Partitioning of key elements within the simulant samples was determined by energy dispersive X-ray spectroscopy (EDX) using a Bruker Quantax EDX system coupled to the SEM. Samples were prepared for SEM-EDX by mounting in cold-setting epoxy resin and polishing with SiC and diamond paste to a 1 µm finish. Samples were sputter coated with carbon to avoid surface charge effects.

RESULTS & DISCUSSION

LFCM Synthesis

Produced ‘Brown’ and ‘Black’ LFCM compositions formed highly crystalline, glassy products. Brown type simulants were dark brown in color with a cracked and mottled surface with low porosity. Black simulant compositions formed a dark blue glass with a thin pale-blue surface layer that was glassy in appearance. The pale blue colored surface is not reported as present in the actual LFCM samples, found in the Chernobyl sub-reactor rooms, and the bulk was much darker in coloration. However, one particular LFCM variant, termed polychromatic ceramic, located in the upper levels of the destroyed Unit 4, was described as “a sealing-wax brown color with bright blue veinlets” [10]. Overall, the visual appearance of the simulants is comparable with reported LFCM.

Phase analysis

Results of powder X-ray diffraction analysis showed simulant LFCM to be glassy materials with significant crystalline content, as shown in Figure 1. The strong diffuse intensity is typical of glassy materials and the observed reflections were indexed to zirconium oxide (ZrO_2), a uranium-zirconium oxide solid solution ($U_{0.8}Zr_{0.2}O_2$) and cristobalite (SiO_2). Brown compositions were also found to contain a spinel phase, nominally $Fe(Fe_{1.96}Cr_{0.03}Ni_{0.01})O_4$.

The pale blue surface phase observed on black simulant lava was removed and characterized by XRD however no significant difference compared to the bulk was detected. This phase is believed to contain uranium in the U (IV) oxidation state, due to its blue coloration. A full analysis of the average oxidation state within the lavas will be carried out at a later date.

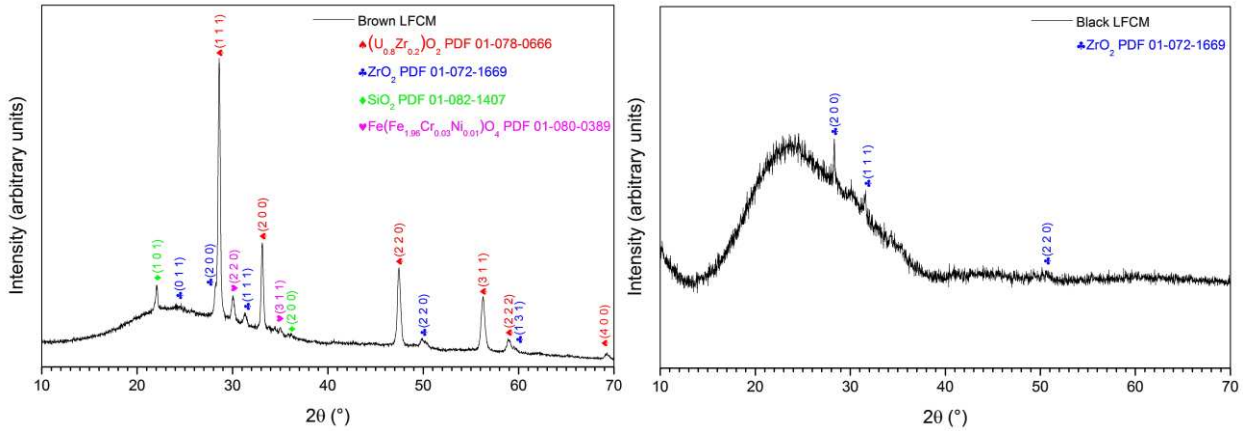

Figure 1. XRD plot of simulant brown (left) and black (right) LFCM

Scanning electron microscopy of black and brown simulant lavas found the microstructure to consist of a majority glass matrix with various minor phases dispersed throughout as distinguished by their contrast. Minor phases rich in U and Zr were present as dendritic and fused crystals. Spherical particles of metal were also found throughout the glass matrix of brown LFCM simulants, likely formed as droplets of molten metal trapped within the glass matrix during melting, as shown in Figure 2. Complementary EDX analysis highlights elemental partitioning with the samples in correspondence with the crystalline phases identified by XRD. EDX maps for the key elements indicate uranium and zirconium are evenly distributed throughout the glass matrix and concentrated within their representative crystal phases as shown in Figure 3.

Comparison of the experimental data presented in this study with the results of analysis of actual LFCM shows good agreement between the simulant and real materials [1], [3], [7]–[9]. Morphology, crystalline content and microstructure were found to be consistent with those observed in actual LFCM samples with the notable exception of the crystalline phase zircon ($ZrSiO_4$). These results would suggest that, although the simulant materials are a good approximation, further refinement is necessary to produce more representative simulant LFCM.

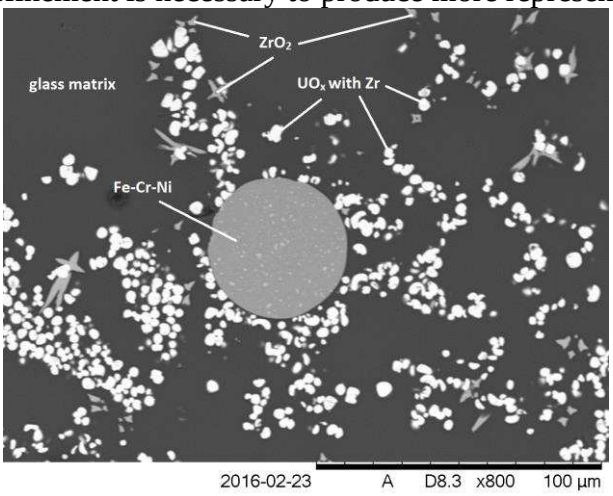

Figure 2. SEM micrograph of simulant brown LFCM labeling the crystalline phases present.

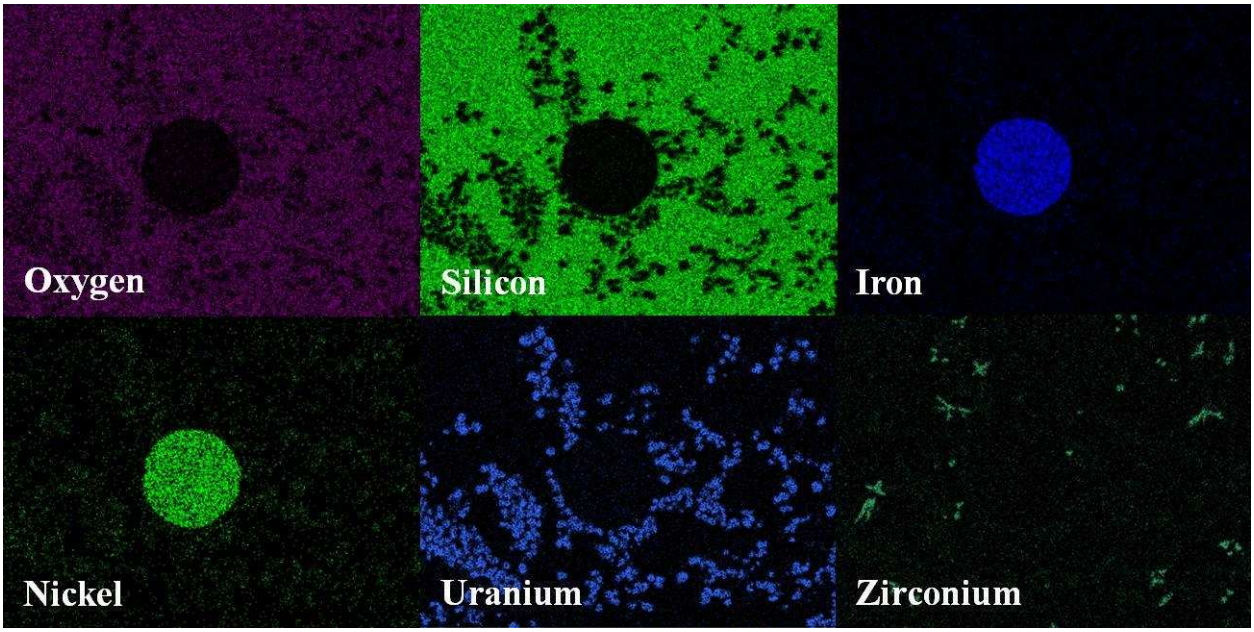

Figure 3. EDS maps of key elements in brown LFCM

Further elaboration of simulant LFCM

The behaviour of LFCM compositions when melting will be further studied by simultaneous thermal analysis (STA). This will allow the glass transition temperature and liquidus temperature of synthesized samples to be determined. The results will allow further refinement of the synthesis process and aid in the production of more representative samples.

The relative durability of simulant LFCM will be studied using standard test protocols to allow direct comparison with both UK and international glass wasteforms for the immobilization of high and intermediate level radioactive waste.

Alteration of samples under simulated shelter conditions, including simulated groundwater and high humidity, will be performed to encourage the formation of secondary uranium phases and allow studying the formation of alteration products observed on actual LFCM samples.

X-ray absorption spectroscopy (XAS) will be implemented to determine the average oxidation state of uranium in synthesized simulants; which is known to have influence on the solubility of U [11]. This will aid in the understanding of U in the dissolution of LFCM.

CONCLUSIONS

This study demonstrates the successful synthesis of simulant ‘lava-like’ fuel containing materials. The morphology and microstructure have both been recreated successfully in the simulant material and the crystalline content has been found to be largely similar with the exception of zircon. Further refinement of the composition and synthesis procedure is ongoing;

production of adjusted LFCM compositions to reproduce the zircon phase is underway with promising results so far.

ACKNOWLEDGMENTS

The authors would like to thank the EPSRC (Grants EP/G037140/1, EP/N017374/1, EP/L014041/1) for financial support for this research, which was performed at the MIDAS Facility, at the University of Sheffield, established with support from the Department of Energy and Climate Change. We also acknowledge financial support from the EPSRC allocation to University of Sheffield from its Global Challenges Research Fund.

REFERENCES

[1] A. Bilyk, A. Novikov, K. Shefer, V. Kashtanov, L. Dodd, and Y. Appolonskyy, "'Shelter' Object Safety Status Report / Отчет О Состоянии Безопасности Объекта « Укрытие »," (2008).

[2] A. S. Baev, Y. A. Teterin, K. E. Ivanov, A. Y. Teterin, and S. A. Bogatov, "X-ray photoelectron Study of the Samples of Fuel Containg Masses Formed as a Result of the Chernobyl Accident," Radiochemistry, vol. 39, no. 2, pp. 169–174, (1997).

[3] E. M. Pazukhin, "Fuel-Containing Lavas of the Chernobyl NPP 4th Block Topography physicochemical properties and formation scenario," Radiochemistry, vol. 36, no. 2, pp. 109–154, (1994).

[4] A. A. Borovoi, "Nuclear fuel in the shelter," At. Energy, vol. 100, no. 4, pp. 249–256, (2006).

[5] I. E. Kuz and V. V Tokarevskii, "Sources and mechanisms of aerosol formation in the Chernobyl 'Sarcophagus,'" At. Energy, vol. 82, no. 2, pp. 130–136, (1997).

[6] B. E. Burakov, E. B. Anderson, S. I. Shabalev, E. E. Strykanova, S. V. Ushakov, M. Trotabas, J. Y. Blanc, P. Winter, and J. Duco, "The Behavior of Nuclear Fuel in First Days of the Chernobyl Accident," Mater. Res. Soc. Symp. Proc., vol. 465, no. August, pp. 1297–1308, (1997).

[7] Y. A. Olkhovyk and M. I. Ojovan, "Corrosion Resistance of Chernobyl NPP Lava Fuel-Containing Masses," Innov. Corros. Mater. Sci., vol. 5, no. 1, pp. 36–42, (2015).

[8] A. A. Borovoi, A. S. Lagunenko, and E. M. Pazukhin, "Radiochemical and Selected Physicochemical Characteristics of Lava and Concrete from Subreactor Room no. 304/3 of the Fourth Block of the Chernobyl Nuclear Power Plant and Their Connection with the Accident Scenario," Radiochemistry, vol. 41, no. 2. pp. 197–202, (1999).

[9] A. A. Shiryaev, I. E. Vlasova, B. E. Burakov, B. I. Ogorodnikov, V. O. Yapaskurt, A. A. Averin, A. V. Pakhnevich, and Y. V. Zubavichus, "Physico-chemical properties of Chernobyl lava and their destruction products," Prog. Nucl. Energy, vol. 92, no. 2016, pp. 104–118, (2016).

[10] E. M. Pazukhin, A. S. Lagunenko, V. A. Krasnov, and V. V Bil, "Fuel at Upper Levels of the Destroyed Fourth Block of Chernobyl NPP . Refining the Formation Scenario of the Polychromatic Ceramics," Radiochemistry, vol. 48, no. 5, pp. 522–534, (2006).

[11] E. R. Weiner, Applications of Environmental Aquatic Chemistry: A Practical Guide, 3rd ed. CRC Press, (2013).