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THE UPDATED MODEL OF MICROSTRUCTURE EVOLUTION IN LAVA-LIKE FUEL-CONTAINING MATERIALS IN UNIT 4 OF CHORNOBYL NPP. BROWN CERAMICS

The model of microstructure evolution of lava-like fuel-containing materials (LFCM) in Unit 4 of the Chornobyl NPP has been updated by an example of brown ceramics. It was confirmed that the behavior of the LFCM is not only governed by a single or a few physical and chemical processes, but also by their interrelation and mutual influence. The list of physical and chemical processes taking place in the LFCM was supplemented with two new ones. The influence of another, previously known process on the LFCM behavior was clarified, and new stages of microstructure evolution are added. The durations of the known evolution stages are refined and those of new stages were determined. The state and behavior of the LFCM were forecast. In particular, there will be no destruction of the LFCM shortly soon, but in the long run, they will be destroyed. The time required for the destruction of the LFCM and the size of particles obtained after the glass phase will have destroyed are evaluated. All inclusions of uranium oxides will escape beyond the LFCM. The uranium oxide grains will be broken down to a size of several microns, and some of them, possibly, to the submicron level. Up to 50 metric tons of micro-sized particles of uranium oxide powders will inevitably participate in the formation of aerosols. The latter will pose the main hazard to humans. Some methodological and technological approaches to the development of new methods for solid-phase conditioning of the LFCM are proposed.

Keywords: lava-like fuel-containing materials, evolution model, microstructure, physical and chemical processes, forecast, methodological and technological approaches, New Safe Confinement, oxidation, radiation-stimulated phase formation, crystallization.

1. Introduction

The nuclear, radiation, and environmental safety of the destroyed Unit 4 of the Chornobyl NPP depends on the properties of lava-like fuel-containing materials (LFCM) since the moment of the accident on April 26, 1986. The LFCM were formed in the course of the nuclear reactor accident, when the nuclear reactor got out of control. During the first decade after the accident, experts determined and analyzed the phase composition of those materials, clarified the conditions and “initial” components required for the formation of all crystalline and vitreous (amorphous) phases, identified the corresponding physical and chemical processes, as well as their sequence, and proposed a scenario of LFCM formation. It is generally agreed that the LFCM are a result of the interaction of uranium oxide contained in nuclear fuel tablets (the latter also contain other fission and activation products) with the zirconium alloy in the fuel rod shells and silicates in the composition of the re-

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actor structural materials (the serpentinite backfill, sand, concrete, and others) [1–11].

Some experts consider that the zirconium alloy in the fuel rod shells had melted from the inside on the first day of the accident and began to dissolve uranium oxide fuel tablets, which resulted in the formation of the zirconium-uranium-oxygen melt [1–5, 7–10]. It happened due to the intensive heat generation and the low heat removal in the fuel rods after the introduction of a positive reactivity. The explosion destroyed the active zone, which allowed the uranium-containing phases to interact with structural materials [1, 2, 5–8, 10, 11]. As a result, the ternary system UO_2–SiO_2–ZrO_2 was formed. In the process of lava formation, owing to the interaction of irradiated fuel with structural materials, a considerable amount of elements – in addition to uranium, zirconium, silicon, and oxygen – was included into the composition of LFCM. Some other experts [12] hold to the idea that the interaction began between the zirconium alloy of fuel rods and silicate materials, and only afterward, uranium oxide of the nuclear fuel was involved in the process.

A large number of physical and chemical processes took place in the LFCM after the accident, and they still continue to run. Among them, there are some that crucially affect the physical properties and the microstructure of the LFCM. Those processes had to be identified. Making use of them as a basis, an attempt to predict the behavior of those materials in the short and long terms should be done. However, in 2001, i.e.15 years after the accident, experts claimed [13, 14] that the understanding level of the whole set of complicated physical and chemical processes running in the LFCM was definitely insufficient for the creation of a scientifically substantiated forecast concerning the LFCM state in the future. In spite of the fact that, at that time, the LFCM were considered as a vitreous matrix containing crystalline inclusions with a characteristic size of several microns and a known phase composition, the scientists thought that all those phases comprised only a very small fraction of the total material and could crucially affect neither the LFCM properties in whole nor the forecast of the LFCM state. The main role was assigned to the radiation-induced damage owing to the self-irradiation in the silicate glass matrix. It was suggested that the LFCM would be totally destroyed, and their whole mass would be transformed into fine dust, which always happens with highly irradiated brittle insulators. At that time, the ability to forecast the LFCM state was limited because of the lack of knowledge about some of their specific properties and did not allow the moment of their catastrophic destruction to be exactly predicted. The catastrophe of such a kind was considered to be dangerously probable within the next 10 to 50 years.

However, some experts [15] held to the idea that the internal self-irradiation by a particle flow could not initiate the LFCM destruction. It is known that α-decay can stimulate both the growth and the reduction of the volume of highly active glasses within the limits of $\pm 1.2\%$. The corresponding changes reach their saturation at a dose of $(1 \div 2) \times \times 10^{18}$ decay/cm^3. Such a value is considered as the lower limit, above which the properties of the silicate matrix undergo substantial changes. The cited authors estimated the time needed for this dose to be reached in the LFCM and found it to be equal to at least 10000 years. However, already in 2002, the LFCM became more fragile and began to collapse. In work [15], it was noted that the decisive role in the processes of property degradation was probably played by storage conditions: temperature differences, high humidity, chemically aggressive washing solutions, and so forth.

Some experts [16] came to the conclusion that the LFCM destruction induced by external and internal processes should be gradual, rather than sudden. The interaction of the LFCM with water was considered as the main origin of their changes. It was noted that the processes of silicate matrix dissolution run slowly. No dangerous tendencies were observed in the integrated emissions and discharges from the Shelter object. A long-term tendency to a regular reduction in the amount of radionuclides going beyond the Shelter boundary was predicted for aerosol emissions, as well as a tendency to a slight increase in the contents of radionuclides and uranium in water in the indoor area.

In 2006, it was claimed [17, 18] about the absence of a generally accepted LFCM model that would allow temporal changes in the LFCM characteristics to be forecast at that time. In this connection, there was no substantiated forecast for the LFCM behavior as well, in spite of a considerable number of relevant studies.

The authors of work [1] arrived at the conclusion that the main danger of the LFCM destruction is their interaction with water. After the creation of the New

Safe Confinement, the corresponding hazard should substantially diminish. A possibility of the destruction under the action of own radiation, as it occurs with strongly irradiated brittle insulators, was also considered. The cited authors estimated the volume changes for glasses containing radionuclides and their dependence on the self-irradiation dose. The inhomogeneities in the vitreous matrix, i.e. inclusions that were formed during the matrix cooling, were considered. The swelling of inclusions can induce the destruction of the LFCM, because the main activity of the latter is concentrated in the former.

The authors of work [8] pointed to several mechanisms that are important for the degradation. These are the self-irradiation, thermomechanical formation of cracks, water leaching, and interaction with atmospheric gases and vapors. A conclusion was made that the self-irradiation is not a serious problem for the LFCM. The cited authors marked the presence of cracks around large inclusions of uranium oxide UO_2 and the zirconium-uranium-oxygen phase Zr–U–O. They also pointed at the interaction of the LFCM with water and atmospheric gases, which had led to the formation of secondary uranium minerals on the LFCM surface inside the Shelter object. In their conclusions, the cited authors marked that the degradation degree and the associated radiological danger of the LFCM remained uncertain.

However, in works [1, 8, 13–18] cited above, which were published from the moment when the necessity to forecast the degradation of LFCM was realized (2001) to 2016, no information was provided concerning the LFCM models that would allow the LFCM behavior in the nearest (years) and far (decades) future to be predicted. Experts have indicated from one to several processes that may affect the degradation of the LFCM. The estimates and forecasts of the LFCM behavior turned out unrealistic. Moreover, they did not allow one to explain and predict the behavior of the LFCM.

Only in 2016, i.e. thirty years after the accident, the authors of work [19] presented for the first time a model of the LFCM microstructure degradation. In work [20], this model was expounded systematically and comprehensively. Among the variety of physical and chemical processes that take place in the LFCM, seven processes were distinguished, which are crucial for the microstructure formation. One of the most important of them, in our opinion, is the formation of open pore channels in the LFCM via the joining of at least some of the tracks left by α-particles that emerged owing to α-decay of radionuclides [20–22]. The nano-sized pore channels provided the formation of materials with open porosity by connecting the gas pores with one another and with the environment. It is nano-sized pore channels that are a determining factor governing the formation of the microstructure, its evolution, and, as a result, the physical and mechanical properties of the LFCM.

The other six processes are as follows [20]: penetration of air oxygen into the LFCM up to the uranium oxide inclusions through the open nano-sized pore channels, oxidation of uranium oxide UO_x in the inclusions by air oxygen, formation of cracks in the LFCM owing to the growth of the uranium oxide inclusions, penetration of water into the LFCM to the uranium oxide inclusions via the cracks, destruction of the LFCM by temperature fluctuations owing to the changes in the aggregate state of water in gas pores and cracks, and interaction of water and dissolved salts and gases with uranium oxides and activation products, which gives rise to the formation of hydrates and soluble compounds of uranium and transuranium elements.

The proposed evolution model for the LFCM microstructure [20] differed from all previous attempts to describe the behavior of those materials. Not only one, two, or three, but seven processes were taken into account. However, the main emphasis in the model was made on the revealing of interrelation among and mutual influence of the physical and chemical processes in order to elucidate their sequence and/or simultaneity. Based on this analysis, a forecast was made about the behavior of the LFCM in the short and long term.

During the last four years, new data on the phase composition of brown ceramics were obtained and new processes in the LFCM were identified at the Institute for Safety Problems of Nuclear Power Plants of the National Academy of Sciences of Ukraine (ISF NPP NASU) [23–28]. There arose a necessity to further develop the evolution model of the LFCM microstructure to improve the quality of prognosis concerning the LFCM state and behavior in the future.

The aim of this work is to update the model of the LFCM microstructure evolution in order to forecast the state and behavior of the LFCM when estimating the nuclear, radiation, and environmental safety of the complex New Safe Confinement–Shelter object in the near and far future. In view of the fact that the LFCM were formed as a result of the accident, the updated evolution model of the LFCM microstructure should take into account all physical and chemical processes: those that took place during the LFCM formation and those that took place in the LFCM after the accident for more than 34 years, during which the LFCM were in the Shelter object and the New Safe Confinement.

2. Formation of LFCM during the Accident

The emergency situation at Unit 4 of Chornobyl NPP on April 26, 1986, led to intensive heat generation and low heat removal in the fuel rods [1–11]. This circumstance stimulated a substantial increase of the temperature (to 2500–2600 °C) of uranium oxide UO_2 in fuel tablets and in the contact areas between uranium oxide and zirconium alloy Zr + 1 wt%.Nb. As a result, there emerged two layers between them. One of the layers included uranium oxide with zirconium (UO_x with Zr) due to the diffusion of the latter into the former. The other consisted of zirconium-uranium-oxygen melt Zr–U–O formed due to diffusion of uranium and oxygen into zirconium. Metallic zirconium was also in the molten state. When being cooled down to 1900 °C, the Zr–U–O melt solidified and transformed into the amorphous phase $(Zr,U)O_x$. As a result of explosion, the reactor core was destroyed and became able to contact with the environment. This led to the oxidation of a considerable part of each uranium-containing phase (UO_2, UO_x with Zr, and $(Zr,U)O_x$) and metallic zirconium. The materials of the destroyed reactor core entered into a reaction with the structural materials of the reactor [1, 2, 6–12] and formed a melt on the basis of the ternary system UO_2–SiO_2–ZrO_2. Besides the elements of this system, the melt also included a substantial number of other elements [1, 2, 7–9, 11]. Under those conditions, crystalline zircon containing uranium–the so-called "chornobylite" $(Zr_{1-x}U_x)SiO_4$ [6–8, 10] was synthesized in a temperature interval of 1600–1660 °C owing to the interaction between the $(Zr,U)O_x$ phase and silicon oxide in the multi-component melt. Metallic globules were formed when the multi-component melt based on silicon oxide got into contact with the metallic components of the reactor. The gradual temperature decrease gave rise to the formation of a silicate glass phase as a result of solidification of the multi-component melt on the basis of silicon oxide. The glass phase contained silicate dendrites [8].

Experts distinguish the following physical and chemical processes taking place at the formation of LFCM in the course of the accident (during 4–5 days), which determined the LFCM phase composition and microstructure [1–11]:

1) residual energy release in uranium oxide of nuclear fuel as a result of the fission reaction of uranium nuclei ^{235}U;

2) heating of uranium oxide in the nuclear fuel with the zirconium alloy of the fuel rod shells to temperatures of 2500–2600 °C;

3) melting of the inner part of the nuclear fuel shells made of the zirconium alloy;

4) interaction of uranium oxide in the nuclear fuel with the zirconium alloy melt formed from the fuel rod shells and the formation of uranium oxide with zirconium (UO_x with Zr) and the zirconium-uranium-oxygen melt Zr–U–O;

5) formation of the amorphous zirconium-uranium-oxygen phase $(Zr,U)O_x$ in the course of cooling of the zirconium-uranium-oxygen melt Zr–U–O;

6) oxidation of uranium oxide UO_2, uranium oxide with zirconium (UO_x with Zr), the amorphous zirconium-uranium-oxygen phase $(Zr,U)O_x$, and metallic zirconium at their contact with oxygen after the reactor destruction;

7) crystallization of zirconium silicate containing uranium (chornobylite $(Zr_{1-x}U_x)SiO_4$) at the interaction of the amorphous phase $(Zr,U)O_x$ with silicon oxide in the multi-component melt;

8) interaction of uranium oxide UO_2, uranium oxide with zirconium (UO_x with Zr), and the amorphous phase $(Zr,U)O_x$ with silicates of the reactor structural materials, and the formation of a multi-component melt followed, as the temperature decreased, by the formation of a silicate glass phase of the LFCM;

9) formation of silicate dendrites in the course of glass phase devitrification.

3. Phase Composition and Microstructure of LFCM According to Data Obtained Until 2016

The LFCM (brown ceramics) comprise a heterogeneous solid solution [1–4, 7, 8, 10–12, 19]. The silicate glass phase has a substantial number of inclusions of uranium phases: uranium oxides UO_x, uranium oxides with zirconium (UO_x with Zr), zirconium-uranium-oxygen phases $(Zr,U)O_x$, and uranium-containing zirconium silicate (chornobylite $(Zr_{1-x}U_x)SiO_4$). The glass phase also contains silicates (in the form of dendrites) and metallic globules. Most often, the sizes of inclusions amounted to 3–10 μm. The LFCM glass phase is a silicate glass containing potassium, calcium, aluminum, magnesium, zirconium, iron, uranium, and other elements [1, 2, 7, 8, 11]. The distribution of elements over the glass phase volume is inhomogeneous.

Glass phase. A comparison of the composition, microstructure, and "fabrication" parameters of the LFCM and silicate glasses testifies that the LFCM are "half-done" glass [20]. In terms of glass manufacturing technology, the LFCM glass phase has almost completely passed the stage of silicate formation. But only 50–70% of the stage of glass formation has been passed because the LFCM contain particles of initial materials that have not reacted. The bleaching stage has not been passed at all because the material has not freed itself from bubbles [29, 30]. Homogenization is out of the question because the distribution of elements over the material is inhomogeneous [1, 31]. If, for some reason, the temperature of the LFCM had not decreased in time during the accident but had been constant at a level of 1400–1500 °C for several tens of hours, then all crystalline inclusions would have been dissolved in the silicate glass phase, and we would have had multi-component silicate glass containing uranium.

The uranium content in the glass phase is lower (often by a factor of 2–5) than the corresponding average value for the LFCM: 60–70% in the inclusions and 30–40% in the glass phase [1]. However, in the later work [32], it was reported that the spatial distributions of α-radiation and the total activity are uniform on the scale of tens of microns, i.e. the separation and activation products are distributed more or less uniformly over the material.

Inclusions of uranium oxides containing zirconium (UO_x with Zr) [2–4, 8, 12] are responsible for the brown color of this type of "lava". The morphology of inclusions of the phase UO_x with Zr is very diverse. There are particles with the condensed morphology, cubic and cuboctahedral crystals, as well as dendrites. Those inclusions of UO_x with Zr may probably be of various origins. Particles with the fused morphology are residues of solidified droplets of the initial melt UO_x with Zr. Crystalline inclusions are the products of crystallization of the UO_x with Zr melt. Small inclusions 1 to 3 μm in size located in the bulk of uranium-containing zircon crystals are the product of the reaction between the zirconium-uranium-oxygen phase $(Zr, U)O_x$ and the silicate melt. Dendrite-like particles are the product of crystallization at the cooling of that part of uranium that was initially dissolved in the silicate melt. The zirconium content in those inclusions amounts to 2.5–7.1 wt%.

In the vast majority of publications [2–4, 7, 8, 10, 12], the inclusions of uranium oxide and uranium oxide with zirconium are presented in the form of an oxide UO_x with an indefinite stoichiometric coefficient x. In works [2, 8], it was noted that according to the results of X-ray phase analysis, the structure of most of those inclusions corresponds to oxide UO_{225}. In work [10], making use of the same method, it was found that besides UO_2 grains, some other grains can be classified to UO_{2+x}.

Inclusions of the $(Zr, U)O_x$ phase [2, 7, 8] are practically amorphous according to the results of X-ray phase analysis. This phase is a precursor of chornobylite. Inclusions of the $(Zr,U)O_x$ phase contain zirconium oxide in two different crystalline modifications: monoclinic and tetragonal [8]. The presence of those zirconium oxide phases was also marked by the authors of work [10].

Inclusion of zirconium silicate containing uranium, i.e. *chornobylite* $(Zr_{1-x}U_x)SiO_4$ [2, 4, 6, 7, 10–12]. Chornobylite was synthesized at the accident owing to the interaction of the $(Zr,U)O_x$ phase with silicon oxide in the multi-component melt. The uranium content x in chornobylite falls within the interval $0.05 \leq x \leq 0.1$, i.e. $Zr_{0.96\div0.9}U_{0.05\div0.10}SiO_4$ [7]. The chornobylite inclusions sometimes contain inclusions of monoclinic zirconium dioxide ZrO_2 with a uranium admixture up to 6–7 wt%. The inclusions are several microns in size [2].

Dendrites of silicates. The authors of work [8] mark the presence of silicates in the form of dendrites in the glass phase. They consider those dendrites as consisting of pyroxene with the probable composition $(Ca_{0.08}Fe_{0.02}Cr_{0.02}Zr_{0.02})Al_{0.18}Mg_{1.86}Si_{1.82}O_{5.67}$. The presence of dioxide $CaMg(Si_2O_6)$ is also marked.

Metallic globules [1, 4, 11] are mainly represented by iron with Cr, Ni, Zr, U, and so forth, admixtures.

Pore space. Brown ceramics has an open porosity of 3–13 vol% [1, 21]. Its pore space consists of the following components: large and small gas pores, cracks, and nano-sized pore channels [21,22]. Large and small gas pores are close to spherical (see Table) [20]. The gas pores were formed when the LFCM were cooled down at the final stage of the accident, owing to the lower solubility of gases in the silicate glass phase when the temperature decreased [21, 22].

The volume of the cracks is relatively small (see Table). Their estimated number amounts to about 10^5 cracks per cm^3. The average distance between them is about 200 μm. The main part of the cracks were formed owing to the volume growth of the crystalline inclusions of uranium oxides in the course of their oxidation. A substantially smaller part of the cracks have a thermal origin, being a result of the rapid cooling of the surface layers in the LFCM.

The volume of nano-sized pore channels is almost identical to the volume of cracks (see Table). Their average diameter belongs to the nanoscale interval. The nano-sized pore channels are undoubtedly a result of defect accumulation in the course of LFCM self-irradiation. They are a result of joining the tracks of α-particles that were formed owing to the α-decay of radionuclides [21, 22].

4. Phase Composition and Microstructure of LFCM According to New Data Obtained in 2018–2020

Within the period from 2017 to 2020, the phase composition of the LFCM was studied at the ISP NPP NASU with the help of the X-ray phase analysis [23–28]. The following uranium-containing phases were revealed: uranium oxide $UO_{2.34}$ and potassium uranyl silicate hydrate (weeksite) $K_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$. The LFCM also contained cubic and tetragonal zirconium oxides, zirconium silicate $ZrSiO_4$, aluminum silicate Al_2SiO_5, and probably calcium silicate Ca_2SiO_4, as well as some phases of silicon oxides. The contents of those crystalline phases were as follows: 4.5–5.5 wt% for uranium oxide $UO_{2.34}$; 3–5 wt% for orthorhombic (1) silicon oxide SiO_2; 3–4 wt% for potassium uranyl silicate hydrate (weeksite) $K_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$; 1–2 wt% for cubic and 1–1.5 wt% for tetragonal zirconium oxide ZrO_2; 0.25–0.35 wt% for zirconium silicate $ZrSiO_4$; 0.4–0.6 wt% for aluminum silicate Al_2SiO_5 and probably 0.4–0.6 wt% for calcium silicate Ca_2SiO_4; 0.45–0.75 wt% for orthorhombic (2) silicon oxide SiO_2; 0.3–0.5 wt% for trigonal silicon oxide SiO_2; and probably 0.8–1.2 wt% for tetragonal silicon oxide SiO_2.

Uranium oxide in the inclusions [23–25, 27, 28] corresponds to oxide $UO_{2.34}$. It has a cubic lattice and a stoichiometric coefficient of 2.34 for oxygen. Perhaps, the larger fraction of uranium oxide in the inclusions contains zirconium, and the smaller one may not contain it. The oxidation of these inclusions took place both during the accident and for a long time after it. The uranium oxide inclusions are in the compressed state. Hence, at least some growth of their volume ocurred due to oxidation under conditions when the glass phase was hard, i.e. already cooled down after the accident. In work [2] published in 1997, it was reported that the content of uranium oxide in the inclusions corresponded to $UO_{2.25}$. Probably, we may assume that owing to oxidation during the accident, the stoichiometric coefficient of oxygen in uranium oxide increased from 2 to 2.25, and after the accident, it continued to increase and reached a value of 2.34.

According to the equilibrium diagram for the U–O systems in the interval where their composition varies from UO_2 to UO_3, the cubic structure exists within the interval from UO_2 to $UO_{2.25}$ [33, 34]. Therefore, in the case of LFCM destruction, the glass phase will not squeeze the uranium oxide inclusions, so this compound will transform into an equilibrium mixture of oxides $UO_{2.25}$ and U_3O_8. The share of U_3O_8 will amount to 20–25%.

Zirconium silicate $ZrSiO_4$ (zircon) [23–28] in the inclusions may probably contain uranium in its crystal lattice, which is available in the glass phase and in lots of crystalline phases of brown ceramics. This is zirconium silicate with uranium, or chornobylite $(Zr_{1-x}U_x)SiO_4$ [2, 4, 6, 7, 10].

Zirconium oxides ZrO_2 (cubic and tetragonal) in the inclusions [23–28]. It is known that zirconium oxides ZrO_2, both tetragonal and monoclinic, were also formed during the crystallization of chornobylite

Volumes and diameters of the pore space components in the LFCM [21, 22]

Component	Large gas pores	Small gas pores	Cracks	Nanochannels
Volume, %	5–11	0.6–1.3	0.3–0.6	0.3–0.7
Diameter, μm	40–200	6–12	2–2.5*	0.04–0.06

*The thickness value is given. The length equals 65–200 μm.

$(Zr_{1-x}U_x)SiO_4$, when the zirconium-uranium-oxygen phase $(Zr,U)O_x$ was in contact with silicon oxide SiO_2 of the multi-component silicate melt [6–8]. However, according to our data, the share of zirconium silicate $ZrSiO_4$ is small (0.25–0.35 wt%), and the share of zirconium oxides ZrO_2, as a result of chornobylite crystallization, cannot exceed a few tenths of a percent. At the same time, the share of zirconium oxides ZrO_2 (cubic and tetragonal) in the LFCM is equal to a few percent.

In our opinion, the main amount of zirconium oxides ZrO_2 with the cubic and tetragonal structures is a result of crystallization of the amorphous zirconium-uranium-oxygen phase $(Zr, U)O_x$ within the time interval elapsed after the accident, i.e. during several decades. It is possible that the crystallization is not complete, but remains partial. This assumption is confirmed by the fact that in the 1990s [7, 8] this phase contained grains of monoclinic and tetragonal zirconium oxides ZrO_2, which could promote the crystallization process by playing the role of crystalline nuclei. Perhaps, those phases may contain uranium as an additive that stabilizes the cubic and tetragonal lattices. It is possible that calcium and magnesium may also be available as stabilizing additives. The existence of two phases of zirconium oxide ZrO_2 can also be explained as a result of the inhomogeneous distributions of uranium and zirconium in the LFCM.

Silicon oxides SiO_2. We found a few phases of silicon oxide SiO_2: orthorhombic (1), orthorhombic (2), trigonal, and probably tetragonal. Those crystalline phases of silicon oxide SiO_2 could be formed during the accident (at its cooling stage) as a result of crystallization of the multi-component silicate melt, as well as at the crystallization of the silicate glass phase during thirty-three years after its formation. The crystallization of various silicon oxide SiO_2 phases can be explained by a high content of this compound in the glass phase of the LFCM. It is possible that the crystallization process of the glass phase was stimulated by self-irradiation of the LFCM. Such phases as α-cristobalite and α-tridymite, which crystallize in silicate glasses, were not revealed in the glass phase of the LFCM [35].

Silicates. We detected the presence of aluminum silicate Al_2SiO_5 and probably calcium silicate Ca_2SiO_4 in the LFCM [27, 28]. Those compounds could also be formed during the crystallization of the multi-component silicate melt during the accident (at its cooling stage) and during the crystallization of the glass phase within the thirty-three-year interval after its formation. Aluminum silicate and probably calcium silicate crystallized in the LFCM glass phase owing to a high content of silicon oxide and the presence of calcium and aluminum oxides in the glass phase. We also know about the detection of other silicates in the glass phase [8]: pyroxene with the approximate composition $(Ca_{0.08}Fe_{0.02}Cr_{0.02}Zr_{0.02})Al_{0.18}Mg_{1.86}Si_{1.82}O_{5.67}$ and diopside $CaMg(Si_2O_6)$.

Potassium uranyl silicate hydrate. We revealed the presence of potassium uranyl silicate hydrate $K_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$ (mineral wicksite) in brown ceramics [23–28]. A considerable amount of potassium can be substituted by sodium [36]. In the 1990s, sodium-potassium uranyl silicate hydrate was not detected in the LFCM [1, 7]. We demonstrated that this compound was formed after the accident as a result of interaction of uranium oxide UO_x (from the uranium oxide inclusions), silicon oxide, potassium, and sodium (from the silicate glass phase of LFCM), and water. Sodium-potassium uranyl silicate hydrate $(Na, K)_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$ was formed during a long time period (thirty-three years) at ambient temperatures. The formation process of this compound was stimulated by a substantial number of defects that were accumulated in the LFCM during prolonged self-irradiation.

5. LFCM Microstructure Evolution (Model of the Year 2016)

According to the evolution model developed in 2016 [20], brown ceramics has the following microstructure. It is a material consisting of the glass phase containing the crystalline inclusions of uranium oxides UO_x, zirconium-uranium-oxygen phase $(Zr,U)O_x$, chornobylite $(Zr_{1-x}U_x)SiO_4$, and others. The glass phase is a "half-done" glass and has an inhomogeneous distribution of elements. The material contains gas pores, as well as micro- and macro-sized defects. The microdefects are formed by nano-sized pore channels. The material is permeated by nano-sized channels that connect the gas pores with one another and with the external environment. The nano-sized pore channels are nonuniformly distributed over the material. Their concentration is higher at places with an enhanced content of α-active radionuclides and near crystalline inclusions of uranium oxides. The macrodefects are cracks. They permeate the material. The schematic diagram of the microstructure of brown LFCM ceramics (the model of the year 2016) is shown in Fig. 1.

6. LFCM Microstructure Evolution (Updated Model of the Year 2020)

The schematic diagram of the microstructure of brown LFCM ceramics, in which new data are taken into account, is exhibited in Fig. 2 [37]. Now, the inclusions of uranium oxides are represented by uranium oxide $UO_{2.34}$ (cf. Figs. 1 and 2). Instead of the inclusions of the zirconium-uranium-oxygen phase $(Zr,U)O_x$, the microstructure includes the inclusions of zirconium oxide ZrO_2 with the cubic and tetragonal structures. The crystalline phases of zirconium oxides ZrO_2 (at least some part of them) are a result of crystallization of the amorphous zirconium-uranium-oxygen phase $(Zr_{1-x}U_x)O_x$ after the accident. One can also see the inclusions of zirconium silicate $(Zr_{1-x}U_x)SiO_4$ known as chornobylite. Potassium-sodium uranyl silicate hydrate $(Na, K)_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$ (mineral wicksite), which has been revealed recently, is most probably located in the contact zone of uranium oxide $UO_{2.34}$ and silicate glass phase at the surface of uranium oxide inclusions. This compound was formed as a result of interaction of uranium oxide UO_2; the inclusions of uranium oxide and silicon, sodium, and potassium oxides in the glass phase of the LFCM; and water. The silicate glass phase of the LFCM contains a number of previously unknown phases of silicon oxide SiO_2: orthorhombic (1), orthorhombic (2), trigonal, and probably tetragonal. The silicate glass phase also includes aluminum silicate Al_2SiO_5 and probably calcium silicate Ca_2SiO_4. All silicon oxide phases and silicates were partially formed as a result of crystallization of the multi-component silicate melt at its cooling during the accident and partially as a result of crystallization of the glass phase during a long time period after the accident.

The pore space in brown ceramics has the following components: large and small gas pores, cracks, and nano-sized pore channels (see Figs. 1 and 2) [21, 22]. The volume of gas pores did not change. No substantial growth in the volume of cracks and nano-sized pore channels was observed. The nanoscale pore channels penetrate the glass phase and all crystalline inclusions in brown ceramics. The pore channels connect the gas pores and the cracks with one another and with the external environment (see Fig. 2).

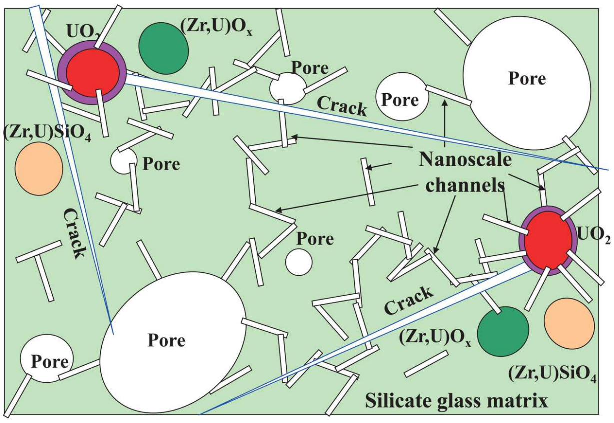

Fig. 1. Schematic representation of the microstructure of brown ceramics of the LFCM (model of the year 2016 [20])

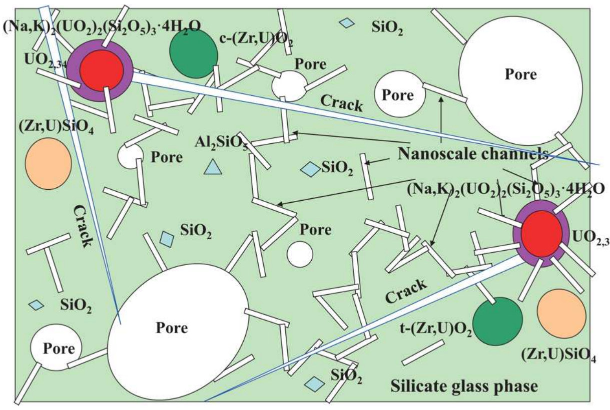

Fig. 2. Schematic representation of the microstructure of brown ceramics of the LFCM taking new data into account

7. Physico-Mechanical Properties

In 2011, the compressive strength of the specimens of brown ceramics of the LFCM was within an interval of 40–70 MPa [20]. Taking the measurement accuracy into account, this parameter did not change in both 2015 and 2020. But those valuesare 4–5 times lower than the valuesof the LFCM strength obtained in 2004. A substantial reduction in the values of Young's modulus and microhardness within the period of 2004–2011 was also observed.

8. Radiation-Induced Defects in LFCM

According to the calculation-theoretical estimates [38], among the kinds of radiation-induced damage created in the LFCM by all possible types of radiation under the conditions of the Shelter object (α- and β-particles, γ-quanta, neutrons, and so forth), the main contribution to the formation of microstructure defects is made by the damage stimulated by α-particles and heavy recoil nuclei. It is generally accepted that 90% of all radiation-induced defects arise owing to heavy recoil nuclei. However [22], among all components of the pore space, only the open nano-sized pore channels are the microstructure defects that appeared as a result of LFCM self-irradiation. They were formed due to the joining of at least some of the α-particle tracks created in the material.

9. Water and Pore Space in LFCM

Our experiments showed that immersion of the LFCM into a vessel with water for 7 days led to the penetration of water into the pore space of LFCM [20, 39]. As a result, the gas pores and the cracks became filled with water, whereas the nano-sized pore channels remained empty. The gas pores were filled through the cracks rather than via the nano-sized channels. Experiments showed that multiple (7 cycles) cooling (to −10 °C) and heating (to +5 °C) of the LFCM specimens that were previously and forcedly filled with water led to the increase in the thickness and volume of the cracks available in the material. At the same time, the volume of gas pores and nanochannels did not change. After each cooling-heating cycle, material fragments up to 0.1–0.3 mm in size detached from the specimen.

10. Previously Known and Newly Discovered Physico-Chemical Processes Governing the LFCM Microstructure

In 2016, when creating a model for the microstructure evolution in lava-like fuel-containing materials, among a large number of physical and chemical processes that took place in the LFCM for thirty years after the accident, we distinguished the following ones, which crucially affected the formation of LFCM microstructure [28]:

1) formation of open pore channels in the LFCM via joining the α-particle tracks, at least some part of them, that emerged owing to the α-decay of radionuclides;

2) penetration of air oxygen through the LFCM to the inclusions of uranium oxides UO_x via the open nano-sized pore channels;

3) oxidation of uranium oxide UO_x in the inclusions by air oxygen;

4) formation of cracks in the LFCM owing to the growth of the volume of uranium oxide inclusions;

5) penetration of water through the LFCM to the inclusions of uranium oxides UO_x via the cracks;

6) destruction of the LFCM by temperature fluctuations as a result of changes in the aggregate state of water available in the gas pores and the cracks;

7) interaction of water and dissolved salts and gases with uranium oxides UO_x and activation products, formation of hydrates and soluble compounds of uranium and transuranic elements.

Below, we present data that confirm the running of each of those processes in the LFCM.

Process 1. The volume of open pore channels in brown ceramics was determined by evaporating water from the pore space [21]. The pore diameter was evaluated to equal 40–60 nm on the basis of the time required to remove water from them. In so doing, the method based on the evaporation of water from the pore space in order to determine the total volume of pore channels in powders and porous bodies [40, 41] was applied. It was shown that the nano-sized pore channels, as well as the α-particle tracks, became closed under the heat treatment in air at 150 °C [22].

Processes 2, 3, and 4. The presence of indicated processes was confirmed by the irreversible volume growth (by more than 0.5%) of LFCM brown ceramics subjected to slow isothermal annealing at 500 °C for 54 h (7 cycles) and the worsening of mechanical parameters followed by the destruction of the specimens into small fragments [20].

Processes 5 and 6 were studied by us making use of real LFCM specimens. It was shown that water can fill the gas pores and the cracks, but not the nano-sized pore channels. The gas pores are filled via the cracks, but not via the nano-sized channels [20, 39]. Experiments on multiple (7 cycles) cooling (to −10 °C) and heating (to +5 °C) of the LFCM specimens that were previously and forcedly filled with water testified to the increase in the thickness and volume of cracks in the material and the detachment of material fragments from the specimens.

Process 7 was confirmed by detecting uranium oxides UO_x as well as the hydrates and soluble compounds of uranium and transuranium elements, on the surface of LFCM clusters. It was the double salt of uranium $Na_4UO_2(CO_3)_3$ with admixtures of sodium carbonate Na_2CO_3, sodium sulfate Na_2SO_4, sodium hydroxide NaOH, and water, where sodium atoms were partially substituted by potassium ones [42]. Uranium is known to migrate in the form of the double alkaline-carbonate complex $Na_4[UO_2(CO_3)_3]$. Carbonates, sulphates, halite, and probably sulphate-carbonates were revealed. An assumption was made about the formation of sodium uranyl carbonate $Na_6(UO_2)(CO_3)_4$ [43, 44]. The following secondary uranium minerals were detected: studtite $UO_4 \cdot 4H_2O$, epiianthinite $UO_3 \cdot 2H_2O$, rutherfordine $UO_2 \cdot CO_3$, and sodium uranyl carbonate $Na_6(UO_2)(CO_3)_4$. Those compounds were identified together with the phases of sodium carbonates $Na_3H(CO_3)_2 \cdot 2H_2O$ and $Na_2CO_3 \cdot H_2O$. The indicated minerals were formed owing to the interaction of LFCM, water, and air [45].

Hence, new data obtained for the phase composition of crystalline inclusions in the LFCM confirmed the oxidation process of uranium oxide UO_x in the LFCM inclusions (process 3). At the accident, uranium oxide UO_2 was oxidized to $UO_{2,25}$ [2]. In 2018, i.e. 22 years later, uranium oxide in the inclusions was in the form of oxide $UO_{2.34}$ [25,27,28]. Our data agree with the data of work [46] published in 2000, where the possibility of oxidation of uranium oxide UO_2 at room temperature was estimated to take place not earlier than in 15–20 years.

Let us estimate the volume ratio between uranium oxide and oxygen required for this process to run. Every mole of uranium oxide $UO_{2.25}$, i.e. every 274 g, has reacted with $2.34 - 2.25 = 0.09$ moles of oxygen. Knowing the density of uranium oxide (10.97 g/cm^2 [33]), we obtain that one mole of uranium oxide has a volume of 24.61 cm^3. The volume of required oxygen amounts to $22.4\ l/mol \cdot 0.09\ mol = 2.02\ l$ under normal conditions. The indicated amount of oxygen is contained in about 10 l of air. So the air volume equals 400 times the volume of uranium oxide. And this air penetrated into the LFCM. This fact confirms the validity of process 2 in the list of physical and chemical processes in the model of microstructure evolution developed in 2016. It also confirms the relevance of process 1 in the same list because, in the case of dense and strong LFCM (within the first decade after the accident, their volume practically did not contain cracks), air could penetrate in such quantities only through the nano-sized pore channels. Of course, a considerable time interval (several years) was required.

The results obtained in 2018–2020 [25,27,28] testify that the inclusions of uranium oxide $UO_{2.34}$ in brown ceramics are in a compressed state. Uranium oxide UO_x in the inclusions was oxidized when the glass phase was hard rather than plastic. The increase in the volume of the uranium oxide UO_x inclusions at oxidation induced the appearance of cracks. In 2014 [21, 22], we showed that the cracks are a component of the pore space in the LFCM. Hence, the new data confirmed the existence of the crack formation process (process 4 in the list).

The authors of work [8] claimed that cracks were observed near the inclusions of uranium oxides UO_x and zirconium oxides ZrO_2. They emphasized that crack formation was mainly stimulated by the phase transition of tetragonal zirconium oxide ZrO_2 into the monoclinic form. In our opinion, crack formation was induced by the volume growth of the uranium oxide UO_x inclusions due to their oxidation. This is unambiguously evidenced by both the increase of the oxygen stoichiometric coefficient to 2.34 and the squeezed state of the uranium oxide $UO_{2.34}$ inclusions in the silicate glass phase.

The results obtained in 2018–2020 make it possible to prove the presence of new, previously unknown physical and chemical processes in the LFCM. In particular, the revealed by us sodium-potassium uranyl silicate hydrate $(Na, K)_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$ (mineral wicksite) [23–26] was formed in brown ceramics after the accident. Its content in brown ceramics equals 3–4 wt%, which is comparable with the content of uranium oxide $UO_{2.34}$ (4.5–5.5 wt%). If this compound had been synthesized during the accident, it would have been detected as long ago as in the 1990s.

We experimentally found [25] that the heat treatment of LFCM brown ceramics in an air furnace at 600 °C for 10 h led to the growth of the share of anhydrous sodium-potassium uranyl silicate $(Na, K)_2(UO_2)_2(Si_2O_5)_3$ from 3–4 wt% to 10–14 wt%. At the same time, the share of uranium oxide $UO_{2.34}$ decreased by a factor of about 3 and that of the silicate glass phase by a factor of about 2. This fact testifies that the formation of anhydrous sodium-potassium uranyl silicate took place, in which only some parts of uranium oxide and silicate glass phase were used. A relatively low temperature of 600 °C is obviously insufficient for the synthesis to be complete. The reaction took place between some part of uranium oxide UO_x in the uranium oxide inclusions and silicon oxide in some part of the silicate glass phase, the both phases possessing a substantial amount of radiation-induced defects that had been accumulated in them during a long time period elapsed after the accident. Such a scenario would be impossible if we suppose the α- and γ-active radionuclides to be uniformly distributed over the LFCM [32]. Instead, we tend to assume that the distribution of α- and γ-active radionuclides in the LFCM is inhomogeneous [1], although it is hardly possible that so much (60–70%) of those radionuclides can be located in the uranium oxide inclusions.

In our case, the radiation-stimulated formation of sodium-potassium uranyl silicate hydrate $(Na, K)_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$ began in brown ceramics some time after the accident and continues until now. So the list of physical and chemical processes that took place in the LFCM during the thirty-three years after the accident and crucially affected the formation of the LFCM microstructure should be extended by the process of radiation-stimulated formation of sodium-potassium uranyl silicate hydrate $(Na,K)_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$ (process 8).

We also revealed zirconium oxides ZrO_2, both cubic and tetragonal, in brown ceramics in amounts of 1–2 wt% and 1–1.5 wt%, respectively [23–28]. In the 1990s, researchers marked an insignificant presence of tetragonal and monoclinic zirconium oxide ZrO_2 [6, 7], but the cubic modification was not mentioned.

The amorphous zirconium-uranium-oxygen phase $(Zr,U)O_x$ was found in the LFCM as a result of solidification of the zirconium-uranium-oxygen melt Zr–U–O [3]. The uranium content in it was 18 wt%, which is sufficient for the stabilization of cubic zirconium oxide ZrO_2. It is quite probable that the crystallization of cubic zirconium oxide from the amorphous zirconium-uranium-oxygen phase Zr–U–O occurred after the accident. The crystallization of tetragonal zirconium oxide ZrO_2 could also take place in the case of inhomogeneous uranium distribution in the amorphous zirconium-uranium-oxygen phase Zr–U–O. Perhaps, this process has not terminated until now so that the LFCM still contain the amorphous zirconium-uranium-oxygen phase $(Zr,U)O_x$.

It is known [47–49] that amorphous zirconium oxide ZrO_2 containing 3.6 wt% of yttrium oxide Y_2O_3 completely crystallizes at a temperature of 500 °C within 36 min with the formation of tetragonal zirconium oxide ZrO_2. Amorphous zirconium oxide ZrO_2 with no other oxides completely crystallizes at a temperature of 450 °C within 26 min and also forms tetragonal zirconium oxide ZrO_2. Fifty hours are required for 20% of pure amorphous zirconium oxide ZrO_2 to crystallize at a temperature of 350 °C. Depending on the nucleation character, type, and the content of stabilizing oxides, the crystallization of amorphous zirconium oxide ZrO_2 at ambient temperatures in the Shelter object could be complete within the time period from several years to decades.

Let us include the probable crystallization of the amorphous zirconium-uranium-oxygen phase $(Zr, U)O_x$ as process 9 into the list of processes that took place in the LFCM during thirty-three years after the accident and affected the formation of the LFCM microstructure.

The presence of several phases of silicon oxide (orthorhombic (1), orthorhombic (2), trigonal, and probably tetragonal), as well as aluminum silicate Al_2SiO_5 and probably calcium silicate Ca_2SiO_4, in brown ceramics testifies that the crystallization process took place in the silicate glass phase during thirty-three years after the accident, and it continues until now. This process is stimulated by self-irradiation of the LFCM. We also include this process as process 9 into the list. It also has to be included in the list of processes that took place during the accident. In 1990–1993, silicates, pyroxene, and dioxide were found in the LFCM. Those compounds were formed during the accident in the multi-component silicate melt at its cooling.

When considering the crystallization process in general, the time dependences of the relative volume of crystalline phase (s-like crystallization curves) are divided into the initial stage, the stage of stable development, and the rapid (or avalanche-like) stage. The total content of phases formed in the LFCM owing to crystallization in brown ceramics is estimated as 5–9 wt%. The indicated value means that this process is at its initial stage. The crystallization process has already been included in the list as process 9.

Hence, when updating the model of the LFCM microstructure evolution, two new processes should be included in the list of already identified physical and chemical processes that took place in the LFCM during thirty-three years after the accident and affected the formation of the LFCM microstructure:

8) radiation-induced phase formation of sodium-potassium uranyl silicate hydrate $(\mathrm{Na, K})_2(\mathrm{UO}_2)_2(\mathrm{Si}_2\mathrm{O}_5)_3 \cdot 4\mathrm{H}_2\mathrm{O}$;

9) crystallization of the orthorhombic (1), orthorhombic (2), trigonal, and probably tetragonal phases of silicon oxide SiO_2, aluminum silicate $\mathrm{Al}_2\mathrm{SiO}_5$, and probably calcium silicate $\mathrm{Ca}_2\mathrm{SiO}_4$ in the silicate glass phase; crystallization of the cubic and tetragonal forms of zirconium oxides ZrO_2 in the zirconium-uranium-oxygen phase $(\mathrm{Zr, U})\mathrm{O}_x$ is also possible.

11. The Sequence and Interrelation of Physico-Chemical Processes that Govern the Microstructure Evolution in the Bulk of LFCM

Let us update the scenario of evolution in the LFCM microstructure, as well as the sequence and interrelation of relevant physico-chemical processes, by taking into account new data obtained for the phase composition and newly discovered physico-chemical processes [20].

Within the first months after the Chornobyl accident, the LFCM comprised a composite. The silicate glass phase included the crystalline inclusions of uranium oxides UO_x, uranium oxides with zirconium (UO_x with Zr), the zirconium-uranium-oxygen phase $(\mathrm{Zr,U})\mathrm{O}_x$, and zirconium silicate with uranium (chornobylite $(\mathrm{Zr}_{1-x}\mathrm{U}_x)\mathrm{SiO}_4$), as well as silicates in the form of dendrites and metallic globules. The LFCM are a result of interaction of the uranium oxide UO_2 in the nuclear fuel tablets with the zirconium alloy of the fuel rod shells and silicates entering the composition of the reactor structural materials. The material possessed closed round pores.

During the following years, the LFCM accumulated tracks of α-particles, which emerged owing to the α-decay of radionuclides, so that their concentration increased in time. In 10–12 years after the accident (in 1996–1998), when, perhaps, the concentration of α-tracks exceeded a certain value, at least some of them joined to form a framework of open nanoscale pore channels. As a result, air became able to penetrate into the LFCM through nano-sized pore channels and reach the inclusions of uranium oxides. Uranium oxide UO_x in the inclusions began to oxidize, and the mass of inclusions and, accordingly, their volume began to increase. The volume growth of inclusions was restrained by the glass phase. As a result, the inclusions were in the squeezed state, and the glass phase around them in the stretched one.

After the tensile strength of the glass phase had been exceeded, the formation of cracks began. The presence of cracks in the glass phase led to a reduction of mechanical stresses. The further volume increase of the uranium oxide UO_x inclusions stimulated the growth of mechanical stresses, which, in turn, stimulated the development of the crack system. Namely, the number of cracks and/or their length and width increased. The mechanical properties of the LFCM became substantially worse. This happened within a period from 2004 to 2011 [20]. Air got an opportunity to reach the inclusions of uranium oxides UO_x not only through the nano-sized pore channels, but also via the cracks. The oxidation process became much more active. Starting from 2004 (i.e. during 15 years) or 2011 (i.e. during 8 years), uranium oxides UO_x were oxidized to oxide $\mathrm{UO}_{2.34}$.

Since that moment, water became able to penetrate through cracks into the LFCM, fill the gas pores, and chemically interact with uranium oxides UO_x in the inclusions. This led to the formation of various hydroxides and carbonates, and ultimately to the washing out of uranium compounds, as well as fission and activation products, from the LFCM. Furthermore, owing to the water volume growth in the cracks and gas pores at the freezing, the LFCM were destroyed. The cracks in the LFCM cut off the material fragments as large as 50–500 μm in size (with an average size of 100–200 μm). During the LFCM destruction, the particles of uranium oxides from the crystalline inclusions were released into the environment. Since the average size of the inclusions was 3–5 μm, and they were composed of at least a few grains, the uranium oxide particles outside the LFCM had micronic – and some of them, probably, submicronic – sizes.

The inclusions of zirconium silicate ZrSiO_4 containing uranium, i.e. chornobylite $(\mathrm{Zr}_{1-x}\mathrm{U}_x)\mathrm{SiO}_4$, and the metallic globules did not change substantially.

The formation of sodium-potassium uranyl silicate hydrate $(\mathrm{Na, K})_2(\mathrm{UO}_2)_2(\mathrm{Si}_2\mathrm{O}_5)_3 \cdot 4\mathrm{H}_2\mathrm{O}$ began after the accident. Perhaps, this process began after a certain number of radiation defects has been accumulated or after the nano-sized pore channels had been formed. The formation of silicate hydrate could be started after the formation of cracks through which water could penetrate to the inclusions. The formation of this compound might occur in several stages. At present, the formation of sodium-potassium uranyl silicate hydrate continues.

Let us evaluate the change of the LFCM volume in the regions, where sodium-potassium uranyl silicate hydrate $(Na,K)_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$ was formed. The chemical formula of this compound tells us that uranium oxide (from the uranium oxide $UO_{2.34}$ inclusions), silicon oxide, sodium oxide, and potassium oxide (from the glass phase), as well as water (from the environment via the cracks), were involved in its formation. The densities of the indicated phases are as follows: 2.786 g/cm^3 for potassium silicate hydrate, 10.97 g/cm^3 for uranium oxide UO_2, and 2.1–2.4 g/cm^3 for LFCM glass phases and silicate glasses. The density of uranium oxide $UO_{2.34}$ is lower than the density of uranium oxide UO_2, maybe by a few percent (up to 10%). As a result, the volume of LFCM regions, where uranyl silicate hydrate was formed, has to increase substantially, which should lead to the growth of mechanical stresses in the glass phase.

Thus, one can see that both processes – the oxidation of uranium oxide UO_x in the inclusions and the formation of uranyl silicate hydrate $(Na,K)_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$ in the region, where the inclusions of uranium oxide and the glass phase are in contact – affect each other. Both processes lead to the growth in the volume of the uranium oxide inclusions and the uranyl silicate hydrate layer located between the uranium oxide inclusions and the glass phase. As a result, they favor the development of a system of cracks in the LFCM.

The amorphous zirconium-uranium-oxygen phase $(Zr,U)O_x$ began to crystallize as early as during the accident. At that time, this phase contained tetragonal and monoclinic zirconium oxide ZrO_2. After the accident, this process continued. In 2018, the crystallization process manifested itself in the presence of 1–2 wt% of cubic and 1–1.5 wt% of tetragonal zirconium oxide ZrO_2 in the LFCM. We do not know yet, whether this process terminated in 2018 or is still continuing.

The glass phase began to crystallize during the accident. This process is continuing now. The presence of several phases of silicon oxide SiO_2 and aluminum silicate Al_2SiO_5, as well as, probably, calcium silicate Ca_2SiO_4, in brown ceramics testifies to that.

So, one can see that the behavior of the LFCM is governed not only by one or more physical and chemical processes, but also by their interrelation and mutual influence. The accumulation of α-particle tracks formed at the α-decay of radionuclides during 10–12 years allowed the nano-sized pore channels to be formed. The penetration of air through the nano-sized pore channels to the inclusions of uranium oxide UO_x allowed the oxidation process of uranium oxide in the inclusions to begin. The inclusions, in turn, after having increased in size, provoked the process of crack formation. The presence of cracks allowed water to penetrate to the inclusions of uranium oxide UO_x and provided the interaction of uranium oxides with water, dissolved salts and gases, which resulted in the formation of hydrates and soluble uranium compounds. The radiation-stimulated phase formation of sodium-potassium uranyl silicate hydrate $(Na,K)_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$ became possible after the accumulation of a required concentration of radiation-induced defects in the LFCM. The crystallization process was also stimulated by a substantial concentration of radiation defects.

12. Stages of the LFCM Microstructure Evolution and Their Duration

In the framework of the model of the LFCM microstructure evolution developed in 2016, the following stages in the evolution of the LFCM bulk microstructure were distinguished, their sequence was determined, and their duration was estimated [20]:

1) formation of copen porosity as a result of the joining of closed spherical pores and newly formed nano-sized pore channels, the latter being a result of joining the α-particle tracks accumulated in the material;

2) oxidation of uranium oxides UO_x in the LFCM inclusions due to the air penetration through the open nano-sized pore channels;

3) formation of cracks in the LFCM owing to the volume growth of the uranium oxides UO_x inclusions at their oxidation;

4) penetration of water into the LFCM via the cracks, its interaction with the inclusions of uranium

oxides, the exit of uranium salts from the inclusions into the environment, destruction of some part of the LFCM due to multiple freezing-thawing cycles of water in the pores and cracks, and exit of uranium oxide UO_x particles into the environment.

Stage 1 began after the accident and continued up to 10–12 years.

Stage 2 began after the termination of stage 1 (in 1996–1998) and continues till now. The duration of this stage is 3–5 decades till the destruction of the LFCM.

Stage 3 began between 2004 and 2011 and continues till now. The duration of the stage is 3–5 decades till the destruction of the LFCM.

Stages 1 and 2, as well as 2 and 3, may partially overlap.

Stage 4 began within the period from 2004 to 2011 and continued to 2018. After the construction of the New Safe Confinement had been completed, this stage practically terminated. The penetration of water in the form of precipitations into the New Safe Confinement was shut down, and the stage-4 processes became substantially slower.

New data on the phase composition of the LFCM, which were obtained from 2016 to 2020, allow two more stages in the evolution of the LFCM bulk microstructure to be identified:

5) radiation-stimulated phase formation of sodium-potassium uranyl silicate hydrate $(\mathrm{Na,K})_2(\mathrm{UO}_2)_2(\mathrm{Si}_2\mathrm{O}_5)_3\cdot 4\mathrm{H}_2\mathrm{O}$;

6) crystallization of amorphous phases of the LFCM: the glass phase with the formation of a few phases of silicon oxide SiO_2, aluminum silicate Al_2SiO_5, and probably calcium silicate Ca_2SiO_4; and the amorphous phase $(\mathrm{Zr,U})\mathrm{O}_x$ with the formation of cubic and tetragonal zirconium oxides.

Stage 5 began in 1996–1998 (or later, within the period from 2004 to 2011). The stage-by-stage development of the process of radiation-stimulated phase formation of sodium-potassium uranyl silicate hydrate is possible. The stage continues till now. Its duration is 5–7 decades till the complete “burning out” of uranium oxide in the inclusions.

Stage 6 began after the accident and continues till now. The duration of the stage is 4–6 decades until the glass phase of the LFCM and the amorphous phase $(\mathrm{Zr,U})\mathrm{O}_x$ transit into the crystalline state.

Stages 2, 3, 5, and 6 are currently active in brown ceramics.

13. Forecast of the LFCM Behavior

The proposed updated model of microstructure evolution makes it possible to predict the behavior of the LFCM in the short and long runs.

The self-irradiation of the LFCM (including the α-decay of radionuclides) will continue. It is difficult to say whether the volume of nano-sized pore channels will increase or not. It remained almost constant within the last five years. The process of uranium oxide UO_x oxidation in the inclusions will continue. The volume of cracks, their length, and perhaps their number will increase due to the volume growth of the inclusions of uranium oxides. The penetration of water into the LFCM to the inclusions of uranium oxides via the cracks has already slowed down considerably in the New Safe Confinement. The interaction of water with uranium oxide UO_x and the formation of hydrates and soluble uranium compounds have been practically stopped. The radiation-stimulated phase formation of sodium-potassium uranyl silicate hydrate $(\mathrm{Na,K})_2(\mathrm{UO}_2)_2(\mathrm{Si}_2\mathrm{O}_5)_3\cdot 4\mathrm{H}_2\mathrm{O}$ will continue. The crystallization of the silicon oxide SiO_2 and silicate phases in the silicate glass phase will also continue. The crystallization of cubic and tetragonal zirconium oxides ZrO_2 in the amorphous zirconium-uranium-oxygen phase $(\mathrm{Zr,U})\mathrm{O}_x$ is also possible.

Let us consider, in more details, the influence of each of the physical and chemical processes in the LFCM on the changes in their microstructure and their behavior in general.

According to the uranium-oxygen equilibrium state diagram [33], uranium oxides within the range from UO_2 to $UO_{2.25}$ have a cubic lattice. In our case, uranium oxide $UO_{2.34}$ in the inclusions of brown LFCM ceramics has a cubic lattice, because those inclusions are in the squeezed state in the glass phase. However, as the oxidation process continues, the stoichiometric coefficient of oxygen, the volume of inclusions, and the number, length, and width of cracks will increase. After the concentration of cracks and their length in the LFCM reach the corresponding threshold values, the LFCM will start to break down into particles from 50 to 500 μm in size with an average size of 100–200 μm, because they will not be able to withstand even their own weight. Those glass-phase particles will contain uranium, as well as fission and activation products. All inclusions of uranium oxides will escape beyond the LFCM. There will be no squeezing stresses for the inclusions in the destroyed material. Cubic uranium oxide UO_x with $x > 2.34$ will transform into a mixture of cubic uranium oxide $UO_{2.25}$ and orthorhombic uranium oxide U_3O_8. The reconstruction of the cubic lattice into the orthorhombic one will destroy the uranium oxide grains to a size of several microns, and some of them, probably, to several submicrons [51, 52]. Those particles of uranium oxide U_3O_3 are the most dangerous. The experience obtained in the USA, the Soviet Union, Germany, and Japan showed [51] that the volume oxidation of the spent fuel results in that the latter releases 99.5% of tritium, 40–70% of krypton, 25–40% of iodine, and 90% of ruthenium in the form of oxide. The destruction of the grains of uranium oxide UO_x inclusions will lead to the exit of the indicated radionuclides from uranium oxide beyond the LFCM.

When the oxygen stoichiometric coefficient reaches the value $x = 2.66$, uranium oxide in the inclusions will completely transform into uranium oxide U_3O_8 with the orthorhombic lattice. Therefore, the density of uranium oxide in the inclusions will decrease to 8.39 g/cm^3 [33], and the volume of inclusions will increase by 23.5%. As a result, the LFCM will be completely destroyed. All inclusions of uranium oxide U_3O_8 will escape beyond the LFCM. The increase of the oxygen stoichiometric coefficient from $x = 2.25$ to $x = 2.34$ (by 0.09) was achieved during 7–14 years within the period from 2004–2011 to 2018. Provided the current oxidation rate and the growth of the oxygen stoichiometric coefficient x to 2.66 (by 0.32), the LFCM destruction will occur in 25–50 years, i.e. within the period between 2043 and 2068. At the same time, it should be borne in mind that the oxidation rate may increase since the size of the cracks may become larger with the growth of the uranium oxide inclusions in size.

Let us evaluate the time interval after which the radiation-induced phase formation of sodium-potassium uranyl silicate hydrate $(Na, K)_2(UO_2)_2(Si_2O_5)_3 \times \times 4H_2O$ will be complete. In 2018, the content of this compound in the LFCM was 3–4 wt%, i.e. 3–4 g per 100 g of the LFCM. Such an amount of uranyl silicate was formed approximately during 7–14 years (within the period from 2004–2011 to 2018) and 1.5–2 g of uranium oxide UO_2 was spent for its "production". Accordingly, provided the current formation rate of uranyl silicate hydrate, all available uranium oxide (4.5–5.5 wt%) will be consumed in 20–41 years, i.e. before 2038–2059.

However, it should be taken into account that, although the heat treatment of LFCM brown ceramics (in air at a temperature of 600 °C for 10 h) led to the growth in the content of anhydrous sodium-potassium uranium silicate from 3–4 wt% to 10–14 wt% [25], the LFCM were not destroyed. Let us evaluate the time interval during which there will be no destruction of the LFCM associated with the volume growth. The required increase in the volume of uranyl silicate hydrate will occur in 9–16 years, i.e. before 2027–2034.

Two simultaneous processes – oxidation of uranium oxide UO_x in the inclusions and radiation-stimulated formation of the sodium-potassium uranyl silicate hydrate phase $(Na, K)_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$ – affect each other. Both processes lead to the volume growth of the uranium oxide or uranyl silicate inclusions and enhance the crack formation and the LFCM destruction. Uranium oxide and uranyl silicate hydrate from the inclusions will escape from the LFCM. The simultaneous running of those processes can reduce the duration of stages 5 and 6 and lead to a more rapid destruction of the LFCM.

If we assume that not six, but only one phase crystallizes, the time dependence of the relative volume of the crystalline phase (s-shaped crystallization curves) [50] makes it possible to evaluate the time needed for the LFCM destruction to begin, if the process of the glass phase crystallization develops. The calculations show that the crystallization process can approach the rapid (or avalanche-like) stage in 14–21 years (before 2032–2039). In this case, a considerable part of the glass phase in the LFCM can be destroyed into particles 10 to 120 μm in dimensions (with an average size of 20–50 μm).

The crystallization of several phases can lead to a situation where there can be several (up to six) rapid crystallization stages (six is the number of currently known phases resulting from the crystallization). However, several rapid stages may not transform into the avalanche one. The multiphase crystallization in the LFCM has to be researched further.

14. Methodical and Technological Approaches to the Creation of Methods of Solid-Phase Conditioning of LFCM

When performing works on switching Unit 4 of the Chornobyl NPP into the safe state, experts faced the necessity to develop a technology for handling the hazard materials, e.g., the methods of solid-phase conditioning. The studies of the microstructure and physicochemical properties of the LFCM and the forecast of their evolution led to the accumulation of an experience in the working with such materials. The LFCM microstructure also suggests us some ways to deal with them.

The LFCM are thermodynamically metastable, because their dominating (by mass) phase, i.e. the glass phase, is amorphous. In it, the process of crystallization, i.e. a transition from the metastable amorphous state into the stable crystalline one, takes place. If the phase tends to transform into a more stable state, we can intensify this process. It is expedient to perform the controlled crystallization of the glass phase of the LFCM by carrying out the heat treatment of those materials, controlling the nucleation of crystalline nuclei, monitoring their controlled growth, preventing the material destruction by activating the sintering of the already crystallized material, and determining, if possible, the phases that are necessary for the crystallization, as well as the implementable sequence of their crystallization.

The analysis of the LFCM microstructure and the physical and chemical processes that are responsible for it testifies that the challenging element of the microstructure is the inclusions of uranium oxide UO_x. They increase their volume as a result of the oxidation of uranium oxide UO_x and the radiation-stimulated formation of sodium-potassium uranyl silicate hydrate $(Na,K)_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$. Therefore, any means that would allow uranium oxide UO_x in the LFCM to be transformed into compounds that do not interact with oxygen and water can be regarded as useful for transiting the LFCM into a more stable state. It is also important, if possible, to reduce the size of uranium oxide UO_x inclusions (preferably to a size less than 1 μm) by redistributing them in the LFCM. In particular, uranium oxide and its compounds can be redistributed among the pore space, cracks, and gas pores.

By the heat treatment of the LFCM, we can activate the radiation-induced phase formation of sodium-potassium uranyl silicate hydrate $(Na,K)_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$, thereby binding uranium oxide UO_x in a compound that may possess a higher corrosion resistance, than uranium oxide has. The experiments showed [21, 22] that the heat treatment of the LFCM also makes it possible to completely close the nano-sized pore channels (at 150–400 °C) and the cracks (at 200–530 °C). As a result, the pore space will be closed and, accordingly, the surface area of the LFCM will be smaller.

15. Conclusions

The model of the LFCM microstructure evolution in Unit 4 of the Chornobyl NPP has been updated by an example of brown ceramics. The behavior of the LFCM is not only governed by one or more physical and chemical processes, but also by their interrelation and mutual influence. The list of seven known physical and chemical processes that govern the microstructure evolution in the LFCM was extended by two new ones: radiation-stimulated phase formation and crystallization. The course of oxidation of uranium oxides UO_x in inclusions was refined. Two more stages were added to the list of already known four stages of microstructure evolution. The durations of the known microstructure evolution stages were determined more exactly, and the durations of new ones were found.

In the near future (tentatively, till 2027–2034), there will be no destruction, even partial, of the LFCM. The volume growth of the inclusions of uranium oxide UO_x and sodium-potassium uranyl silicate hydrate $(Na,K)_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$ will only result in the increase of the crack concentration and lengths.

In the long run, the behavior of the LFCM will be determined by three processes: oxidation of uranium oxide UO_x in the inclusions, radiation-induced phase formation of sodium-potassium uranyl silicate hydrate $(Na,K)_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$, and crystallization of silicate glass phase.

Provided that the current oxidation rate will not change, the transformation of uranium oxide $UO_{2.34}$ into uranium oxide U_3O_8 will lead to the destruction of the LFCM in 25–50 years, i.e. within the period between 2043 and 2068. The LFCM will be completely destroyed into glass-phase particles 50–500 μm in dimensions (with an average size of 100–200 μm). As a result, all inclusions of uranium oxides UO_x will exit from the LFCM. The grains of uranium oxides UO_x from the inclusions will be destroyed to a size of a few microns, with some of them, probably, to a few submicrons. The micro-sized powders of uranium oxides UO_x (in an amount of up to 50 metric tons) will inevitably participate in the formation of aerosols, which will pose the main danger for humans.

Provided the current formation rate for sodium-potassium uranyl silicate hydrate $(\mathrm{Na, K})_2(\mathrm{UO}_2)_2(\mathrm{Si}_2\mathrm{O}_5)_3 \cdot 4\mathrm{H}_2\mathrm{O}$, all available uranium oxide UO_x (4.5–5.5 wt%) will "burn out" in 20–40 years, i.e. before 2038–2059. The simultaneous running of the uranium-oxide oxidation processes in the inclusions and the radiation-stimulated phase formation of sodium-potassium uranyl silicate hydrate can reduce the time required for the complete destruction of the LFCM.

The crystallization process (assuming that only one phase crystallizes) can approach the rapid (or avalanche-like) stage in 14–21 years (in 2032–2039). A considerable part of the glass phase in the LFCM can be destroyed at that with the formation of particles 10–120 μm in dimensions (with the average size of 20–50 μm). However, the crystallization of a lot of phases may not have the avalanche stage.

Some methodological and technological approaches were proposed to create the methods of solid-phase conditioning of the LFCM. It is reasonable to perform the controlled crystallization of the glass phase of the LFCM in order to transit this phase into a thermodynamically stable state. Attempts should be made to transform uranium oxides UO_x into compounds that do not react with oxygen and water. It is also important, if possible, to redistribute UO_x oxides and uranium compounds over the cracks and the gas pores. The heat treatment of the LFCM will make it possible to close the nano-sized pore channels (at 150–400 °C) and the cracks (at 200–530 °C), which will make the LFCM surface smaller.

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ОНОВЛЕНА МОДЕЛЬ ЕВОЛЮЦІЇ МІКРОСТРУКТУРИ ЛАВОПОДІБНИХ ПАЛИВОВМІСНИХ МАТЕРІАЛІВ 4-го БЛОКА ЧАЕС. КОРИЧНЕВА КЕРАМІКА

Модель еволюції мікроструктури лавоподібних паливовмісних матеріалів (ЛПВМ) 4-го блока Чорнобильської АЕС оновлено на прикладі коричневої кераміки. Підтверджено, що поведінка ЛПВМ визначається не одним або декількома фізичними і хімічними процесами, а їх взаємозв'язком і взаємовпливом. Фізичні та хімічні процеси, що протікають в ЛПВМ, доповнено ще двома новими. Уточнено вплив на поведінку ЛПВМ ще одного раніше відомого процесу. Додано нові стадії еволюції мікроструктури. Уточнено тривалості відомих і визначені тривалості нових стадій. Представлено прогноз стану та поведінки ЛПВМ. У найближчій перспективі руйнування ЛПВМ не буде, у віддаленій – вони повністю зруйнуються. Оцінено терміни руйнування ЛПВМ, розміри частинок, на які зруйнується склофаза. Всі включення оксидів урану потраплять за межі ЛПВМ. Зерна оксиду урану зруйнуються до кількох мікрон, а частина з них, можливо, і до субмікронного рівня. До 50 т мікронних порошків оксидів урану неминуче будуть брати участь у формуванні аерозолів, які й представлятимуть основну небезпеку для людини. Запропоновано деякі методичні та технологічні підходи до створення методів твердофазного кондиціонування ЛПВМ.

Ключові слова: лавоподібні паливовмісні матеріали, модель еволюції, мікроструктура, фізичні та хімічні процеси, прогноз, методичні та технологічні підходи, Новий безпечний конфайнмент, окислення, радіаційно-стимульоване фазоутворення, кристалізація.