

Chernobyl fuel microparticles: uranium oxidation state and isotope ratio by HERFD-XANES and SIMS

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Abstract

Fuel "hot" particles are the most unpredictable dose-forming components in the soils of uranium contaminated regions, such as Chernobyl Exclusion Zone. Over time in the environment, "hot" particles undergo gradual dissolution with the release of uranium as well as fission and neutron-activation products trapped inside the uranium-oxide fuel matrix. The environmental fate of fuel particles depends not only on the environmental conditions but mainly on the conditions of their formation in the reactor and during the accident. In the present work micromorphology, fuel burnup and uranium oxidation state of several fuel "hot" particles, collected on the Western trace of Chernobyl fallout, were studied using a combination of non-destructive or semi-non-destructive techniques: gamma-spectrometry, secondary-ion mass-spectroscopy, scanning electron microscopy with energy-dispersive X-ray spectroscopy, the X-ray absorption near-edge structure and the high-energy resolution fluorescence-detected X-ray absorption near-edge structure spectroscopy. An attempt has been made to assess the contribution of the conditions of particle formation and the conditions of being in the environment to the current state of particles after more than a quarter of a century of history in the environment.

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Graphical Abstract



Keywords Fuel "hot" particles · HERFD-XANES · Uranium oxidation state · Fuel burnup

Introduction

The accident that occurred at the 4th power unit of the Chernobyl nuclear power plant on April 26, 1986, became the most widescale accident in nuclear energy ever. According to the IAEA International Nuclear and Radiological Event Scale, it belongs to the highest, i.e. 7th Level, Major Accident,—with widespread health and environmental effects and external release of a significant fraction of reactor core inventory. The 4th power unit of the Chernobyl NPP was an RBMK-1000 (high power–1000 MW—channel reactor with water cooling) with low-enriched (about 2%) ceramic structure UO₂ fuel [1].

Due to changing meteorological conditions and the ten-day duration of accidental radioactive release, multidirectional contamination spots were formed. The proportion of radioactive material released to the environment depended on the form of radionuclides: gases were released from the reactor core completely, volatile components—to a significant extent, while the release of the fuel component, according to estimates of non-volatile nuclides, was 1.5% [2–4]. For more than 37 years after the accident, various aspects of the impact of this accident on humans [5] and the environment [6–10] were studied, one of the most common study was radioactive Cs and Sr distribution and migration [6, 11–13].

The most important characteristic of nuclear fuel during reactor operation is its burnup. Fuel burnup determines the degree of fuel utilization; it can take values of more than 100 MWd/kg(U) for various modern reactors with high uranium enrichment. For RBMK-1000 in the fourth power unit of the Chernobyl NPP, the commonly used maximum burnup value was 20 MWd/kg(U) while the average burnup value was 10.9 MWd/kg(U) [14]. As a result of burnup, the oxygen potential of the fuel increases due to the fission of uranium and formation of fission products with valent state lower than 4 in the sublattice and the resulting formation of free oxygen [15]. When the fuel rod burns out, intragranular fission gases (Xe, Kr isotopes) form submicron bubbles in the ceramic structure of the fuel. Intragranular gases migrate to the periphery of the fuel grain making intergranular gas outlet channels [16–18]. The most studied phenomenon in UO_2 fuel is so called the high burnup structure in the outer region of UO₂ fuel pellets which is not the case for Chernobyl reactor but for reactors with burnup values more than 60 MWd/kg (U). This microstructure is a result of recrystallization of UO_2 ceramic with decreasing in the size of fuel grains, formation of high-density faceted pores, which can lead to the local degradation in thermal conductivity of fuel pellets and enhanced fuel swelling [19–21]. The environmental fate of RBMK reactor fuel particles depending on their fuel burnup has not yet been studied.

Among various forms of accidental fallout into the environment, special attention was attracted to the particles of high radioactivity, so called "hot" particles, widely distributed in the different directions. In the first years after the accident, condensed particles (Cs, Ru), had the highest dose, and they were carefully studied. Later fuel U-(Zr)-O micro- and submicroparticles [22-24] and their long-term role in the environment began to be studied more closely. Different investigations of radioactive "hot" particles are carried out: "hot" particles composition at first [25, 26], their size and activity distribution [27-30], further - extracting of "hot" particles and their morphology determination [30, 31], uranium oxidation state determination [32, 33], "hot" particles dissolution kinetics [34–36], "hot" particles migration peculiarities [37-39] and dose formation [28, 34, 40].

The development of analytical methods has contributed to the intensification of research on fuel "hot" particles. Gamma-spectrometry and radiography techniques were the only tools for "hot" particle research in the first years after the accident. Over time, fine studies began to be used to analyse individual "hot" particles using advanced techniques. Knowledge of the "hot" particle morphology, its elemental composition, various isotope ratios and oxidation states of uranium in the particles will help reconstructing the accident scenario and investigating the melting gradient of the fuel, temperature at the moment of its release from the reactor and Red/Ox conditions during the accident [32, 41–43]. Fuel burnup – one of the most important characteristics of the fuel "hot" particles can be calculated from different radionuclides ratio. In earlier works the most popular method used was ¹³⁴Cs/¹³⁷Cs ratio measurement by gamma-spectrometry [44]. It was an express and nondestructive method. But this way had high measurement inaccuracy and now it cannot be used for Chernobyl "hot" particles analysis due to small half-life of ¹³⁴Cs [45]. One more radionuclide set which ratio can be measured with gamma spectrometer and used for fuel burnup determination is following: ¹⁵⁵Eu/¹⁴⁴Ce versus ¹⁵⁴Eu/¹⁴⁴Ce [45, 46]. The ratios ¹⁵⁴Eu/¹⁵⁵Eu and ²³⁸Pu/^{238,240}Pu were also measured and used for burnup estimation [47]. For ²⁴¹Am/Pu and ^{243,244}Cm / Pu isotopes ratios determination sample dissolution for alpha-spectrometry is required [44, 48]. Currently, the most accurate and most used method for determining fuel preparation, while SIMS [49-54] is conditionally nondestructive method. The ratio of plutonium isotopes can also be determined for the same purpose, using resonant-laser secondary neutral mass-spectrometry (rL-SNMS). SIMS and rL-SNMS can be also used for "hot" particle isotope mapping [41, 55, 56]. Sometimes mass spectrometry is combined with other methods to comprehensively analyse a "hot" particle. In the research [57] Raman spectroscopy was used to determine the oxidation state together with mass spectrometry to assess the burnup of the fuel - material of the "hot" particle. In addition to Raman spectroscopy, synchrotron XANES spectroscopy is used to determine the oxidation state of uranium in "hot" particles. XANES L_3 U edge spectroscopy was used to prove the presence of uranium in Fukushima "hot" particle [58]. In the research by Salbu and co-authors [32] the combination of micro-XANES L₃ U edge spectroscopy and micro-XRD was used to characterize the "hot" particle composition and difference between inner composition and the surface. In the research by Batuk and co-authors [59] XANES and EXAFS were used for establishing the form of uranium in "hot" particles and assessment of the degree of ordering of atoms in a crystal in the Chernobyl "hot" particle.

burnup is mass spectrometry: ICP-MS [48] requires sample

Based on the fine studies, Chernobyl fuel "hot" particles can be divided into two large groups: uranium oxide and uranium-zirconium oxide. At the same time, separate subgroups are distinguished within each group: stoichiometric UO₂ particles, partially oxidized UO_{2+x} particles and particles with a wide U/Zr ratio range [60]. As the distance from the reactor increases, the mass and size of the fuel particles decrease since particles with a larger mass sediment already at shorter distances, so the selection of particles takes place more efficiently in the immediate vicinity of the reactor [61]. Particles taken from various traces of Chernobyl fallout differ considerably: in the soils of the northern trace particles are more oxidized, while uranium dioxide particles were found in the western trace [32]. The rate of half-dissolution for different kind of "hot" particles varies: 1-14 years for UO_{2+x} group of particles and 7–70 years for UO_2 particles [35, 62]. In addition to the oxidation state of uranium in fuel particles, the rate of fuel particles half-dissolution also depends on the pH value of the environment, which was shown in laboratory experimental modelling.

"Hot" particles research is carried out for a number of applied reasons, including health physics and dosimetry as well as radioecology. A detailed study of micro- and nanoparticles will make it possible to obtain information about their health effects in case of inhalation or ingestion [63–68], as well as the behaviour of various radionuclides contained in "hot" particles in environmental conditions [11, 36, 62, 69, 70] and therefore assess this long-term risk. Many fuel parameters have been studied previously, while the burnup using uranium isotope ratio has not previously been systematically investigated in complex with uranium oxidation state for Chernobyl fuel "hot" particles.

The purpose of this work is to establish the exact characteristics of fuel uranium oxide microparticles by non-destructive advanced techniques as an example of a methodological approach to the analysis of unique micro objects. In this work the fuel burnup value using SIMS together with morphology using SEM, elemental composition using EDS and oxidation state of uranium in individual particles using XANES-SR is studied for the first time.

Experimental

Sampling

Soil and moss samples were collected in the immediate vicinity of the reactor: in the Red Forest, which is located 1–2 km to the west from Chernobyl NPP. Sampling was carried out in 2016 (30 years after the Chernobyl accident). Group of particles "T_" was extracted using digital and alpha-track radiography from moss samples. Group "SL_" single particles were isolated using quartering method with gamma spectrometry from soil samples and placed on double-sided tape.

"Hot" particles detection, extraction and characterization

"Hot" particles were localized using digital radiography with SR-type (super-resolution) Imaging Plates, Cyclone Storage Plus System scanner and OptiQuant software, as well as alpha-track radiography using poly-allyl diglycol carbonate detector MTrack GMScientific Ltd., UK. The scanning electron microscope Jeol JSM-6480LV with INCA Energy-350 spectroscopy in the back-scattered electron mode detected particles by bright areas in the image resulting from the high Z-contrast for atoms of heavy elements and established the particles morphology and elemental composition. Particle extraction on custom tungsten needles was carried out in an ESEM (Philips XL30, remX GmbH, Bruchsal, Germany) with an EDS detector (SDD-Detector, remX GmbH, Bruchsal, Germany) and a micromanipulator (Kleindiek Nanotechnik MM3A, Reutlingen, Germany). The particles were attached to the needles using an electron beam curing glue (SEMglu, Kleindiek Nanotechnik Reutlingen, Germany) [71]. Uranium isotope ratios were established using timeof-flight secondary-ion mass spectrometer TOF–SIMS.5, IONTOF [49]. The fuel burnup of "hot" particles (B) was calculated using the empirical Eq. (1) from Mironov et al. [72].

$$154 \cdot B^{-1.346} - 4180 \cdot \left(\frac{235}{238}U\right)_{nat}$$
$$\cdot B^{-0.817} = \frac{\left(\frac{235}{238}U\right)_{sample} - \left(\frac{235}{238}U\right)_{nat}}{\left(\frac{236}{238}U\right)_{sample}}$$
(1)

where B is the fuel burnup value, ${}^{235}\text{U}/{}^{238}\text{U}$ and ${}^{236}\text{U}/{}^{238}\text{U}$ are uranium isotope ratio values in natural uranium (*nat*) and in the investigated sample (*sample*).

The content of fission products and minor actinides was determined by gamma spectrometry using an ORTEC gamma-spectrometer with an HP Ge detector and software LSRM.

Determination of uranium oxidation state was carried out using X-ray Absorption spectroscopy on the base of synchrotron radiation. The X-Ray Absorption Near Edge Structure (XANES) spectra on the L₃ uranium edge were obtained at the STM beamline of Kurchatov Synchrotron Radiation Source [73]. Pellet with UO₂ powder was used as reference sample. High-resolution measurements took place at ROBL [74] (Rossendorf Beamline, BM20) at European Synchrotron Radiation Facility (ESRF) on a high-resolution X-ray spectrometer [75] (XES). The X-ray emission spectrometer consists of 5 crystal analysers and a detector located together with the sample along the Rowland cycle in Johann-type geometry with 0.5- radius was used for high resolution measurements. The highenergy resolution fluorescence-detected X-ray absorption near-edge structure (HERFD-XANES) measurements performed by scanning the incident energy along the absorption edge of the selected element at the X-ray line maximum. The X-ray spectra are measured by scanning the emitted energy at a fixed incident energy. The recording time for one particle spectrum at U L₃-edge were obtained using Si (220) crystals was 15 min, while at U M_4 -edge, using Si (880) crystal reflections the recording time was 25 min. 3 scans were obtained for each spectrum. Pellet with UO_2 powder was used as reference sample.

For data evaluation the IFFEFIT package was used [76]. The analysis of raw data was performed in the ATHENA software. Each scan was deglitched and aligned and several scans were merged to improve signal-to-noise ratio. Linear combination of XANES spectra on U M_4 -edge was performed using ITFA software [77, 78]. HERFD XANES spectra of uranium oxides UO₂ and UO₃

registered in the same conditions and "hot" particles were used as references for the linear combination.

Results and discussion

Particles morphology and elemental composition

Morphologically, based on size, two groups of studied particles can be distinguished: more than $20-25 \ \mu m$ (Fig. 1), which were subjected to further spectroscopy analyses and less than $20 \ \mu m$, for which only radiography and SEM studies were carried out (Fig. 2).

Particles vary in the shape and the surface morphology. The particle SL10 has smooth surface particle and faceted shape with clear edges, it has no external signs of damage and destruction. The other 7 particles have uneven surface (see Fig. 1 and Fig. 2 for SEM images of the particles). More specific insight into the particles' morphology helps to distinguish four particles with more or less distinct layering: SL6, T1, T5 and T2. The SL6 and T1 particles are morphologically similar to each other, as evidenced by their layered structure and cracks on the surface. The T4 particle has a shape similar to the shape of a fuel grain, it shows a large number of intragranular pores as a result of the release of fission gas, and there are no signs



Fig. 1 SEM-images of "hot" particles in BSE-mode a, b, c, d and SE-mode e, f, g, h: a, e–SL10, b, f–SL6, c, g–T1, d, h–T4. Scale bars: yellow–10 μ m, red–5 μ m



Fig.2 SEM images of "hot" particles in BSE mode a, b, c, d and SE mode e, f, g, h: a, e,-T5, b, f-T2, c,g-T7, d,h-SL12. Scale bars: blue-2 μ m, red-5 μ m

Table 1 "Hot" particlesmeasured properties

	SL10	SL6	T1	T4
²³⁵ U/ ²³⁸ U (SIMS)	0.02062 ± 0.00018	0.01113 ± 0.00009	0.01201 ± 0.00007	Not measured
²³⁶ U/ ²³⁸ U (SIMS)	0.00078 ± 0.00004	0.00212 ± 0.00004	0.00221 ± 0.00003	Not measured
A(²⁴¹ Am)/ A(¹³⁷ Cs)	0.008	0.05	0.07	0.09
Zr atomic% (EDX)	0	0.1	0.1	0.2

of destruction such as cracks and laminations. Particle SL12 is composite: it consists of micrometer grains with submicron pores on their surface. Particle T7 is the smallest of the studied particles and it consists of several tens of spherical submicron fragments.

According to SEM–EDX data, all the particles, except SL10, contain small amounts of zirconium—less than 1 percent from the sum of (U+Zr) (see Table 1), so these particles can be categorized into the uranium-oxide group of particles [60].

Fuel burnup of "hot" particles

According to the SIMS data (Table 1), particles SL6 and T1 have similar uranium 235, and uranium 236 fractions while the respective fractions of particle SL10 differs sharply.

The obtained values of the uranium isotope ratio correlate with the data on fuel burnup in RBMK-1000 [48], while high content of ²³⁵U and low content of ²³⁶U indicative the fuel burnup in the SL10 particle is minimal. The burnup value, calculated according to Eq. (1) for the SL10 particle was 3.9 MWd/kg (U).

The uranium isotope ratios of the remaining particles also correspond to fuel burnup in RBMK reactors during long-term operation of the fuel, since the content of 235 U decreased from 2% to close to the natural ratio of ca. 0. 7%, while 236 U was detected (Table 1). The burnup values for SL6 and T1 were 13.2 MWd/kg (U) and 14.5 MWd/kg (U) correspondingly.

The presence of a small amount of ²⁴¹Am—0.19 Bq in the SL10 particle, compared to other particles, in which the specific activity of americium is approximately an order of magnitude higher, also indicative a low burnup value, since this radionuclide is a decay product of ²⁴¹Pu, which is produced in large amounts only during extended operation of nuclear fuel.

Uranium enrichment values of the extracted "hot" particles lie between 2.00 and 2.02% [48] (Fig. 3), which corresponds to uranium enrichment in the 4th unit of ChNPP [14].

Uranium oxidation state in "hot" particles

The SL10 U L_3 -edge XANES spectrum absorption peak (Fig. 4a) is at the same position as the peak of the



Fig. 3 Uranium isotope ratio of RBMK-1000 fuel with different enrichments [83] (*-literature data for fuel with varying burnup) [48]. Uranium isotope ratio of Chernobyl fuel "hot" particles established by secondary ion mass spectrometry–red dots



Fig. 4 a HERFD XANES L_3 U edge spectra of "hot" particles SL6, T1 and T4 and XANES U L_3 -edge spectrum of "hot" particle SL10 along with reference spectra of uranium (IV) and uranium (VI) compounds, **b** HERFD-XANES U M_4 -edge spectrum of "hot" particle SL6 along with spectra of reference uranium compounds

reference UO_2 spectrum indicative that in this particle uranium has valence state not higher than (IV). The SL6 U M₄-edge HERFD XANES spectrum along with U L₃-edge XANES spectrum absorption peaks (Fig. 4a, b) are in the same position as the peaks of the UO₃ spectra indicative uranium is oxidized in this particle. It should be mentioned that U M₄-edge HERFD XANES spectrometry is the unique method of determining the oxidation states of trace amounts of elements [79–81], and for the analysis of "hot" particles it is used for the first time in this study. The HERFD-XANES at U L₃-edge spectrum of T1 shows a correspondence between the position of the white line and its position for standard U(VI) oxide. The HERFD XANES L₃ U edge spectra of SL6 and T1 particles correspond to the UO₃ form of uranium + 6, since the spectra of compounds containing uranyl cation exhibit the first post-edge feature, which is absent in the spectrum of uranium trioxide [82]. The position of the white line of the T4 particle HERFD XANES XANES spectrum (U L3-edge) coincides with the position of the white line for U(IV) oxide.

The absorption peaks of SL6 and T1 HERFD-XANES U L_3 -edge spectra (Fig. 4a) are broader than the absorption peaks of standard uranium oxides, which can be explained by the particles' smaller size and a greater disorder of the structure.

Quantitative analysis of SL6 particle composition was performed by spectral decomposition using ITFA software. The experimental HERFD-XANES U M_4 -edge spectra of the oxides and particle SL6 were sufficiently reproduced (Fig. S1a) by using linear combinations of the three extracted component spectra (Fig. S1b). The first two eigenvectors show a non-zero signal, the eigenvector 3 is on zero-level (Fig. S1c), then all the three components are necessary to describe the spectrum of SL6 particle. The extracted components spectra refer to (IV) and (VI) uranium valence states. It was calculated that SL6 particle consists of 0.2% U(IV) and 99.8% U(VI).

Generalization of results

Using XANES and SIMS combination, the following behaviour of four particles was established over 30 years under the same environmental conditions. Since U/Zr ratio in all the fuel particles studied in the present work ranges from 0 to 0.2 at.%, these particles can be accounted as uranium-oxygen [26, 84]. XANES spectra proved that uranium oxidation state in SL10 and T4 particles is tetravalent, that is they belong to the UO₂ particles subgroup, which is relatively stable in the environmental conditions with dissolution half-life up to 70 years [62]. The SIMS data along with intact surface morphology confirmed extremely low burnup value of the fuel matter of the particle SL10. The surface of the particle T4 is porous, with fission gas channels, which, together with the high ²⁴¹Am content, makes it possible to assume a high burnup of the fuel material of the particle. At the same time, it should be noted that the overall shape of the particle T4 is similar to that of fuel grains and the faces and edges retain. Thus, two particles in which uranium is in the tetravalent state, have not undergone significant morphological changes over 30 years of being in the environment, regardless of their fuel burnup value.

The other two particles (SL6 and T1) in which uranium is present in the hexavalent state differ sharply in morphological peculiarities, in some places, layering typical of U(VI) oxides and oxy-hydroxides[85] can be seen. Based on the SIMS results, their burnup values were high for Chernobyl fuel. According to the same fuel particles classification [26, 84], SL6 and T1 particles can be classified as the UO_{2+x} particles subgroup, which is less stable, and its half-dissolution time was estimated in a range from 1 till 14 years [62]. The HERFD-XANES data proved the recent oxidation state of uranium in SL6 and T1 particles, which in 30 years after accidental fallout corresponds not UO_{2+x} , but to $U^{VI}O_3$.

Detailed studies of several fuel particles that have located for the same duration in the same spot of the exclusion zone confirm that the rate of destruction of particles in all probability depends not on the environmental conditions, but on the initial state of the particles, namely, on the uranium oxidation state. According to our data, fuel burnup doesn't seem to have any significant effect on the behaviour of particles, although, fuel burn-up cannot be completely excluded from the causative factors list for the behaviour of "hot" particles. The oxidation state of uranium is one of the major factors, to this list, but the importance of environmental and burn-up factors should not be neglected.

Conclusions

The complex of instrumental techniques: HERFD-XANES, SIMS and SEM-EDX makes it possible to compare uranium fuel "hot" particles to each other in following characteristics: uranium oxidation state, uranium isotope ratio and therefore fuel burnup, particle morphology and element composition, respectively. The impact of uranium in different oxidation states in "hot" particle using HERFD XANES M₄ U edge spectroscopy was calculated for the first time. Two particles in which uranium is in the tetravalent state have not undergone morphological changes over 30 years of being in the environment, regardless of their fuel burnup value. Two particles in which uranium was present in the hexavalent state stratified and the process of their morphological destruction began, while their burnup values were high for Chernobyl fuel. The studies carried out show that the combination of the used spectroscopy techniques can be a successful tool for radioecology research and nuclear forensics.

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Data availability The datasets generated and analysed during the current study are not publicly available since the given spectral data are sufficient to understand the operation but they are available from the corresponding author.

Declarations

Conflicts of interest There are no conflicts to declare.

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