Deliverable No. D5.3:
Redox processes in radionuclide transport in contaminated systems
(FINAL REPORTING)

REDOX PHENOMENA CONTROLLING SYSTEMS
ReCosy

COLLABORATIVE PROJECT (CP)

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The Final reporting includes the updated versions of previous Deliverables No. D5.3 (scheduled to be in months 24 and 36).

Particle transport is one of the possible mechanisms determining radionuclide speciation and migration behavior in environment. There are different sources of radionuclide containing particles such as technologies associated with SNF treatment, nuclear tests, fires, thermal explosions, accidents on nuclear power plants etc. It is known from literature that speciation of actinides mediated by particle transport could be source-dependent and source-independent. Source-dependent term means that species are not at thermodynamic equilibrium with their surroundings but remain in forms that are influenced by the source of particles. Source-independent speciation is determined by thermodynamics. Several methods exist which provide information from macroscopic (localization of radionuclide containing particles) to microscopic levels (chemical composition and speciation). These methods are alpha track analysis (search and localization of actinide containing particles), SEM-EDX (morphology and major element composition), SIMS (isotope composition), synchrotron based μ-XRF (elemental mapping), μ-XANES/EXAFS (chemical speciation), μ-XRD (phase composition), single particle chemical analysis (trace element, radionuclide composition).

In this report we are presenting results of application of methods mentioned above for investigation the actinide speciation in colloids collected in different industrial ponds from Russian SNF treatment plant PA “Mayak”. A number of samples of surface water and bottom from different Lakes of cascade of industrial basins at the Mayak site sediments have been obtained. Organic and inorganic colloids were characterized by methods of DOC analysis, ICP-MS, ICP-AES, SEM, AsFIF, TEM, STEM-HAADF, EELS and XAFS.

**Alpha-activity microdistribution**

One of the powerful methods for localization of actinide bearing particles is alpha track analysis (ATA). An example of localization of such particles by methods of optical microscopy and ATA is shown in Fig. 1.
The general elemental distributions in collected soils are presented in Fig. 2. These elemental maps were obtained by synchrotron based micro-X-ray fluorescence spectroscopy.

The concentration of Pu of soil samples is lower than the detection limit using the SB-XRF data. The microdistribution of $^{239}$Pu could be roughly estimated using ATA technique so long as the considerable part of alpha-activity of soils samples is due to the presence $^{239}$Pu. The comparison of ATA-image (Fig. 1) and the XRF-uranium map of the same place (Fig. 2, opposite hand view) show the noncoincidence of U- and Pu-bearing microparticles location.

**Uranium partitioning. The comparison of elemental micromaps**

![Fig. 2. Distribution of U and Fe in soils collected from Old Swamp.](image)

It was detected by $\mu$-XRF analysis that in many cases that no clear correlation of U with major elements (at least with the detected elements: Ca, Fe, Mn,) (Fig. 3, 4).
Fig. 3. Micro-XRF elemental mapping and SEM-SDX of one of the Old Swamp U particles (U (IV)), sample #SB-2-2.

Examination of some of U-containing particles reveal that U distribution is governed by the presence of Ca and Fe. For regions containing actinides more precise elemental mapping were carried out with higher resolution and for more elements. Comparison of U, Ca and Fe distribution for different regions in collected samples are presented in Fig. 5, 6 and 7.
Fig. 5. Comparison of U, Fe and Ca distribution in collected from Old Swamp samples.

Fig. 6. Comparison of U, Fe and Ca distribution in collected from Old Swamp samples.
It was shown that U distribution is correlated with distribution of Ca in some cases. One of the possible explanations of such behavior of uranium is possible formation of U-Ca mineral-like compounds. As it was noticed U and Pu speciation and local distribution does not correlate with each other. Different U redox species are present as well that is due to the presence of source-dependent and source-independent species.

**Uranium speciation in microparticles**

The XANES results revealed that among 15 U-containing microparticles there are 6 U particles in which U is present as U(IV) and 11 U particles having U(VI). Even after several decades of pond existence under oxic conditions there are some particles of nano- and micro-size which are remained in the state (IV), so they are source-dependent particles.

**Organic colloids**

Two main fractions of OM have been detected in the surface water, sampled from the lakes using AsFIFFF: particles having size around 1.5 nm (probably FA) and 10-15 nm. The main plutonium content was found to be bond to low-molecular weight fraction, that was attributed to a metal-induced colloidal organic matter agglomeration, mainly with FA and HA. It was unfortunately not possible to detect in the present conditions the Pu-240, Np-237 and Am-241 fractograms, according to the very low concentrations of these elements in the different water samples. Analysis of HA (MHA) extracted from the bottom sediments of the Mayak site have been performed regarding functional analysis. Total acidity of MHA was found to be two times higher then for leonardite HA (CHP), that correlates with the reducing capacity of these HA.

As the result the speciation of actinides (U and Pu) was studied in organic-rich bottom sediment from one of the industrial reservoirs at PA “Mayak” (Russia). Elemental mapping shows only isolated uranium particles with no associations with other elements ≥Ca, neither evenly distributed within the particles nor as an agglomerate that would imply U sorption on a mineral surface that nucleated further growth of a U-containing precipitate on the surface.
The XANES and the EXAFS spectra and curve-fit results unambiguously show that the particles consist of chemically homogeneous $\text{UO}_{2+x}$, $\text{U}_3\text{O}_8$, and schoepite ($\{(\text{UO}_2\text{O}_2\text{OH})_2\}(\text{H}_2\text{O})_{12}$ with metrical parameters within the range exhibited by these compounds within the lab and other environmental and geological sources. What is surprising is the tremendous range of speciation in these particles that were within mm of each other in the soil. There are no indications even after several decades of environmental exposure of any convergence of these species towards the most stable schoepite form. It can therefore be safely assumed that these species are the original source terms from multiple waste streams and that they unexpectedly were highly inert under these conditions.

The other purpose within the ReCosy project was to define the mechanisms of redox reactions of plutonium upon its sorption onto mineral oxides. Hematite ($\alpha$-$\text{Fe}_2\text{O}_3$), magnetite ($\text{Fe}_3\text{O}_4$), silica ($\text{SiO}_2$) and titania ($\text{TiO}_2$) colloids were used in sorption experiments. The samples were characterized by X-ray diffraction indicative no foreign phases present in the sample. The specific surface area was determined by BET method. To study plutonium sorption at different total concentrations, isotopes with different specific activities were used – $^{237}\text{Pu}$ ($T_{1/2} = 45.2$ d) and $^{239}\text{Pu}$ ($T_{1/2} = 2.41\cdot10^4$ a). In this study $\text{Pu(IV)}$ and $\text{Pu(VI)}$ pH sorption edges, kinetics and redox speciation were examined at different radionuclide concentration ranges, i.e. femtomolar ($\sim10^{-14}$ M), nanomolar ($\sim10^{-10}$ M) and micromolar ($\sim10^{-6}$ M).

At different total concentration range kinetics of sorption, pH-edges, leaching behavior were studied to derive mechanism of Pu sorption. The plutonium redox speciation on the colloid surface was studied using solvent extraction technique with TTA and HDEHP. HR-TEM and XAFS were used for local distribution analysis and spectroscopic speciation of plutonium. It was found that $\text{Pu(V,VI)}$ is reduced upon sorption onto mineral oxides and $\text{Pu(IV)}$ is stabilized on the particle surface. It was observed that sorption of Pu at nano- and micromolar concentrations is much slower than sorption at femtomolar concentration that could be explained by formation of polymeric species of Pu upon sorption at concentrations higher than $10^{-9}$ M. This assumption was confirmed by EXAFS through Pu-Pu interaction in EXAFS spectra. HR-TEM also support this assumptions - formation of $\text{Pu}_2\text{O}_3$-$n\text{H}_2\text{O}$ nanoparticles onto hematite surface were observed after equilibration at total concentration of plutonium equal $10^{-6}$ M and $10^{-9}$ M.

**Dissemination**