Study of the oxidation state of uranium in individual particles of abandoned mine tailings

A. Alsecz, J. Osán, V. Groma, S. Török and G. Falkenberg[1]

KFKI Atomic Energy Research Institute, P.O. Box 49, H-1525 Budapest, Hungary

[1] Hamburger Synchrotronstrahlungslabor (HASYLAB) at Deutsches Elektronen-Synchrotron (DESY), Notkestr. 85, 22607 Hamburg, Germany

One uranium ore deposit exists in Hungary. It is located in the south of the country at the foot of the Mecsek Mountains at the Western border of the city of Pécs. Before 1989, production was 500 - 550 tonnes of uranium per year from ores at grades of 0.1 % and was completely shipped to the Soviet Union. The production stopped in 1997. Since then, a project started in order to decrease and eliminate the damages caused mostly by the waste ore tailings and mill tailings. The majority of the tailings ponds were recultivated and covered with clay and loess. The recultivation of tailings pond No. I is not yet finished. Nuclear spectroscopical methods are well established in order to study the problem concerning radionuclides [1]. However, very limited information is available on the distribution and chemical form of uranium in the tailings sludge.

Tailings samples were collected from the uncovered part of tailings pond No. I, dried in air and prepared on Nuclepore polycarbonate filter. Fragments of the uranium ore provided by the mine remediation company was prepared similarly.

In order to identify the uranium containing particles in tailings samples efficiently, the particle-containing sample substrate was attached to a Solid State Nuclear Track Detector (SSNTD) [2]. The sample–detector system was irradiated with fast neutrons for 5 min in the research reactor of AEKI (fast neutron flux: 9.5×10^8 n/cm^2/s). Based on the tracks on the detector, the localization of U-rich particles was possible with a precision of ±100 µm.

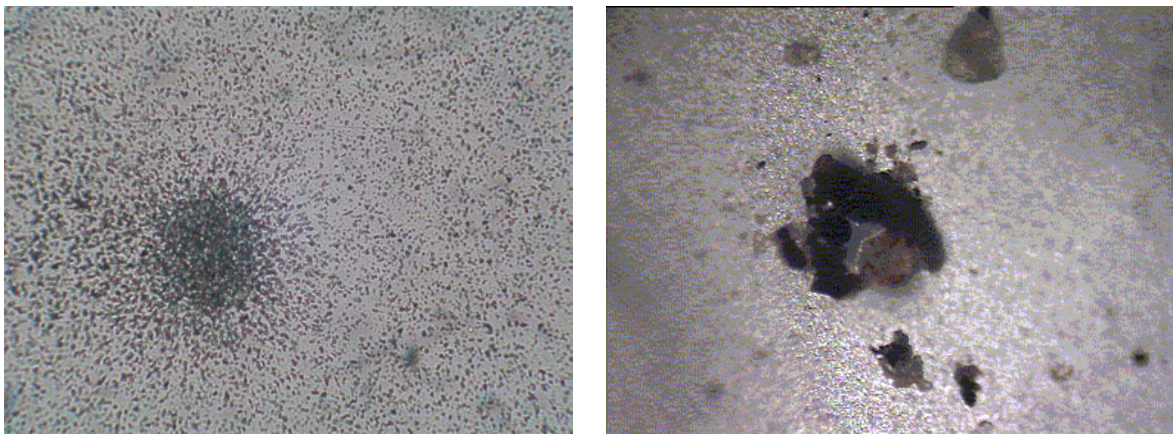

Figure 1: Optical images of the SSNTD (left) and the corresponding part of the sample (right)

The oxidation state of uranium in the pre-selected individual U-rich particles was investigated at the micro-fluorescence beamline L at HASYLAB using µ-XANES. The white beam of a bending magnet was monochromatized by a Si(111) double monochromator. A polycapillary half-lens (X-ray Optical Systems) was employed for focusing a beam of 1×1 mm^2 down to a spot size of 15 µm diameter. The absorption spectra were recorded in fluorescent mode, tuning the excitation energy near the L_3 absorption edge of U (17167 eV) by stepping the Si(111) monochromator, while recording the Lα fluorescent yield of the element of interest using an energy-dispersive GRESHAM Si(Li) detector. The used energy step size varied between 0.5 (edge region) to 2 eV (more than 50 eV above edge). UO_2, UO_3 and U_3O_8 particles prepared and tested in house were used as standards. The diameter of the standard particles was between 5 and 20 µm. The measuring time for each

energy point varied from 5 s to 30 s depending on the concentration of the element of interest. The U-L_3 μ-XANES spectra of the particles separated from tailings and ore samples was evaluated using linear combination of standard spectra of UO_2, UO_3 and U_3O_8.

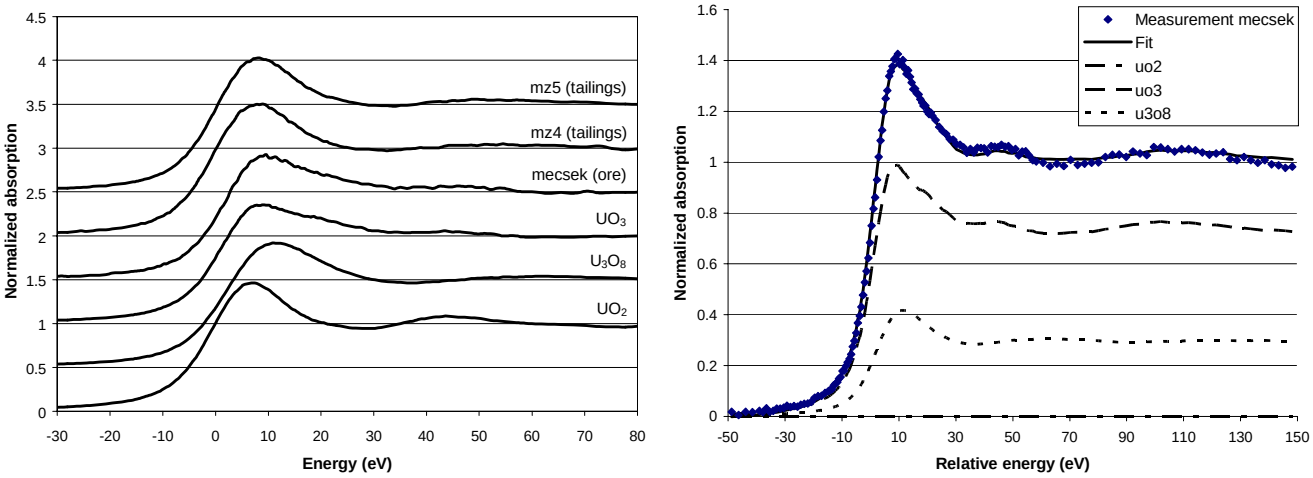

Figure 1: Comparison of μ-XANES spectra of separated U - rich particles and the standards

Table 1: Result of the linear combination of standard μ-XANES spectra of the individual U particles

Standard	Abandoned mine tailings					Mecsek uranium ore				
	mz4	mz5	mz4_8	mz5_9	mz5_10	ore	ore_1	ore_2	ore_5	ore_8
UO_2 (%)	77	69	62	60	47	-	-	-	-	92
U_3O_8 (%)	23	31	38	40	53	29	47	40	61	8
UO_3 (%)	-	-	-	-	-	71	53	60	39	-

Uranium in the mine tailings particles were 50–80 % in the less mobile U(IV) form and 20–50 % in the more mobile U(VI) form. In the original ore, the oxidation state of the uranium was found to vary in a wide range in the measured individual particles. A wide variety of uranium minerals exist in the Mecsek Mountain, containing U in +4 and +6 oxidation state, that supports our observation. Uranium in the tailings particles was found to be in more reduced form than main forms in the original ore, which was expected from the uranium mining technology. Depleted uranium particles separated from soil contained uranium in even more reduced form, mostly as U(IV) [3], resulting in lower environmental risk than in case of mine tailings particles.

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