ROBL-CRG	**Experiment title:** **Studies of the chemical forms of actinides and fission products adsorbed on nanocrystalline magnetite**	**Experiment number**: **20-01-658**
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Names and affiliations of applicants (* indicates experimentalists):

Dr. NIKITENKO Serguei*, C.N.R.S. - UMR 5084, CENBG, Domaine du Haut Vigneau, B.P.120, F-33175 Gradignan Cedex, France
Dr. SCHEINOST Andreas, ROBL

Speciation of selenium and uranium adsorbed at superparamagnetic magnetite by XAFS

Magnetite nanocrystals were obtained by co-precipitation of Fe(II) and Fe(III) in basic solutions in the presence of argon under the effect of power ultrasound (f= 20 kHz, I= 30 W/cm^2, P_{ac}= 0.75 W/mL, T=30-32°C). Transmission electron microscopy (Philips SM 120) reveal that the average particles size is equal to 4-6 nm (Fig.1a). Mössbauer spectroscopy (MS, ^{57}Co as a γ-source, with respect to metallic iron) show the superparamagnetic behaviour (Fig. 1b).

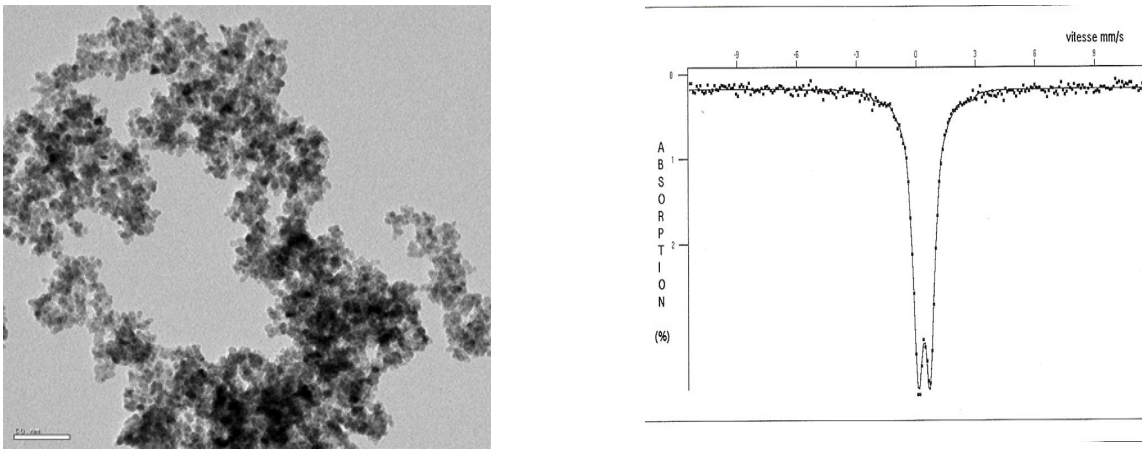

Fig. 1. TEM (left) and Mössbauer spectra of nanocrystalline magnetite.

Table 1.

Experiment	Adsorbent	Initial chemical form	pH	Time of contact to reach an equilibrium, min
1	Fe_3O_4 (4-6 nm)	Se(IV) ($HSeO_3^-$, SeO_3^{2-})	7.9	15
2	Fe_3O_4 (4-6 nm)	Se(VI) (SeO_4^{2-})	7.9	15
3	Fe_3O_4 (4-6 nm)	U(VI)	6.5	60

4	Fe_2O_3 (5-30 nm)	Se(IV) ($HSeO_3^-$, SeO_3^{2-})	5.5	15
5	Fe_2O_3 (5-30 nm)	U(VI)	4.0	60
6	Fe (≅ 5 μm)	U(VI)	5.4	12 hours

Sorption was performed in an inert atmosphere from 0.1M NaCl solutions at room temperature. The phase ratio solution (L)/solids (S) was equal to L/S= 200. Concentration of adsorbed species was typically about 1000 ppm. XAFS of the slurries of adsorbents were measured in fluorescence mode at 15 K at the Se K-edge and at room temperature at the U-L_{III} edge. The studied systems are summarised in Table 1.

XAFS of the systems 1,2, clearly show the absence of Se(IV) and Se(VI) reduction at the surface of nanomagnetite at the studied experimental conditions (Fig. 2). From the thermodynamic point of view Fe(II) of magnetite is able to reduce selenium. It can be assumed that reduction is very slow in basic solutions. The experiment will therefore be repeated at pH≅ 5. Metallic iron reduces U(VI) to U(IV) hydroxo-species immobilised at its surface (experiment 6, Fig. 3). By contrast, U(VI) adsorption at the magnetite occurs without chemical reduction (Fig. 3, left). Appearance of XANES band typical for U(IV) after several scans (experiment 3) most probably is related to U(VI) photoredution rather than reduction with magnetite. XAFS studies of this system at 15 K is necessary to minimise the photoreduction effect.

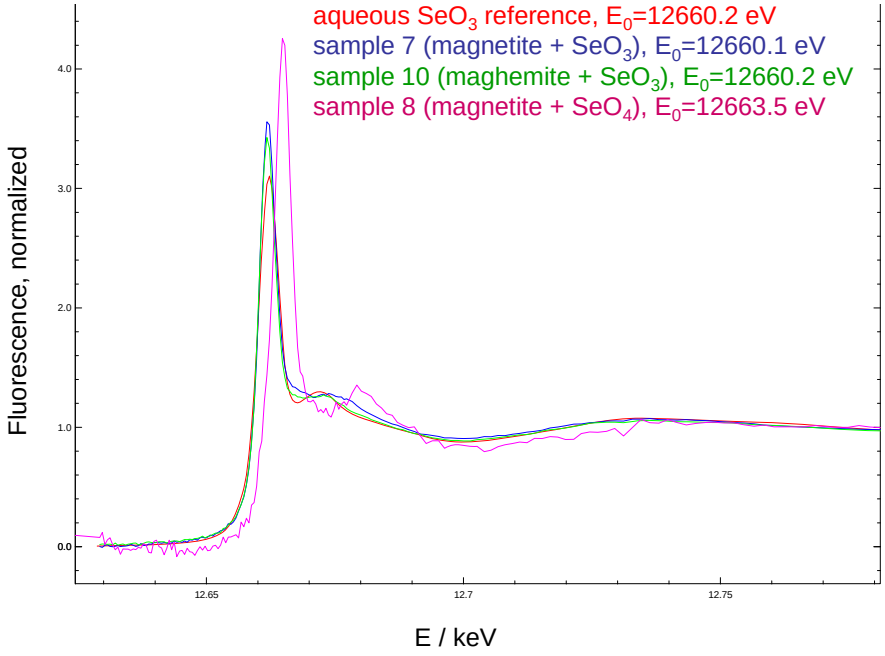

Fig. 2. Se K-edge XANES at 15 K

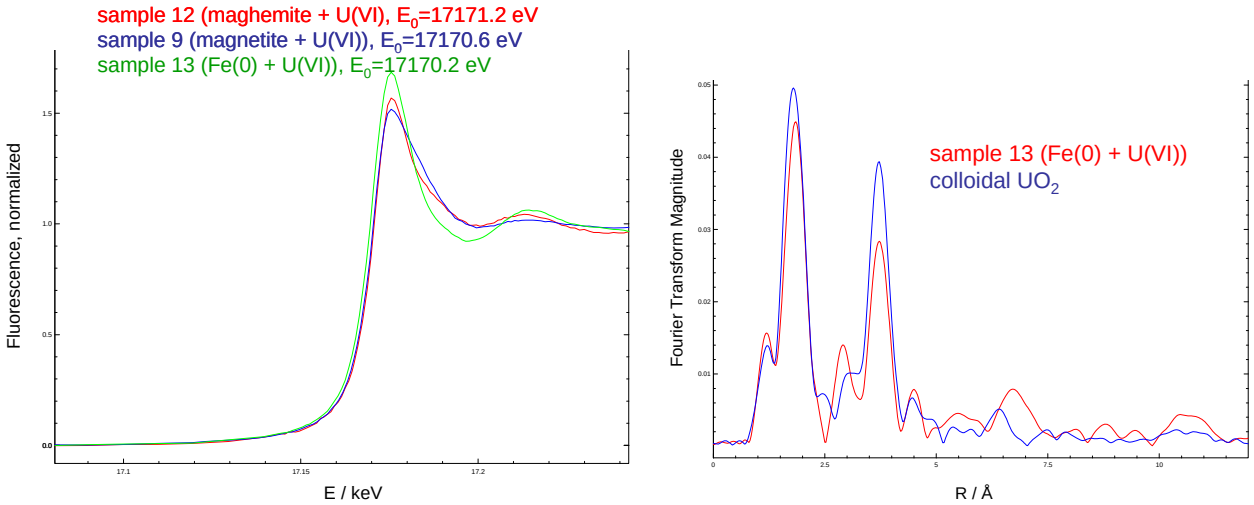

Fig. 3. U L_{III}-edge XANES (left) and EXAFS (right) measured at RT.