



Experiment title: Technetium chemistry: speciation in non-complexing and carbonate media, and coprecipitation with siderite (FeCO₃).

Experiment number:
30 02 801

Beamline: BM 30B	Date of experiment: From : 30/08/2007 to: 05/09/2007	Date of report: 25/09/2007
Shifts: 18	Local contact(s): Olivier Proux	<i>Received at ESRF:</i>
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Purpose

The purpose of this experiment was to characterize the chemical environment of technetium by means of EXAFS/XANES techniques in order to determine if technetium is mobile or not under the specific conditions of a nuclear waste storage in deep geological formation. On another hand, the detection trace elements present in different prepared samples by solid characterization and spectroscopic techniques was also carried out.

The samples

Two kinds of samples were prepared: technetium (IV) solutions in acidic non-complexing and 1M bicarbonate media, and technetium coprecipitate with siderite (FeCO₃).

Solutions of ammonium pertechnetate are electrochemically reduced by potentiometry in two media: HTFMS (trifluoromethanesulfonic acid) (pH < 0) and bicarbonate (pH = 8.5). In these conditions, the first medium will enable us to study the non-complexing form of Tc(IV), the second will allow to characterize Tc(IV) under conditions close to those of the natural environments.

Siderite and coprecipitates are synthesized by an electrochemical two-step protocol [1]. The first step consists in the electrochemical reduction of Fe³⁺ into Fe²⁺ in chloride medium pH 1 and the second is the coprecipitation of technetium with siderite under reducing and anoxic condition from N₂ bubbling at constant pH (8.5) under a redox potential equal to -300 mV/NHE.

The technetium and iron concentrations used in this experiment was 10 ppm and below.

The setup

Caution: technetium-99 is a β -emitter ($E_{max} = 293$ keV, $T_{1/2} = 2.13 \cdot 10^5$ years). Samples were bordered in specific tight cells in order to respect the radioprotection rules.

The X-ray absorption spectroscopy experiment was performed using monochromatic beams set at Tc K-edge (21 keV) and Fe K-edge (7 keV). We used a 30-elements Germanium detector to collect fluorescence photons. Each spectrum was obtained for energies varying in the range from 20.9 to 22.4 keV at the Tc K-edge, from 7 to 8 keV at the Fe one. The fluorescence signal was recorded counting 2s in the zone before element absorption, 4s in XANES zone, and with and increasing counting time in the EXAFS zone from 6 at the beginning to 12s at the end.

The data collection was carried out under inert atmosphere using an over-pressured nitrogen filled bag.

The experiment

The study of speciation of technetium (IV) in an acidic and non-complexing medium by X-ray absorption spectroscopy highlighted the formation of polymer complexes. Figure 1 presents Tc K-edge EXAFS spectra of two technetium species.

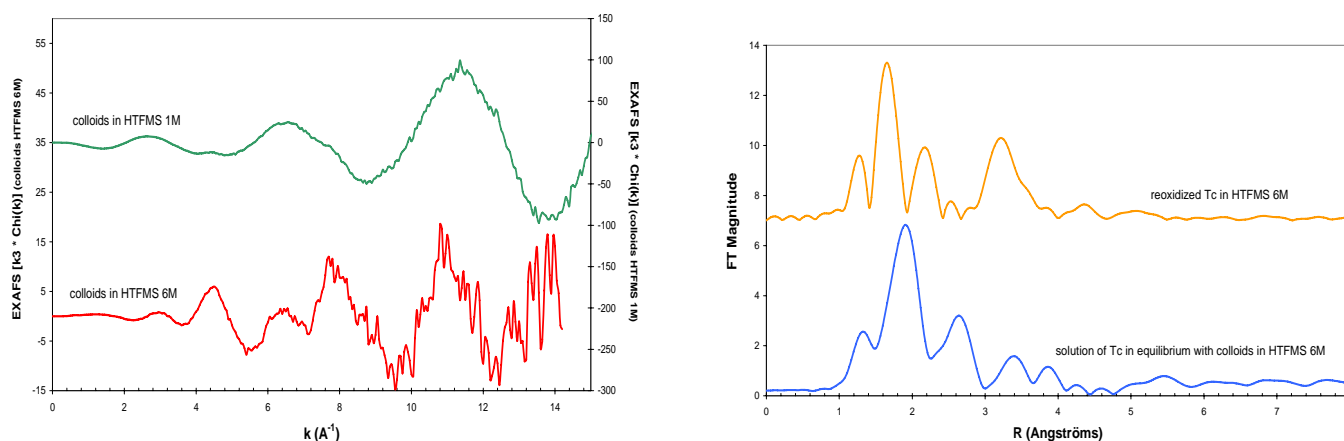


Figure 1: Tc K-edge EXAFS of colloids in 1 M and 6 M HTFMS (left) and Tc K-edge Fourier transformed of polymer and associated equilibrium solution in 6 M HTFMS (right) .

From an experimental point of view, the difficulty of the analysis is clearly shown. Firstly, the formation of colloids leads to a strong decrease of the signal-to-noise ratio. The quality of the data is worst for the 6M solution than for the 1M one. Secondly, we have observed the oxidation of polymer technetium species in 1M HTFMS due to the beam irradiation. Analyse of such solution requires reducing maintaining conditions. Normalized XANES spectra illustrated this evolution are presented in figure 2. Finally, the characteristic of the beamline allowed to detect concentrations down to 10 ppm, even if uncertainties (due to the cell) prevent from a quantitative analysis of the results.

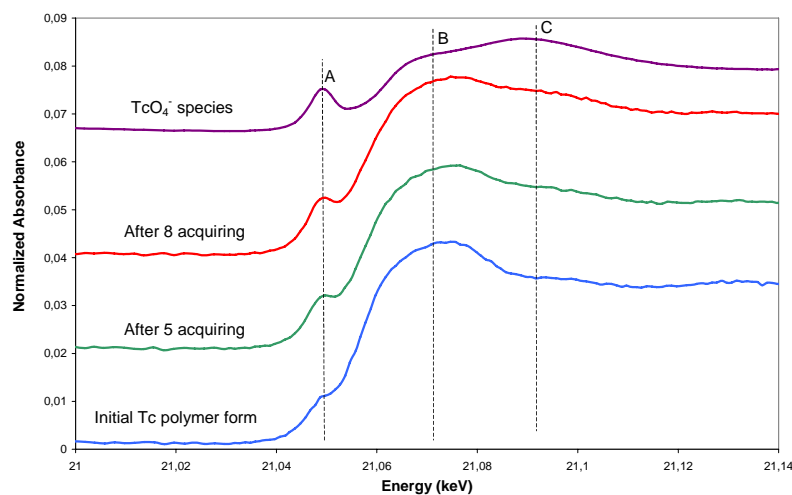


Figure 2: Evolution under beam irradiation of the polymer species in 1M HTFMS solution.

Concerning the interaction of technetium with siderite, K-edge of Tc and Fe EXAFS spectra have been obtained and are presented on figure 3 (EXAFS spectra at the Tc K-edge) and figure 4 (XANES spectra at the Fe K-edge). The direct comparison of the Fe K-edge XANES spectrum of the siderite with model compounds suggests an oxidation of this sample. Concerning the high Tc concentration coprecipitate, the pre-edge analysis shows the formation of an iron (III) phase.

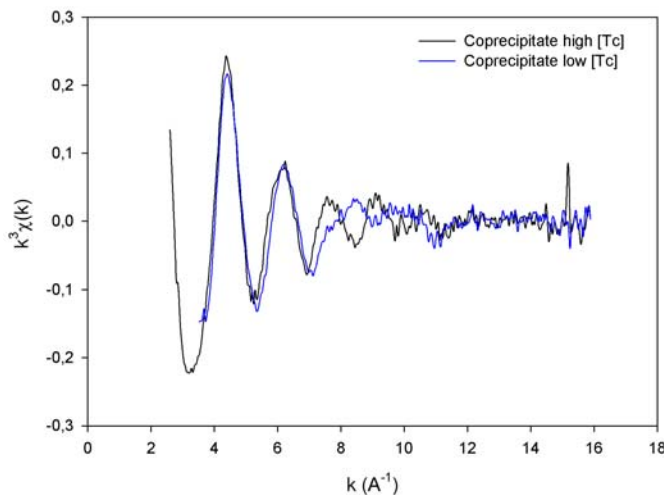


Figure 3: Tc EXAFS spectra in coprecipitates with two different Tc concentration.

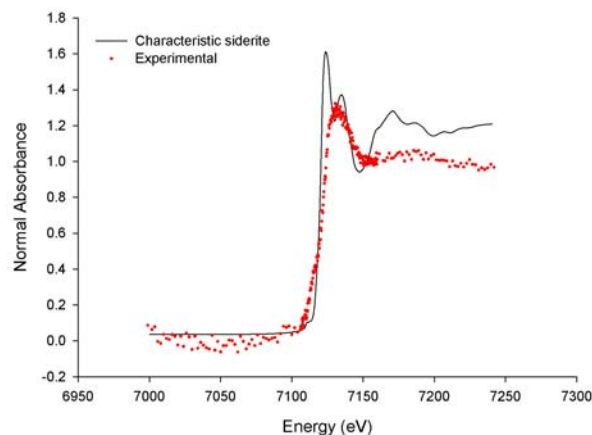


Figure 4: comparison of Fe XANES spectra of synthetic siderite with a siderite spectrum (personal communication of BM30 b)

Conclusions

This experiment shows the feasibility of EXAFS and XANES spectroscopy for the study of coprecipitation and adsorption of trace element in mineral phase and the speciation of trace element in aqueous solution (1-5 ppm). More technetium standard samples are necessary to determine the exact chemical speciation of Tc in acidic non-complexing medium. Experiments using electrochemical cell are also necessary to study the speciation of technetium (IV) in carbonate medium.

Preliminary measurements were carried out at Fe K-edge during the last two days of the experiment in order to characterize siderite by XAS and to determine the oxidation state of iron in a coprecipitate with a high Tc concentration. The quality of the acquired spectra makes their interpretation nevertheless delicate. In spite of all our caring, XAS cell contains large quantities of iron, which can have hinder data collection. The as obtained spectra for the coprecipitate, in spite of statistic of the measure, confirm the existence of an iron (III) phase (as had let us of it think the Mössbauer spectroscopy). These encouraging results show that a new series of measure at Fe K-edge would be necessary, with an optimized cell for this element (in lead screening for instance) and an optimized thickness of the sample (much lower than in the case of these tests where the important thickness, optimized for Tc, led to a following scattered beam).

References

- [1] I. Llorens, M. Fattahi, P. Deniard, P. Leone, S. Jobic and B. Grambow: Electrochemical synthesis and characterization of siderite. *Materials Research Bulletin* pp (accepted).