



	Experiment title: EXAFS/XANES studies on speciation of Tc-99 under reducing conditions	Experiment number: CH - 1050
Beamline: BM -20	Date of experiment: from: 28/03/2001 to: 31/03/2001	Date of report: 14/8/2001
Shifts: 9	Local contact(s): André Rossberg	<i>Received at ESRF:</i>
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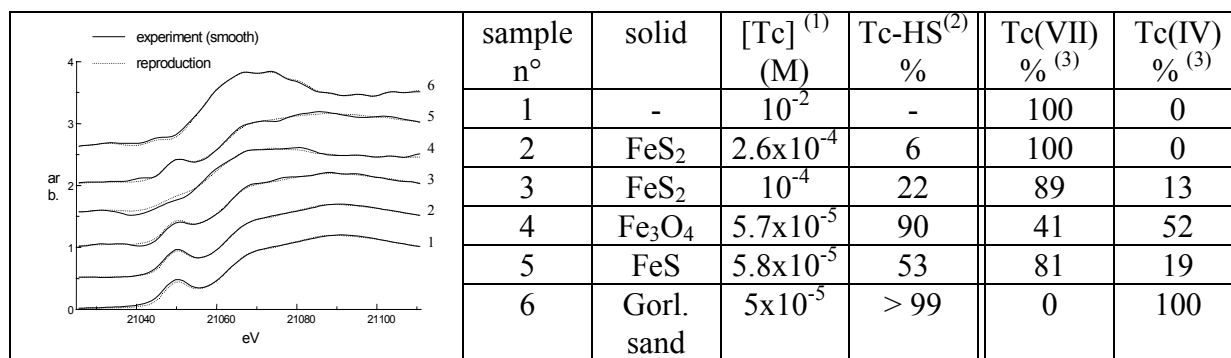
Report:

The redox-sensitive fission product technetium-99 is of great interest in nuclear waste disposal studies because of its potential of contaminating the geosphere due to its very long half-life and high mobility. Under oxidising conditions, technetium is present as pertechnetate, a highly soluble, anionic species, that does not sorb significantly on minerals or sediments [1]. Under suitable reducing conditions, eg. in the presence of a reducing solid phase which can act as an electron donor, the solubility can be limited by the reduction of pertechnetate followed by the formation of a surface precipitate [2]. However, in presence of soluble (mobile) humic substances, reduced technetium might be soluble due to the formation of Tc-HS complexes [3]. One of the main questions related to the behaviour of Tc-99 under natural reducing conditions and in presence of humic substances is the one concerning the oxidation state of reduced technetium. So far no direct proof of the oxidation state and the speciation of Tc has been given neither in the solution phase nor in solid phases (surface precipitate, sorbed species).

Four series of samples were prepared at K.U.Leuven. Series 1 consisted of reduced forms of Tc adsorbed or precipitated onto 3 different reducing surfaces (FeS, Fe₃O₄ and FeS₂) in absence and presence of humic substances added as real Gorleben water. Series 2 consisted of concentrated reduced forms of Tc in precipitated humic substances. Series 3 were the humic substances containing supernatant solutions of the above mentioned samples of series 1 and series 4 were the supernatant solutions of samples which contained Gorleben sand as the reducing solid phase. For security reasons, it was not allowed to measure series 1 and 2 because of problems with the containment. The remaining 2 series of samples, however contained a Tc concentration too low to be measured by EXAFS, and therefore, only XANES studies were performed.

The 9 allocated shifts were used to measure the XANES spectra of 5 liquid samples (see Table 1) in the fluorescence detection mode and 1 reference sample (pertechnetate) both in transmission and fluorescence mode. The 5 liquid samples (from series 3 and 4) were collected from batch experiments, in which different solids (magnetite, pyrite, ironsulphide and Gorleben sand) were contacted with humic rich pertechnetate solutions in an anoxic atmosphere. The Tc concentrations in samples 2 till 6 were extremely low for X-ray

absorption spectroscopy (see Table 1), however the obtained spectra could all be well analysed. The raw (pre-edge subtracted) data were smoothed (spline estimation savitzky-golay with nurbs) and normalized at an energy level of 21111 eV (see Figure 1). The pertechnetate (sample 1) has one important feature: a pre-edge absorption peak, which is recognised as a signature for pertechnetate [4]. In sample 6 this pertechnetate signature has completely vanished and an edge shift of 7.02 eV has occurred. Almahamid et al. [5] found an edge shift of around 7 eV corresponding to a reduction of Tc(VII) to Tc(IV). Therefore sample 6 contains 100% Tc(IV) species. Using a newly developed Tc speciation method [6], the amount of Tc associated with humic substances was also determined in all 5 samples (see Table 1). In sample 6, more than 99% of the technetium present is associated with the humic substances (see Table 1). Hence, it can be concluded that in sample 6, the Tc associated with humic substances are Tc(IV) species.



Figure/Table 1. Overview and results of the different samples of series 3 and 4 (sample 1 till 6).

- ⁽¹⁾ Total concentration of Tc in solution as determined by liquid scintillation counting (LSC)
⁽²⁾ Percentage of Tc in solution associated with humic substances (calculated as the difference between total Tc in solution and Tc of the supernatant after precipitation of the humic substances with La³⁺)
⁽³⁾ Calculated percentage of Tc(VII) and Tc(IV) from XANES spectral analysis

The other samples have spectra with two main features compared to sample 1 and 6: 1) the main absorption edge lies in between sample 1 and 6, and 2) the pre-edge absorption peak is decreasing compared with sample 1. The Tc speciation determined in Leuven is given in Table 1, column 3 and 4. A variable amount of Tc bound to humic substances and free Tc in solution was observed. Assuming that only Tc(IV) species associate with humic substances and the unbound Tc left in solution is mainly unreduced pertechnetate, the spectra of samples 2 till 5 were analysed as a binary mixture of samples 1 and 6. The percentage Tc(IV) associated with humic substances determined by XANES is smaller than the percentage determined by chemical methods. The reason of this is unknown, perhaps a slow oxidation of some samples occurred during transport.

Conclusions

It was unequivocally demonstrated by XANES spectroscopy of samples with very low Tc content, that Tc(IV) is associated with mobile humic substances. In samples containing variable amounts of Tc(VII) and Tc(IV), both fractions could be calculated from the recorded spectra. Further work with EXAFS and XANES is necessary, to unravel both the local environment of Tc in humic substances and in the surface precipitate.

References

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