



Experiment title: EXAFS/XANES studies on the speciation of reduced technetium-99 in presence of humic substances

Experiment number:
SI-790

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Report:

Introduction

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 with a low solubility [2]. However, in presence of dissolved humic substances, the solubility may be enhanced due to the formation of Tc-HS complexes [3].

In March 2001, a first series of measurements were performed at ESRF. From these measurements, it was unequivocally demonstrated by XANES spectroscopy of samples with very low Tc content, that Tc(IV) species were formed and were 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. These results were presented in a paper by Geraedts et al., which will be published in Radiochimica Acta [4]. It was the intention from the EXAFS measurements given in the present report to further elucidate the nature and kind of Tc(IV)-humic substances species (Gorleben and Boom Clay humic substances) and to identify Tc(IV) species formed on solid phases (pyrite and magnetite).

Sample preparation

At KULeuven, different series of samples were prepared in batch experiments: series 1 consisted of Tc species in presence of 2 different iron-containing surfaces (acting as the necessary reducing solid phase): pyrite and magnetite. These solid phases were brought in contact with humic rich (Gorleben groundwater) and humic free solutions. This set-up was used to determine the Tc species in presence of the different solid phases. A next series of samples was made to mimic a more natural environment: 1) a suspension of Gorleben sand in Gorleben groundwater and 2) Boom clay sediment in equilibrium with a synthetic

groundwater, resulting in an equilibrium distribution of humic substances and Tc between the solid and the liquid phase. From these last two samples, Tc-HS species could be obtained via centrifugation of the high weighted molecular humic substances. A final series of samples was made using a methodology developed at KULeuven for collecting (and measuring the concentration of) Tc-humic substances species from solution by induced flocculation of the organic matter with the trivalent cation La^{3+} [5].

The 9 allocated shifts were used to measure the XANES/EXAFS spectra of the abovementioned samples in the fluorescence detection mode. For the iron-containing samples, a special chromium filter was used to suppress the influence of the high X-ray absorption from iron.

Results

- 1) No differences were observed between spectra of samples containing Tc associated with solid humic substances and Tc associated with dissolved humic substances which were precipitated by La^{3+} . This indicates that 1) the Tc(IV) association with both solid and dissolved humic substances is alike and 2) La-precipitation of dissolved humic substances did not alter the Tc-HS association.
- 2) Unexpectedly, there were significant differences between the spectra obtained for samples containing Tc species associated with Boom Clay- and Gorleben humic substances, indicating a different interaction between Tc and the different types of humic substances (Boom Clay humic substances versus Gorleben humic substances). Preliminary calculations did not allow to quickly elucidate the chemical environment of Tc in these samples. Therefore, since no EXAFS literature data are available for these types of Tc species, additional EXAFS measurements on carefully chosen reference Tc-complexes are necessary in order to compare them with the obtained results with Boom Clay and Gorleben humic substances.
- 3) The Tc species formed on solid phases (magnetite and pyrite) both in absence and presence of humic substances were tetravalent Tc species. The exact coordination numbers and bond lengths will be calculated and compared with literature values of TcO_2 and TcS_2 in order to identify the formed Tc solid phase species on the different surfaces.

References

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