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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title: EXAFS/XANES studies on the interaction of Tc(IV) with selected chemical components as a reference for Tc(IV)-humic substance interaction**	**Experiment number**: CH 1454
Beamline: BM-20	**Date of experiment**: from: 18/05/2003 to: 21/05/2003	**Date of report**: 29/08/2003 *Received at ESRF:*
Shifts: 9	**Local contact(s)**: André Rossberg	

Names and affiliations of applicants (* indicates experimentalists):

André Maes*, Christophe Bruggeman*, Kathleen Geraedts*
K.U.Leuven, Laboratorium voor Colloïdchemie, Kasteelpark Arenberg 23,
B-3001 Leuven, Belgium

Luc Van Loon
Paul Scherrer Institute, Laboratory for Waste Management, OHLB/409a,
CH-5232 Villigen PSI, Switserland

Report:

Introduction

The redox-sensitive fission product technetium-99 (Tc) is of great interest in nuclear waste disposal studies because of its potential for contaminating the geosphere due to its very long half-life (2.13×10^5 year) and high mobility under oxidising conditions, where technetium forms pertechnetate (TcO_4^-) [1]. Under suitable reducing conditions, e.g. in the presence of an iron(II) containing solid phase which can act as an electrondonor, the solubility can be limited by the reduction of pertechnetate followed by the formation of a surface precipitate [2]. However, by association with mobile humic substances (HS), the solubility of reduced Tc species may be drastically enhanced [3].

A first XANES measuring campaign (performed at ESRF, March 2001, CH-1050) demonstrated for the first time that pertechnetate was reduced to Tc(IV) and Tc(IV)-HS species were formed in Gorleben sand/Gorleben groundwater (rich in humic acids) reducing systems. These results were published in Radiochimica Acta [4].

A second EXAFS/XANES campaign (performed at ESRF, July 2002, SI-790) was then performed on samples in which TcO_4^- was reduced by various solid phases (pyrite, magnetite, Gorleben sand, Boom Clay), both in absence and presence of humic acids (HA). These experiments were set up in order to elucidate the chemical environment of Tc in these systems on atomic scale. The data from these experiments showed very interesting and surprising results, because all spectra could be fitted with a hydrated amorphous Tc(IV) oxide phase, independent of the reducing surface used and of the eventual presence of HA. These results could only mean that Tc(IV) oxide colloids were formed and precipitated upon reduction of TcO_4^-, and that these colloids could also interact with the organic colloidal material from Gorleben and Boom Clay HA. This latter observation was confirmed by batch sorption experiments with Tc and Boom Clay suspensions from which an interaction constant could be derived describing the interaction of a neutral Tc(IV) species and dissolved HA [5]. A paper containing the results from the above described EXAFS/XANES data was sent to Environmental Science & Technology for reviewing [6].

It was the intention from the EXAFS measurements given in the present report to further clarify the nature and kind of Tc(IV)-humic substance species, in terms of complexation or colloid-colloid interaction.

Sample preparation

To investigate the universality of the observed interaction between Tc(IV) colloids and HA for other organic molecules, batch systems were set up at KULeuven in which TcO_4^- was chemically reduced to Tc(IV) and to which 9 reference organic compounds varying in size from small to large (citric acid, hydroxybenzoic acid, pyrogallol, glutaminate, isosaccharinic acid, aurintricarboxylic acid, calconcarboxylic acid, Laurentian fulvic acid, Fluka humic acid) and Boom Clay HA were added. The systems were allowed to equilibrate over a certain time period before preconcentration of the samples, after which aliquots were transferred into the measuring vials.

The allocated shifts were used to measure the XANES/EXAFS spectra of the abovementioned samples in fluoresence (and where possible transmission) detection mode.

Results

The results from this campaign are still being investigated, but the following preliminary conclusions were already drawn :

1) the technique used to reduce TcO_4^- still yielded the same colloidal Tc(IV) spectra in presence of large humic acid molecules (Fluka HA and Boom Clay HA) as observed before, however different spectra were now obtained in the presence of small dissolved organic molecules ;
2) as described in literature [7,8], Tc(IV) species probably formed chelates with most smaller organic molecules by means of a ligand exchange between the hydrolysed Tc(IV) molecules and functional groups present on the organics. Since for all samples a different spectrum was obtained, this reflects the different nature of chelates formed dependent on the availability and geometry of the ligands on the different organic molecules. If the obtained EXAFS spectra can be interpreted correctly, they form the first direct spectroscopic proof for this range of Tc(IV) complexes ;
3) in view of the foregoing results, it is now assumed as a working hypothesis that Tc(IV) can interact with different organic molecules in two ways : the first is by colloidal association between anorganic Tc(IV) and large organic matter (HA) molecules, the second is by making complexes with smaller organic ligands. However, the exact contribution of each interaction mechanism in intermediate HS molecules such as Laurentian FA and in natural waters containing a wide range of organic matter (mixture of HA, FA and low molecular weight organic acids), remains unknown due to the lack of sufficient knowledge concerning the mechanisms and associated constants.

References

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