Experiment Report Form

The double page inside this form is to be filled in for each experiment at the Rossendorf Beamline (ROBL). This double-page report will be reduced to a one page, A4 format, to be published in the Bi-Annual Report of the beamline. The report may also be published on the Web-pages of the HZDR. If necessary, you may ask for an appropriate delay between report submission and publication.

Should you wish to make more general comments on the experiment, enclose these on a separate sheet, and send both the Report and comments to the ROBL team.

Published papers

All users must give proper credit to ROBL staff members and the ESRF facilities used for achieving the results being published. Further, users are obliged to send to ROBL the complete reference and abstract of papers published in peer-reviewed media.

Deadlines for submission of Experimental Report

Reports shall be submitted not later than 6 month after the experiment.

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 / experiment 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.
- bear in mind that the double-page report will be reduced to 71% of its original size, A4 format. A type-face such as ”Times” or ”Arial” , 14 points, with a 1.5 line spacing between lines for the text produces a report which can be read easily.

Note that requests for further beam time must always be accompanied by a report on previous measurements.

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HZDR HELMHOLTZ ZENTRUM DRESDEN ROSSENDORF ROBL-CRG	**Experiment title:** EXAFS investigations on Am(III) complexes formed by the cementitious additives malate and succinate	**Experiment number**: **20-01-772**
Beamline: BM 20	**Date of experiment**: from: 27-Jul-16 (08:00) to: 01-Aug-16	**Date of report**: 1-Feb-17
Shifts: 15	**Local contact(s)**: André Rossberg	*Received at ROBL:*

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Report

The understanding of the interaction of cementitious organic additives with radionuclides in solution is very poor and only a few investigations on the effect of concrete admixtures on the aqueous speciation of actinides are available [1, 2]. Here, the complexation of Am(III) with malate (as cementitious additive) and succinate was investigated in the pH range between 1 and 8 to determine structural properties of these complexes for the first time. Here we report the results for the malate system.

Results

In the EXAFS spectra and the corresponding Fourier transform (FT) of the Am(III)-malate samples shown in Fig. 1 only small variations with rising pH value can be observed. As the use of the iterative transformation factor analysis (ITFA) [3] already showed good results for complexation reactions of similar small organic ligands [4, 5], it was applied here to isolate pure component spectra. In the first step of the ITFA two components were determined. The speciation of Am(III)-malate complexes and the adapted coordination numbers (CN) of these two components, which are needed for the third step in the ITFA, were taken from previously performed time-resolved laser fluorescence spectroscopy (TRLFS) and isothermal titration calorimetry (ITC)

measurements. Also, a chelate and an asymmetrical coordination of malate was assumed. The single spectral components extracted by the iterative target test (ITT) were fitted with EXAFSPAK [6]. Component 1, i.e. Am(III) coordinated by oxygens (water-like) shows an Am-O bond distance of 2.48(4) Å and a CN of 1.2(4).

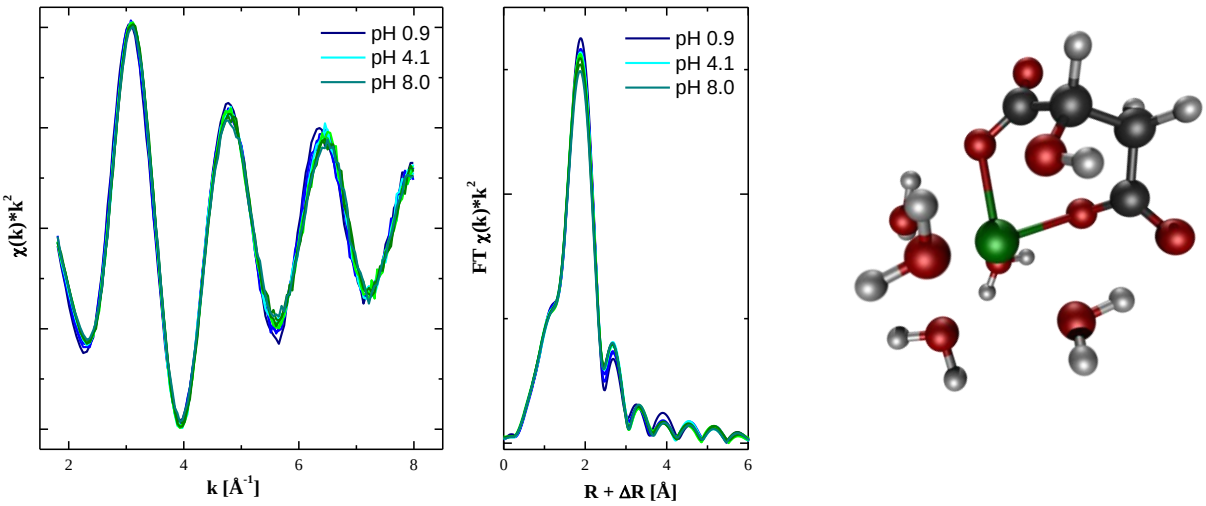

Figure 1: EXAFS spectra and the corresponding Fourier transform (FT) of the Am(III)-malate samples, DFT opimized structure of a proposed 1:1 complex including the 7-membered ring.

Component 2, which represents Am(III) coordinated by malate, shows a Am-O bond distance of 2.39(5) Å (CN of 0.8(6)) and a Am-C bond distance of 3.33(1) Å (CN of 1.8(3)). Note that all spectra can be reproduced by these two isolated spectral components and their corresponding fractions and CN's. The relatively long Am-C bond distance, which also can be observed in the Am(III)-lactate [5] and Cm(III)-succinate [7] system, indicates a monodentate binding of the carboxylate group(s) of malate either including the OH group in a 5- or 6-membered ring or including both carboxylate groups in a 7-membered ring.

References

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