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Application for beam time at ESRF – Experimental Method

This document should consist of a maximum of two A4 pages with a minimal font size of 12 pt.

Title: **Interaction of uranium with characterized organic degradation products of organic waste components including model compounds and microorganisms using XAS**

Aims of the experiment and scientific background

The safe disposal of radioactive waste is an omnipresent and much discussed issue. Within the EU project MIND (Microbiology In Nuclear waste Disposal) we want to contribute to the further development of the safety case knowledge base on the influence of microbial processes on geological disposal of radioactive waste [1]. One topic of interest is the degradation of organic waste polymers (e.g., cellulose, bitumen, and PVC) present in nuclear waste and to evaluate their influence together with their associated degradation products on the current radionuclide speciation. Hence to assess the safety and the long term performance of deep geological repositories it is necessary to know the fate of actinides in- and outside of the waste bins. The degradation processes strongly depend on the surrounding/ambient conditions, e.g. pH, the presence of microbes, and the presence of complexants. We will begin our study with degradation products of cellulosic materials (e.g. acetate, butyrate and isosaccharinic acid) [2, 3] to study the interactions with U(VI) and to determine structural changes by using XAS. The identification of the speciation of U in supernatants of microbial degradation experiments are also in the focus of our study.
Within our last three projects, XAS brought important results [4-6]. We could explore structural parameters of U in species formed with microbially secreted bio-ligands. We were able to determine interatomic distances and coordination numbers of U and partly Pu to its nearest neighbors in cell material from *Desulfovibrio aespoeensis*, *Pseudomonas fluorescens* and from bacterial isolates of Mont Terri Opalinus Clay. We were also able to determine the oxidation state of the actinides in these samples. The results helped to describe the direct and indirect interaction processes of bacteria with U and Pu. This new study is focused on speciation analyses of U with complexants formed by degradation processes of organic polymers present in nuclear waste using XAS. For instance, the EXAFS data sets for one particular ligand, e.g. as a function of pH, will be evaluated using factor analysis (ITFA [7]) in order to ease the determination of the U(VI) speciation based on structural changes. However, also the influence of microbes on the degradation processes and the actinide chemistry as well as U speciation analyses in supernatants of microbial degradation experiments will be addressed in the project. In addition, the interaction of U(VI) with organic polymers itself is in the focus of our investigations. Knowledge about nature and strength of the formed U species is of great importance for the understanding of mobilization or immobilization of U under the conditions of a nuclear repository. To study the complexation of U in our selected systems, XANES and EXAFS will be used in addition to other analytical and spectroscopic methods. X-ray absorption spectroscopy gives important information concerning the oxidation state, site geometry, coordination numbers, neighboring atom type and interatomic distances.

Experimental method

XAS measurements will be performed in order to describe the interaction of degradation products, model ligands, organic polymers, and microbes of interest with U on a molecular level. XANES will be applied to identify the oxidation state of U. EXAFS will be applied to measure coordination numbers and interatomic

distances of U to its nearest neighbors. We also intend to reduce the required U concentration per sample (< 50 mM) to come closer to our other, more sensitive, spectroscopic techniques, e.g. UV-vis and TRLFS. U L_{III}-edge X-ray absorption spectra (17.166 keV) will be measured at room temperature and at low temperature by using a closed-cycle helium cryostat. The spectra will be recorded in the energy range from 16.9 to 18.5 keV. The samples will be mostly liquids encapsulated in a PE container (first confinement) sealed with a polyethylene (PE) foil (second confinement). In addition also measurements of solids and wet pastes could be possible. For all specimens (e.g., solutions and/or solids and wet pastes) sample holders with an approved design will be used to ensure the double confinement. The measurements will be performed in transmission or fluorescence mode by using ionization chambers or a 13 element Ge-detector.

Results expected

As indicated in the project description, we expect to obtain information on the oxidation state of U in different experimental systems. Furthermore, we want to explore the short range order of U in the presence of complexants and also microbes. We expect to detect structural parameters of the U complexes formed. Moreover, we want to apply factor analysis to ease the determination of the U speciation based on structural characteristics of the formed complexes.

References

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