Speciation of Uranium and Arsenic Sorbed onto Scrap Metallic Iron and Shewanella putrefaciens Surfaces: A XANES Fingerprinting Investigation

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The effective design, operation, long term maintenance, performance evaluation and troubleshooting of a permeable reactive barrier filled with elemental iron in mitigating uranium and arsenic require sound understanding of both toxins sorption mechanisms and related mass exchange reactions. To date however, both uranium and arsenic sorption onto zero valent iron (ZVI) is described by seemingly contradictory reaction mechanisms. This paper discusses the mechanisms of uranium sorption onto scrap metallic iron and the versatile bacterium Shewanella putrefaciens surfaces in the presence of arsenic based on X-ray absorption near edge structure (XANES) fingerprinting. Bulk U L3 and As K-edges X-ray absorption fine structure (XAFS) spectra from solid samples of batch sorption experiment were recorded at the INE-Beamline for Actinide Research at the ANKA synchrotron radiation facility.

Shoepite was used as a standard for uranium in valence state +VI whereas arsenic metal foil [As(0)] and powder samples of $As[III]_2O_3$ and $As[V]_2O_5$ were measured as reference compounds. The sorption experiment samples comprised the systems Fe^0-0.1mM U, Fe^0-0.1mM U-0.1mM As and the anoxic Fe^0-0.1mM U- 0.1mM As-DSMZ Shewanella putrefaciens strain 6067 at concentration of 2 optical density units (600 nm) equilibrated for 24 hours in the dark without shaking. The shapes and edge positions of the normalized U L3-edge XANES spectra for all three samples are identical. The energy position of the white lines is typical for U(VI) compounds. A shoulder at the higher energy side of their respective white lines is commonly attributed to multiple scattering of the outgoing photoelectron wave at the two shorter bound axial oxygen atoms in a uranyl compound. The XANES fingerprinting of the normalized As K-edge spectra with reference compounds reveals a clear valence state of +V of the absorbing arsenic atom for both the abiotic Fe-U and Fe-U-As as well as for the biotic Fe-U-As-Shewanella putrefaciens systems. Thus, under this study experimental condition, the prevalence of uranyl and arsenate species reflects macroscopic experimental observations in favor of a dominant precipitation/co-precipitation mechanism of uranium fixation by elemental iron enhanced by arsenic if present rather than reductive sorption.

The facultative Shewanella putrefaciens apparent failure to reduce uranium enzymatically is chiefly interpreted as a metabolic inhibition on the reduction kinetics rate caused by a high arsenic concentration.

1 Introduction

The concomitant occurrence of uranium and arsenic in groundwater at concentrations of up to hundreds of magnitude beyond their respective World Health Organization provisional threshold guidelines of 15 µg/L and 10 µg/L is a major threat to both the natural environment and human health and wellness. While uranium carcinogenicity from exposure to high concentrations has been known for decades, world wide attention on arsenic toxicity has gain much attention following the human mass poisoning in India and Bangladesh due to consumption of arsenic contaminated groundwater. Inside the human body, arsenic targets mainly liver and kidney with carcinogenic effects (REIMANN & DE CARITAT 1998).

While the mining and milling of arsenic rich ore bodies is a main source of the dual occurrence of uranium and arsenic in groundwater, recent studies suggest that inorganic arsenic reaching and coexisting with uranium in groundwater may

originate from a much wider spectrum of sources. For instance, CORTINAS *et al.* (2006) found that 4-hydroxy-3-nitrobenzene arsonic acid (roxarsone), benign and common arsenic based feed additive still in use in North America poultry industry can convert into highly toxic inorganic form within 8 months following chickens litter spread onto field. STOLZ *et al.* (2007) credited a much more rapid (10 days) transformation of roxarsone to inorganic arsenates to microorganisms of the genus Clostridium in chicken litter. In addition the National Research Council (1999) reports that the ingestion of arsenic as either arsenite [As(III)] or arsenate [As(V)] can result in a similar harmful toxicological effects to humans as As(V) can be reduced to As(III).

Therefore, understanding the speciation of both uranium and arsenic in either natural or laboratory settings is paramount since it relates to their mobility in groundwater, reactivity, stability in natural environment and nuclear waste repositories, bio-availability and ultimately their toxicity. However, despite this environmental significance of uranium and arsenic speciation, yet studies solely related to the subject are rare. This scarcity seems to be related to current analytical limitations to reliably characterize species of interest among the wide range of aqueous, surface and minerals species of the natural environment heterogeneous systems (MANCEAU *et al.* 1996; SCHEINOST *et al.* 2002).

Over the last decades, analytical progress and wider availability of synchrotron based spectroscopic techniques has boosted the likelihood of reliable determination of uranium and arsenic speciation in the natural environmental heterogeneous samples. To this end, DENECKE *et al.* (2005) for instance combined confocal micrometer-scale X-ray fluorescence and bulk X-ray absorption fine structure to uncover uranium and arsenic speciation and hypothesized on the geogenic immobilization mechanism of uranium in a tertiary sediment dominated by the system Fe-U-As.

Overall, chemical speciation whether in aqueous, minerals or at the interface liquid-solid systems holds essential information to decipher the major sorption mechanisms controlling the environmental fate of a contaminant of concern. Thus, chemical speciation is a key criterion in the effective design, operation, long term maintenance, performance evaluation and troubleshooting of a passive remediation strategy.

Permeable reactive barrier filled with elemental iron has recently emerged as one of the most promising and effective technology in mitigating uranium and arsenic in contaminated groundwater. To date however, both uranium and arsenic sorption onto zero valent iron is described by seemingly contradictory reaction mechanisms. Uranium immobilization by metallic iron is reported as either controlled by reductive precipitation induced by elemental Fe(O) or structural Fe(II), chemisorption at the surfaces of Fe(O) and corrosion products, precipitation/co-precipitation, or their combination (GU *et al.* 1998; ABDELOUAS *et al.* 1999; BOSTICK *et al.* 1996; FIEDOR *et al.* 1998; NOUBACTEP *et al.* 2003; NOUBACTEP *et al.* 2006). Arsenic removal by ZVI is also commonly described either as co-precipitation of the reduced As (III) from As (V) or as adsorption of both As (V) and As (III) on iron corrosion products or other pre-existent oxyhdroxides (MCRAE *et al.* 1999; MALLANS *et al.* 2002, SU & PULS 2001).

A major drawback of the ZVI technology is the possibility of the immobilized contaminant to be re-oxidized and re-dissolved back into solution. Therefore, much attention has been turned lately to the dissimilatory Fe(III) reducing bacteria such as Geobacter Metallireducens and Shewanella putrefaciens which have the capability to couple the oxidation of organic matter to the reduction of Fe(III) and alternatively various metals/metalloids including uranium and arsenic (LOVLY *et al.* 1992; LOVLY 1995) through typical reactions:

$$CH_3COO + 4U^{6+} 4H_2O \Rightarrow 4U^{4+} + 2HCO_3^- + 9H^+$$

$$H_2 + U^{6+} \Rightarrow U^{4+} + 2H^+$$

However, as pointed out by BROOKS *et al.* (2003), conditions that can inhibit this enzymatically driven bio-transformation are an active research area. Yet, as reported by ABDELOUAS (1998), several authors have claimed that the reduction of U(VI) is an enzymatically mediated reaction and as such independent of experimental conditions.

This contribution revisits and discusses the mechanisms of uranium sorption onto elemental iron emphasizing on the effect of arsenic and Shewanella putrefaciens surfaces on uranium sequestration using X-ray absorption near edge structure (XANES) fingerprinting and geochemical speciation calculations of abiotic and biotic experimental systems conducted in conditions

that theoretically hold potential to inhibit the enzymatic reduction of uranium.

2 Experimental

2.1 Reagents and Solutions

Analytical grade uranyl nitrate 6-hydrate $UO_2(NO_3)_2.6H_20$ (Chemapol, Germany) and sodium arsenate $Na_2HAsO_4.7H_20$ (Baker, Germany) were used to prepare stock solutions of uranium and arsenic. The background electrolyte used in every experiment was prepared from sodium nitrate from Merk (Germany). Reagents used for bacterium growth include yeast extract (Roth, Germany), Peptone (VEB Berlin Chemie, Germany) and NaCl (Riedel-de-Haen, Germany). Water used as solvent throughout was deionized with a Milli-Q Water Purification System (Millipore, France).

2.2 Scrap Metallic Iron

The scrap metallic iron type S69 from Metallaufbereitung Zwickau (Germany) was crushed and sieved and the 0.1 mm fraction used as sorbent. Its elemental composition is 92.8 % Fe, 3.5 % C, 2.1 % Si, 0.9 % Mn and 0.7 % Cr.

2.3 Bacteria Culturing and Harvesting

The dried culture of Shewanella putrefaciens referred to as strain 6067 was purchased from Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH (DSMZ). It was resuscitated following routine DSMZ protocol using an appropriate medium at the laboratory of environmental microbiology at the Technische Universität Bergakademie Freiberg (Germany). The stock culture was maintained through freezing. The active stock cells cultures of S. putrefaciens DSMZ 6067 was thereafter used to inoculate a Petri dish containing yeast extract, peptone and agar and incubated at room temperature (about 23^{o}C). Cells culturing for the sorption batch experiment was carried out aerobically at a similar ambient temperature at the Laboratoire de Chimie Agro-Industrielle of ENSIACET (France) using a set of 250 mL glass Erlenmeyer filled with 100 mL of the growth medium and inoculated with a loopful of S. putrefaciens colonies from Petri dish. The growth medium comprised 2 g/L yeast extract, 5 g/L peptone and 5g/L NaCl adjusted to pH 7 with NaOH prior to sterilization. The culture vessels were put on a shaker and incubated at room temperature until the late exponential growth phase. The cultured cells were harvested by centrifugation at 7000 g for 15 minutes at a temperature of 10^{o}C. The harvested cells were washed twice using a sterile and anoxic 0.01 M KOH solution. The washed pellets were finally resuspended in anoxic 0.01 M $NaNO_3$ background electrolyte solution of the biotic batch sorption experiment reaction vessel.

2.4 Batch Sorption Experiments

The abiotic batch sorption experiments samples selected for the synchrotron radiation investigation comprises the reacted solid phase from the systems Fe^0-0.1mM U and Fe^0-0.1mM U-0.1mM As. The 100 mL polyethylene reaction vessels contained 2 g of 0.1 mm particulate sized scrap metallic iron set to equilibrate in a solid to solution ratio (weight/weight) of 1/50 using a background electrolyte solution of 0.01 M $NaNO_3$ spiked respectively with uranium 0.1mM U alone or with the bi-component 0.1mM U-0.1 mM As adjusted in either case at pH 4.5. The biotic batch sorption experiment consisted of the unique system Fe^0-0.1mM U-0.1mM As-Bacteria cells. All solutions used in this system were adjusted at pH 4.5 and purged with high purity nitrogen gas prior to sterilization. The anaerobic reaction vessel consisted of 75 mL glass bottle capped with rubber crimped with an aluminum seal. The vessel contained a mixture of 1g of 0.1 mm scrap metallic iron particles in 50 mL of a 0.01 M $NaNO_3$ background electrolyte solution. This medium was spiked with S. putrefaciens cells to achieve a concentration of 2 optical density units (600 nm) at the end of the 6 hours hydratation time imposed to both the abiotic and biotic systems. High purity ethanol at concentration of 0.05 % was used as electron donor. In either the abiotic or the biotic experiments, the addition of uranium or uranium and arsenic marked the start of the sorption experiment. The reaction vessels were covered with aluminium foil to minimize photochemical reactions and were only wrists shaken up and down up to 10 times at the beginning and left to equilibrate for 24 hours without further shaking.

2.5 Synchrotron Based XAFS Spectra Collection and Reduction

Bulk U L3 (17.175 keV) and As K-edge (11.867 keV) X-ray absorption fine structure (XAFS) spectra of selected solid samples of abiotic (Fe^0-

0.1mM U and Fe^0-0.1mM U-0.1mM As) and biotic (Fe^0-0.1mM U- 0.1 mM As-S. putrefaciens) batch sorption experiments were recorded at the INE-Beamline for Actinide Research with radiation from the bending magnet port 3.5-2 of the ANKA synchrotron storage ring operating at 2.5 GeV with current intensity spanning 85 and 180 mA. For the bulk U L3-edge XAFS measurements, the Lemonnier type double crystal X-ray monochromator (DCM) equipped with a set of Ge(422) crystals was used with the second crystal detuned to 60% of the maximum intensity. Samples filled into Eppendorf vials and sealed in polyethylene bags were positioned with a goniometer (Huber Diffraktionstechnik, Germany) with respect to the focused beam of 1mm diameter. Full XAFS spectra were recorded in fluorescence mode at ambient temperature (~ 23 C) using 5 pixel low energy fluorescence germanium solid state detector (Canberra). Nine XAFS scans were recorded and later averaged for each sorption sample to increase the signal-to-noise ratio. Schoepite was used as calibration reference for the U-L3-edge excitation energy.

Bulk As K-edge XAFS spectra were collected with the same experimental set up as for U L3-edge XAFS spectra but with the second DCM crystal detuned to 70% of the maximum photon intensity. As K-edge XANES spectra scans of reference compounds comprising arsenic metal foil [As(0)] and powder samples of $As[III]_2O_3$, and $As[V]_2O_5$ were recorded in transmission mode using argon filled ionization chambers. The XANES spectra presented herein for all sorption experiment samples were isolated from the complete XAFS spectra. They were background subtracted and normalized using the Athena XAFS analysis package routines (RAVEL & NEWVILLE 2005). Thus, the uranium spectra were calibrated and aligned with respect to the first inflection point of the first derivative of the schoepite spectrum while arsenic spectra were similarly calibrated with respect to As(0).

3 Results and Discussion

3.1 Initial Aqueous Uranium and Arsenic Speciation

The initial speciation of the aqueous uranium and arsenic from the reacting sorption solution was calculated using the geochemical code PHREEQC (PARKHURST & APPELO 1999) with its embedded Lawrence Livermore National Laboratory (LLNL) thermodynamic database supplemented with the following uranyl-arsenate complexes formation constants given by RUTSCH *et al.* (1997):

$UO_2^{+2} + HAsO_4^{-2} = UO_2(HAsO_4)$ log_*K* 18.76

$UO_2^{+2} + H_2AsO_4^{-} = UO_2H_2AsO_4^{+}$ log_*K* 21.96

$UO_2^{+2} + 2H_2AsO_4^{-} = UO_2(H_2AsO_4)_2$ log_*K* 41.53

Assuming the thermodynamic database used in the simulation is reliable, we speculate that the speciation of the initial mono-component uranium solution in the system Fe^0-0.1mM U was most likely dominated by the aqua cation uranyl UO_2^{2+} by more than 77 % followed in decreasing order of importance by the hydroxylized species

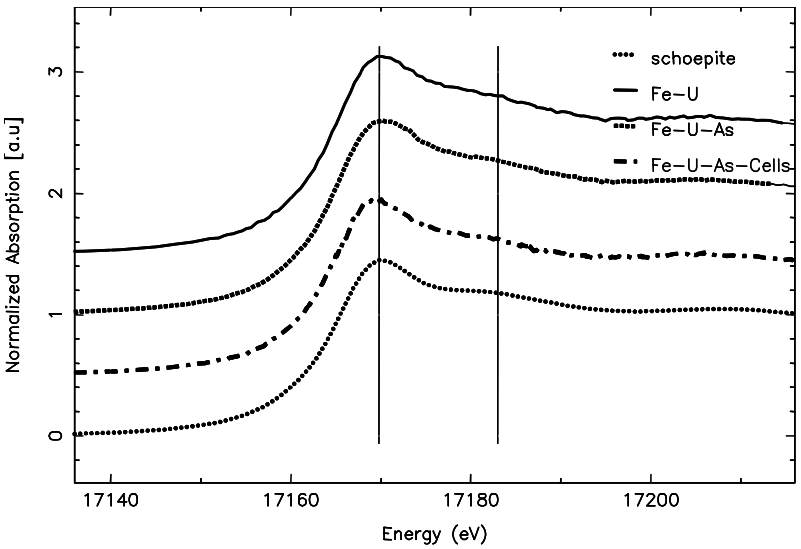

Figure 1: Normalized U L3- edge XANES spectra of the experimental samples Fe-U, Fe-U-As and Fe-U-As-bacteria cells compared to schoepite spectrum.

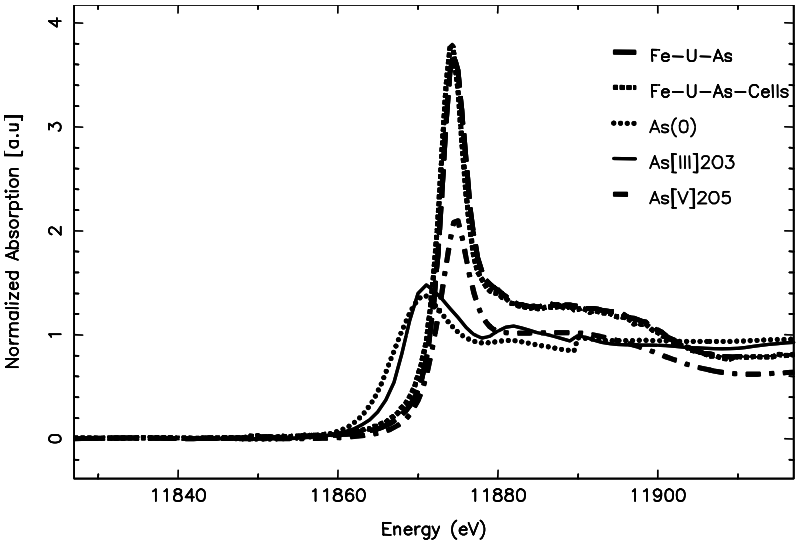

Figure 2: Normalized As K-edge XANES spectra of the samples Fe-U-As and Fe-U-As-Shewanella putrefaciens cells compared to the spectra of the reference compounds [As(0)], $As[III]_2O_3$ and $As[V]_2O_5$.

UO_2OH^+, $(UO_2)_2(OH)_2^{2+}$ $UO_2(OH)_2$ and the uranyl-nitrate $UO_2NO_3^+$. Similarly, the initial speciation of U(VI) in the bi-component uranium-arsenic water used in both the abiotic and biotic systems Fe^0-0.1mM U-0.1mM As seems to have been largely dominated by uranyl-arsenate complexes $UO_2H_2AsO_4^+$ and $UO_2(H_2AsO_4)_2$ followed by the aqua cation uranyl UO_2^{2+}, uranium hydrolyzed species UO_2OH^+ and $UO_2(OH)_2$ and the nitrate $UO_2NO_3^+$. Within this system, arsenic species comprises major and similar uranyl-arsenate species including but not limited to $UO_2H_2AsO_4^+$, $UO_2(H_2AsO_4)_2$, $UO_2(HAsO_4)$, minor arsenate species $H_2AsO_4^-$, $HAsO_4^{2-}$, H_3AsO_4 and AsO_4^{3-} In the biotic system, however, the addition of ethanol has likely resulted in the formation of minor but highly mobile uranyl carbonato complexes.

3.2 Sorbed Uranium Oxidation State

The normalized U L3-edge XANES spectra of samples from the experimental systems Fe-U, Fe-U-As and Fe-U-As-Shewanella putrefaciens cells are presented in figure 1 and compared to the schoepite spectrum.

The shapes and edge positions of the normalized U L3-edge XANES spectra for all three samples are identical. The energy position of the white lines is typical for U(VI) compounds. As pointed out by DENAUWER *et al.* (2003) and DENECKE *et al.* (2005), qualitative characterization of actinides L3-edge oxidation states based on the white line position and intensity alone is not straightforward owing to just minor differences in the dominating white line caused by the 2p→6d transition. Instead multiple scattering features in the XANES regime can be of much value in characterizing actinide cations. In this particular case, a shoulder at the higher energy side of the white lines in all spectra shown in figure 1 (indicated by the line at 17183 eV) is commonly attributed to multiple scattering of the outgoing photoelectron wave at the two shorter bound axial oxygen atoms in a uranyl compound.

3.3 Sorbed Arsenic Oxidation State

Figure 2 shows the normalized As-K edge XANES spectra while figure 3 illustrates the corresponding first derivative of the systems Fe-U-As and Fe-U-As-Shewanella putrefaciens cells compared to reference compounds [As(0)], $As[III]_2O_3$ and $As[V]_2O_5$.

The reference spectra show a systematic shift of the edge position with increasing valence state. Hence, we hypothesize that the sorbed arsenic coordination environment contains oxygen bonding. The edge position and the shape of the spectra of the samples Fe-U-As and Fe-U-As-Shewanella putrefaciens cells fit well those of $As[V]_2O_5$ clearly indicating a valence state of V.

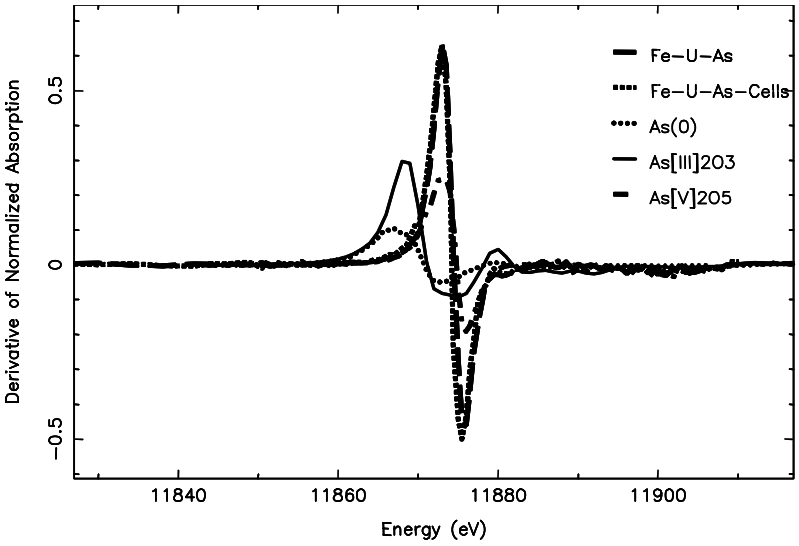

Figure 3: First derivative of the normalized As K- edge XANES spectra of the samples Fe-U-As and Fe-U-As-Shewanella putrefaciens cells compared to the reference compounds [As(0)], $As[III]_2O_3$ and $As[V]_2O_5$.

3.4 Implications of Sorbed Uranium and Arsenic Oxidation States on the Sorption Mechanism

The persistence of the initial uranium and arsenic oxidation states (VI and V respectively) the three reactive systems Fe-U, Fe-U-As and Fe-U-As-bacteria cells may help explaining the mechanism controlling uranium and arsenic fixation onto scrap metallic iron under this study experimental conditions.

The oxidation state VI in case of uranium sorbed onto metallic iron and corrosion products in the system Fe-U with uranium likely linearly linked to oxygen as suggested by the multiple scattering features in the corresponding XANES spectrum rather excludes the prevalence of a primarily reductive sorption mechanism through neither Fe(0) nor the structural Fe(II) or even molecular hydrogen (H_2) as byproducts of iron corrosion as electron donors. Through discrimination, it follows that uranium may have been fixed onto elemental iron through either surface complexation or most likely precipitation/co-precipitation with iron corrosion products enhanced by arsenic if present. This process results in the possible formation of sparingly soluble new mineral phases as the most prevalent mechanism or the combination of both mechanisms. This interpretation which reflects macroscopic experimental observations (MBUDI *et al.* 2007) is expandable to the system Fe-U-As as well as to the anoxic and biotic system Fe-U-As-Bacteria cells.

Furthermore, it may be understandable that the quite short hydratation time of 6 hours and the relative short equilibration time of 24 hours may not have lead to sustainable anoxic conditions prone uranium or arsenic reduction in the systems Fe-U and Fe-U-As. However, the apparent failure of both scrap metallic iron and the facultative Shewanella putrefaciens to reduce uranium or/and arsenic enzymatically needs to be explained.

As reported by ABDELOUAS (1998), some authors have claimed that the microbially mediated reduction of uranium is enzymatically catalyzed regardless of the experimental conditions. In fact, as aforementioned the experiment in the Fe-U-As-Bacteria system was carried out under no growth conditions while using reagents that may be potential inhibitors of uranium dissimilatory reduction such as ethanol as organic carbon source, nitrate as background electrolyte, high concentration of arsenic and possible competition for electrons between Fe(III), U(VI) and As(V) .While common electron donors coupled with Fe(III) reduction by S. putrefaciens include H_2, formate, acetate, and lactate but not ethanol, ABDELOUAS *et al.* (1998) reported the use of ethanol as carbon source that lead to the enzymatic reduction of U(VI) to U(IV) at the highest rate compared to acetate, methanol, glucose and lactate. Worth mentioning in this case is that according to the following reaction, anaerobic corrosion of metallic iron produces molecular hydrogen and Fe(II) which could alternatively have been used to reduce uranium:

$$Fe(0) + 2H^+ \Rightarrow H_2 + Fe^{2+}$$

A second potential inhibitor which might have been active is nitrate NO_3^- dissociated from the 0.01M $NaNO_3$ background electrolyte. This possibility of nitrate inhibition is consistent with COOPER *et al.* (2003) who observed that NO_3^- severely inhibited the reduction of Fe(III) contained in goethite by Shewanella Putrefaciens. Their results indicated that in fact the concurrent bacterial mediated reduction of Fe(III) and NO_3^- to respectively Fe(II) and NO_2^- which is followed by an abiotically reduction of NO_2^- to NO_2 and the oxidation of Fe(II) to Fe(III). The concomitant presence of Fe(III) and U(VI) may in turn lead to competing reactions and hence inhibition when ideal Eh and pH conditions are not met for uranium reduction. The above mentioned potential inhibition conditions fused with the quite high arsenic concentration in the reaction vessel may be the main cause of the metabolic inhibition of the dissimilatory reduction kinetics rate of both uranium and arsenic. In addition, it can be inferred from MYERS & MYERS (1992) that although perfectly facultative microorganism, growing Shewanella putrefaciens under aerobic conditions of this study may have lead to limited production of the necessary amount of cytochromes in the outer cell membranes for higher Fe(III) reductase activity.

4 Conclusion

This study has shown that under its experimental conditions both uranium and arsenic sorbed onto elemental iron in abiotic or biotic and anoxic conditions may have been fixed through precipitation/co-precipitation as predominant mechanism while maintaining the initial oxidation states of respectively U(VI) and As(V). While XANES fingerprinting has been valuable in the determination of the absorbing atoms oxidation states, EXAFS modeling is required to fully uncover the coordination chemistry of the sorbed uranium and arsenic and hence assess the relevance of surface complexation mechanism in order to draw definitive conclusions. A conjunction of inhibition conditions that include the presence of nitrate, possible limited cytochromes Fe(III) reductases, both arsenic and uranium toxicity may have lead to reduced kinetic rates of the expected dissimilatory uranium and arsenic reduction. Future similar sorption studies should be conducted at an appropriate actinides dedicated laboratory in situ at the synchrotron facilities location in order to minimize the possibility of redox reactions between sampling and the actual XAFS spectra collection.

5 Acknowledgements

This work was supported by the European Community – Research Infrastructure Action under the FP6: Structuring the European Research Area (Integrating Activity on Synchrotron and Free Laser Science (IA-SFS) RII3-CT-2004-506008.

We thank the Forshungszentrum Karlsruhe's Institut für Synchrotronstrahlung for providing the Beamtime and the Institut für Nukleare Entsorgung for providing the necessary technical support from the inception of this project.

The first author extends his gratitude to the European Network of Excellence for Actinide Sciences, the European Commission Cost Action 629 and the TU Bergakademie PHD Program in Environment, Material science, Technology and Management for their financial assistance to cover the travel and living expenses related to this project and subsequent training.

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