ELSEVIER

Journal of Alloys and Compounds 223 (1995) 274–279

Journal of ALLOYS AND COMPOUNDS

Synchrotron X-ray absorption spectroscopy: a new tool for actinide and lanthanide speciation in solids and solution

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Abstract

Synchrotron-based X-ray absorption near-edge structure spectroscopy and extended X-ray absorption fine structure spectroscopy are powerful techniques to study many chemical elements in solids, liquids and gases. Information can be obtained on the speciation and complexation of lanthanide and actinide elements and other radionuclides in aqueous and non-aqueous solutions, on adsorption processes at the solid–water interface of these solutions with soils, minerals, mineral assemblies and uranium mill tailings, and on the adsorption and incorporation of these metals in biological materials. A literature review on synchrotron studies of these processes is given. The conceptual design of an experimental hard X-ray synchrotron beam line end station for the investigation of radioactive samples is described.

Keywords: Actinides; Lanthanides; X-ray absorption spectroscopy

1. Radiochemical X-ray adsorption spectroscopy studies

A basic molecular-level understanding is required to describe quantitatively the mechanisms of radionuclide transport in the environment. This microscopic information is used together with chemical–mathematical models to obtain macroscopic transport predictions.

Many different methods are necessary to provide the microscopic information that is mandatory for making macroscopic predictions. In addition to conventional techniques such as resonance (nuclear magnetic resonance, electron spin resonance) and optical spectroscopies (IR, UV–visible), electron microscopy and analytical chemistry, modern highly sensitive methods are needed. They are either laser-based methods (photoacoustic spectroscopy, thermal lensing spectroscopy, time-resolved fluorescence spectroscopy) or synchrotron-based X-ray absorption spectroscopy (XAS).

XAS is a powerful technique to study many chemical elements in solids, liquids and gases. Because of the high intensity of the synchrotron radiation used, lower concentration levels can be reached than with most conventional methods. This is important for real environmental samples where concentrations may be in the milli- and micromolar range, or even lower. XAS is an element-specific method. It provides information about the oxidation state and the coordination and bond length to first, second and even third shell neighbour atoms of a metal absorber. XAS can provide information on the speciation of lanthanides and actinides and other radioactive and non-radioactive heavy metals and of speciation changes that result from changes of their chemical environment. This knowledge is essential to study the interaction of actinides such as uranium, thorium, neptunium, plutonium and americium, and other environmentally important radionuclides such as zirconium, radium, strontium, caesium and technetium with soils, minerals and mineral assemblies. The lanthanides can serve as valuable model systems for some of the homologous trivalent actinides. It is emphasized, however, that working with the non-radioactive lanthanides cannot replace experiments with radioactive actinides. For example, there is no substitute system for investigations of plutonium in environmental solutions at near-neutral pH where four oxidation states can coexist.

The energies for the X-ray absorption edges between approximately 5 and 35 keV that are suitable for XAS using a conventional double-crystal monochromator are given in Tables 1, 2 and 3 for lanthanides, actinides and selected other radionuclides respectively. Table 1 shows that for the lanthanides up to atomic number 66 only the L_I edge can be used for extended X-ray absorption fine structure (EXAFS) measurements because the energy separations between the L_{II} edge and

Elsevier Science S.A.
SSDI 0925-8388(94)09014-9

Table 1
Binding energy E, edge jump $\Delta\mu$ and fluorescence yield ω of the L_I and L_{III} edges of the lanthanide elements (L_{II}–L_{III} and L_{II}–L_I are the energy separations between the L_{II} edge and the L_{III} and L_I edges respectively [1,2])

Z	Symbol	L_{II}–L_{III} (eV)	L_{II}–L_I (eV)	L_{III} edge E (eV)	L_I edge E (eV)	Edge jump $\Delta\mu$ (cm^2 g^{-1})	Fluorescence yield ω_{LX}
58	Ce	441	384		6548	112	0.058
59	Pr	476	395		6835	105	0.061
60	Nd	514	404		7126	99	0.064
61	Pm	554	415		7428	93	0.066
62	Sm	596	425		7737	87	0.071
63	Eu	640	435		8052	82	0.075
64	Gd	687	446		8376	76	0.079
65	Tb	738	456		8708	72	0.083
66	Dy	791	465		9046	67	0.089
67	Ho	847	476	8071		216	0.182
68	Er	906	487	8358		205	0.192
69	Tm	969	499	8648		196	0.201
70	Yb	1034	508	8944		185	0.210
71	Lu	1105	521	9244		177	0.220

Table 2
Binding energy E, edge jump $\Delta\mu$ and fluorescence yield ω of the L_{III} edge of the actinide elements (L_{II}–L_{III} is the energy separation between the L_{III} and L_{II} edges [1,2])

Z	Symbol	L_{III} edge E (eV)	L_{II}–L_{III} (eV)	Edge jump $\Delta\mu$ (cm^2 g^{-1})	Fluorescence yield ω_{LIII}
90	Th	16300	3393	64.8	0.463
91	Pa	16733	3581	63.7	0.476
92	U	17166	3782	58.4	0.489
93	Np	17606	3990	59.4	0.502
94	Pu	18053	4205	56.6	0.514
95	Am	18504			0.526

Table 3
Binding energy E, edge jump $\Delta\mu$ and fluorescence yield ω for the K and L_{III} edges of selected radionuclides (for Bi, Po and Ra, the energy separation L_{II}–L_{III} between the L_{III} and L_{II} edges is given [1,2])

Z	Symbol	Energy E (eV)	L_{II}–L_{III} (eV)	Edge jump $\Delta\mu$ (cm^2 g^{-1})	Fluorescence yield ω_x
38	Sr	16 105, K		99.1	0.690
40	Zr	17 998, K		80.9	0.730
43	Tc	21 004, K		66.5	0.780
55	Cs	35 985, K		28.4	0.897
83	Bi	13 419, L_{III}	2292	88.3	0.373
84	Po	13 814, L_{III}	2430	85.3	0.386
88	Ra	15 444, L_{III}	3040	68.9	0.437

the L_{III} or L_I edges are too small for L_{III} or L_{II} edge EXAFS spectroscopy respectively. From atomic numbers 67–71, this separation is sufficient to allow the use of the L_{III} edge. Compared with the L_I edge, the L_{III} edge is much more favourable because of its much larger absorption and fluorescence yields. Table 2 shows that for the actinides the L_{II}–L_{III} edge energy separation is more than 3000 eV, and therefore, the L_{III} edge can be used for EXAFS spectroscopy. Because of the substantially better fluorescence yield of the actinides compared with the lanthanides, the actinides can be measured in fluorescence mode, thus giving a higher sensitivity than the lanthanides. Table 3 shows the energies for strontium, zirconium, technetium and caesium where the K edge can be utilized for XAS measurements. Also listed are the usable energies of the L_{III} edge for bismuth, polonium and radium. The absorption edges of the elements listed have good fluorescence yield and therefore low sensitivities should be attainable.

Synchrotron-based X-ray absorption near-edge structure (XANES) spectroscopy and EXAFS spectroscopy can be applied for the following research areas:

- speciation and complexation studies of radionuclides in aqueous and non-aqueous solutions pertinent to environmental contamination, pollution risk assessment and remediation strategies;
- adsorption processes at the solid–water interface of radionuclide solutions with soils, minerals, mineral assemblies and uranium mill tailings;
- adsorption and incorporation of radionuclides in biological materials in support of bioinorganic chemistry and bioremediation technologies.

2. Speciation and complexation studies

Speciation describes the chemical state of radionuclides in solutions and solids. It discriminates between the individual radionuclides and provides information on their oxidation state, stoichiometry and structure of ions and dissolved complexes. Radionuclide speciation depends on a variety of factors such as temperature, pH, redox conditions, the ionic strength, initial radionuclide oxidation state and the presence, nature and concentration of complexing inorganic and organic ligands. Exact knowledge of radionuclide speciation is essential and primarily necessary to understand the interaction of soluble radionuclide with the geomedium along their transport path. Different species can have substantially different charges and will exhibit very different adsorption behaviours when they come in contact with soil, rock and mineral surfaces.

EXAFS on solutions can provide microscopic-level structural information of ligands surrounding a central radionuclide ion. Model systems must be used for supporting the structural data in unknown contaminant systems.

It is planned to establish a data base of model systems for the complexation of radionuclides (e.g. UO_2^{2+}, U^{4+}, Th^{4+}, PuO_2^{2+}, PuO_2^{+}, Pu^{4+}, NpO_2^{2+}, NpO_2^{+}, Bi^{2+}, Pb^{2+}) with natural and anthropogenic inorganic ligands (CO_3^{2-}, SO_4^{2-}, PO_4^{3-}), anthropogenic organic ligands (e.g. polycarboxylic acids: NTA, EDTA, DTPA) and natural dissolved organic materials (humic and fulvic acids). Structural information of these systems, if available at all, is largely obtained by comparison of data from indirect measurements, such as pH titration or spectrophotometry, with thermodynamic models that are often based on structural information derived from solid state samples.

For example, UO_2^{2+}, PuO_2^{2+}, or Th^{4+} in carbonate-containing solutions can form monomeric, dimeric and polynuclear carbonate or mixed hydroxide–carbonate complexes [3,4]. Such polynuclear complexes can exist in solution as colloids that may have very different sorption properties than the ionic complex. Colloidal transport provides, in addition to ionic transport, a second mode for radionuclide migration in solution. Particularly in environmental solutions, Pu^{4+} seems to be present as colloid in the absence of strong complexing agents [5,6]. Strong complexing agents such as NTA were shown to depolymerize colloidal plutonium via reduction and complexation [7,8]. Furthermore, PuO_2^{2+} and PuO_2^{+} can be reduced to Pu^{4+} and complexed by NTA. XANES and EXAFS will enable us to follow these processes in situ and to monitor the expected changes in the oxidation state and the coordination sphere of the radionuclide.

3. Adsorption processes at the solid–water interface

The sorption of a dissolved radionuclide describes its distribution between the aqueous or organic phase and the surface of a solid that it is in contact with. Depending on the bonding of the radionuclide to the solid phase, one can distinguish between surface precipitation, adsorption and absorption. Surface precipitation is characterized by the formation of mostly amorphous three-dimensional radionuclide precipitates at several non-linked centres at the surface. Adsorption describes a two-dimensional enrichment of the radionuclide on the solid–solution interface without the formation of a three-dimensional layer. Absorption describes the formation of a chemical reaction of the radionuclide with the solid's surface. This can occur by surface complexation or ion exchange reaction. Also, re-precipitation reactions are possible involving the reaction of the radionuclide together with dissolved material of the solid to form an insoluble compound that precipitates on the solid's surface.

Sorption of a radionuclide to soils and geologic materials can provide a limiting mechanism for the distribution of radionuclides to the environment. There are many studies that have determined the sorption behaviour of radioelements by determining the distribution coefficient K_D between a defined solid and a solution. Such experiments can supply certain qualitative measures about the retaining capability of the solid for the particular radioelement. However, they do not significantly contribute to an improved mechanistic understanding of the sorption phenomena.

XAS is very well suited to provide a molecular-level mechanistic understanding of radionuclide sorption on solid matrices. It was established by Brown and coworkers as a viable technique that can provide molecular-level information of metal ion sorption at mineral–water interfaces [9–14]. For example, the EXAFS study of adsorbed selenate and selenite ions on α-FeOOH (goethite) has shown that selenate forms a bidentate inner sphere complex, whereas selenite forms an outer sphere complex. It was shown also that selenate is strongly and selenite is only weakly bound at the α-FeOOH–water interface. EXAFS investigations of Co(II) on different oxide surfaces have shown that Co(II) polymerizes on the oxide surface and that the degree of polymerization depends on the surface's structure. These differences were observed by comparing the sorption behaviour on TiO_2 (rutile), γ-Al_2O_3 and $Al_2Si_2O_5(OH)_4$ (kaolinite). Lead(II), however, was shown to form only unidentate complexes with γ-Al_2O_3. Brown and coworkers postulate from their results that cations that hydrolyse and polymerize easily in solution may do this preferentially at oxide surfaces too. It would be of great interest if this also applies to actinide and radionuclide mineral–water interface systems.

To date, there are few XAS investigations using radionuclides. Kaindl and others investigated solid uranium and neptunium compounds such as UO_2, UO_3, UF_4, α-U, NpI_3, NpO_2, Na_2NpO_2 and Ba_2CoNpO_6 [15–17]. Recently, uranium solution sorption studies on montmorillonite clay were reported by Combes et al. [18] and by Dent et al. [19]. Combes et al. report

EXAFS measurements investigating the sorption behaviour of dissolved NpO_2^+ on α-FeOOH (goethite).

It is planned to establish a data base for the sorption of radionuclides (as listed above) on solids, soils, minerals and mineral assemblies that are found at and near (1) uranium mines and ore processing facilities in German Saxony and Thuringia, and the Czech Republic, (2) contaminated land surface areas in Russia and the Ukraine and (3) potential low-level and high-level nuclear waste repositories.

XANES and EXAFS are the methods of choice to establish resonance and energy shifts to identify sorption sites and oxidation state changes, as well as information on the coordination environment and bond lengths of the radionuclide. Additionally, the focused, highly brilliant beam provides the ability to resolve spatially microstructures of inhomogeneous samples.

This structural information will be used as input to existing adsorption models to obtain macroscopic predictions on the transport of the contamination [20,21]. If necessary, the models will be improved using the new information at hand.

4. Adsorption and incorporation of radionuclides on biological material

We are investigating biomolecules and their structural derivatives for the accumulation of naturally occurring and artificial radionuclides and long-lived fission products. Several types of metal-ion-chelating biomolecules in the form of proteins, peptides and ribonucleopolypeptides have been isolated from mammalian cells, plants and microorganisms. Their special characteristics are high interaction constants and a remarkable accumulation capability of up to 18 mol mol^{-1} for heavy metal ions. Ultimately, the biosorbents are to be used in bioreactors for removal of radionuclide contaminants from waste and seepage waters of flooded uranium mines and mill tailings, to name only a few applications.

XAS is a unique tool for providing in situ structural information for the radionuclide interaction with the biosubstrate. In particular, the unique capability of this method for determining possible valency changes of multioxidation state radionuclides (such as actinide elements) during the bioaccumulation process can provide valuable mechanistic information. This information is essential for selecting and optimizing the biomolecular systems.

For example, Dodge et al. used XAS for the investigation of uranium oxidation states in anaerobic bacteria that are currently employed for bioremediation purposes [22]. The study indicates that U^{3+} may be incorporated within the microbes in addition to the expected U^{4+} oxidation state.

5. X-ray absorption spectroscopy results

Representative results are XANES investigations to evaluate the efficacy of two unique chemical processes to devise remediation strategies for the environmental contaminants Se and Tc; the suitability of incorporating a reducing agent in pertechnetate (TcO_4^-)-containing cementious waste matrices in order to immobilize Tc and the bioremediation of Se by bacteria [23]. The XAS measurements were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) wiggler branch beam line 4.1 utilizing an Si(220) monochromator at the K edges of Tc (21.0 keV) and Se (12.6 keV).

The Se study was performed in conjunction with an ongoing bioremediation research project on the biological uptake of Se by the common soil bacterium *Bacillus subtilis* in order to determine Se valency changes related to the uptake. *B. subtilis* is known to incorporate Se somewhere within the cell membrane and the microbes are exposed to either an Se(IV) or an Se(VI) solution. The Se XANES spectra of two strains B and K, clearly proved that the bacteria selectively incorporate Se from the Se(IV) solution and reduce the Se(IV) to Se metal, as shown from the near-edge shifts.

More recently, the efficacy of a proposed waste treatment process in which technetium, present primarily at pertechnetate, is reduced to an immobile and insoluble Tc compound by FeS added to the cement waste form matrix has been evaluated in collaboration with S. Clark of the Savannah River Ecology Laboratory in the USA. These XANES measurements from the treated cement, untreated cement and reference compounds exhibited a pre-edge feature arising from a symmetry-allowed transition from the pertechnetate anion present in both cements, thereby indicating that reduction of Tc by FeS has not taken place. TcO_4^-, TcO_2 and Tc metal were used as reference compounds. From the Tc K EXAFS of TcO_2 the first direct crystal structure parameters were determined. They show that TcO_2 has a rutile structure.

These two investigations have yielded valuable information on relevant systems that will help to understand further the redox processes involved in bacterial uptake of Se and help design better chemical processes for Tc immobilization.

6. The proposed beam line at European Synchrotron Radiation Facility and layout of an end station for X-ray absorption spectroscopy with radioactive materials

The proposed beam line at the European Synchrotron Radiation Facility (ESRF) at Grenoble, France, will be installed at the high-field section of the bending magnet. The double-crystal monochromator system will

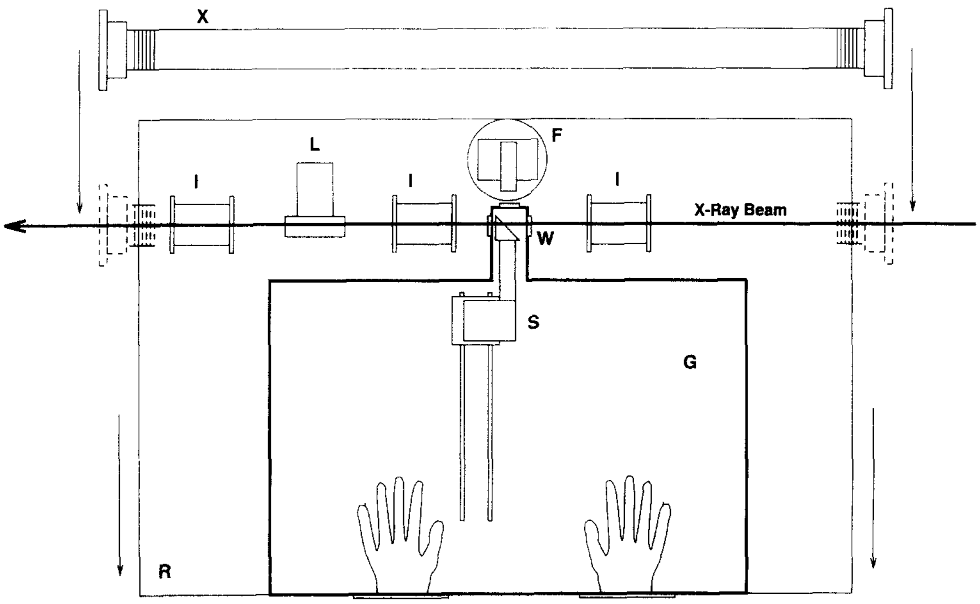

Fig. 1. Layout of the experimental station: F, multielement fluorescence detector; G, glove-box; I, ionization chamber; L, Lytle fluorescence detector; R, table on rail system; S, sample-positioning system; W, beryllium windows; X, X-ray beam tube.

have a usable energy range of about 5–35 keV, with an energy resolution of 0.01%. An unfocussed and a focused beam are planned with an intensity of approximately 10^{13} photons s^{-1} and $0.1\ bw^{-1}$ and a dimension of $1\times1\ cm^2$ and $0.1\times0.1\ mm^2$ respectively.

The end station for XAS measurements on radioactive samples requires a special design to satisfy the radiation protection requirements at ESRF. The radioactive samples that will be measured contain only relatively small amounts of radioactivity and therefore will generate a very weak exterior radiation field at best. Because of the α activity and the potential heavy metal toxicity in case of ingestion, the samples must be handled in a special containment.

This containment can be a simple plastic enclosure for some samples or a sophisticated glove-box for other samples. The glove-box is operated under slightly negative pressure with a double high-efficiency filter system on the vented side. There is the possibility that the regulations may demand a double containment. This redundancy will guarantee that, in the unlikely event of failure of one containment, the radioactive sample is still safely contained in the other. Such a double-containment system can be a plastic-sealed sample in a negative-pressure glove-box, or a negative-pressure glove-box in a slightly negative-pressure room. This containment technology is common worldwide for laboratories working with radioactive α samples. The Institute Laue Langevin (ILL) at Grenoble, France, has such a facility on site. It will be used for receiving, handling, and final preparation of samples that are being shipped from Forschungszentrum Rossendorf to Grenoble. Handling of samples at the ESRF would be kept to a minimum. It is preferable, however, to have the possibility of handling some samples within the glove-box, e.g. for applying an electrical potential to a solution in order to follow the in situ change of solution species etc.

For relatively concentrated samples, standard XAS equipment for transmission measurements will be used. Fig. 1 shows the layout of the experimental station. It consists of three ionization chambers mounted on an optical rail and a remote-controlled sample positioning system. More dilute samples will be measured in fluorescence mode using Stern–Heald type gas ionization chambers (Lytle detectors) or multielement solid state detector systems. The detectors can be mounted outside and only the sample-positioning system must be positioned inside the glove-box. The glove-box itself is mounted on a precision rail system, so that it can be moved in and out of the beam. When the glove-box is moved out of the beam, measurements can be carried out with non-radioactive samples.

The beam and the detectors are connected to the glove-box via transmissive windows of beryllium or any other suitable material. The two windows for the beam are located in the side walls of the glove-box. The structural integrity of the windows in the glove-box is very important. The exit side of the glove-box can be equipped with either a beam stop or an exit window that is connected to a beam tube leading to a beam stop further away from the box. This depends on the amount of scattered light and radiation that will be produced by the interaction of the beam with the beam stop inside the glove-box.

The windows can have an additional renewable protection against possible low-level contamination from inside the glove-box such as a Mylar foil that can be exchanged if the window becomes contaminated. A contaminated window may influence the fluorescence detection because the detector may also respond to the radiation of the contamination.

Acknowledgements

I would like to thank D. Shuh, J. Bucher and N. Edelstein of the Lawrence Berkeley Laboratory, Berkeley, CA, USA, for starting this research jointly with me at the SSRL and for their continued collaboration. Thanks are due to SSRL for providing beam time at beam line 4-1, and to R. Frahm of the Deutsches Elektronen-Synchrotron (DESY), Hamburger Synchrotron strahlungslabor (HASYLAB) for his advice and the use of beam line ROEMO II. I am also indebted to my team at the Forschungszentrum Rossendorf that has created the conceptual design of this proposed beam line.

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