



Ulla Vuorinen & Torbjörn Carlsson

XAS methods in understanding chemical processes relevant to nuclear waste disposal

A literature review

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Keywords nuclear waste management, repositories, X-ray absorption spectroscopy, elements, radionuclides, migration, chemistry, sorption, precipitation, kinetics

Abstract

A limited literature survey is presented. The purpose is not to explore all the possibilities of the technique of X-ray Absorption Spectroscopy (XAS) methods but to illustrate, with a few examples, the contribution it can make to understanding element speciation and chemical processes involved in the radionuclide migration in the environment. The emphasis is research related to radionuclide behaviour in the context of safe disposal of nuclear waste.

The report contains suggestions for the application of XAS methods to chemical systems relevant to Finnish repository conditions. Appropriate experiments are briefly outlined.

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Tiivistelmä

Tämä suppea kirjallisuustutkimus esittelee lyhyesti XAS-tekniikoita (X-ray Absorption Spectroscopy) ja vain muutamien esimerkkien avulla niiden mahdollisuuksia arvioitaessa radionuklidien kulkeutumista ympäristössä. Kulkeutumisen kannalta on oleellista tuntea tutkittavan radionuklidin osalaji (spesiaatio) ja sen osallistuminen erilaisiin kemiallisiin prosesseihin. Tutkimusesimerkit liittyvät ydinjätteen turvalliseen loppusijoitukseen tähtääviin tutkimuksiin. Raportin lopussa on ehdotus XAS-tekniikan soveltamisesta suomalaisia loppusijoitus olosuhteita vastaaviin tutkimuksiin.

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1. Introduction

X-ray Absorption Spectroscopy (XAS) is a powerful, element-specific in-situ technique that can be used to determine the local structure (bond distance, number and type of near neighbours) around a sorbing element, even when the element is present at low concentration (depending on element and matrix as low as = 0.03 to 0.05% by weight (Charlet and Manceau 1993). In most cases XAS studies are limited to elements heavier than Sc, (i.e. elements with $Z > 21$). For many first row transition elements, XAS studies yield information about the site geometry of an absorber, which is commonly related to the oxidation state.

The purpose of this brief literature survey is not to explore all the possibilities of XAS methods, but to illustrate, with some examples, the contribution that XAS can make to understanding element speciation and chemical processes involved in radionuclide migration in the environment. The emphasis is research related to radionuclide behaviour in the context of safe disposal of nuclear waste. There is, nevertheless, a broader reference to many other areas where understanding of element speciation is important.

In the field of nuclear waste disposal studies, knowledge of radioactive elements released from the wastes and their possible migration to the human accessible environment is of key importance. Without understanding the fundamental physical and chemical behaviour of the key radionuclides in nuclear waste, the evaluation of radionuclide parameters needed in performance assessments can never be satisfactory. The most important factor influencing the physical and chemical behaviour of an element in the environment is speciation, which also determines its bioavailability. The oxidation state of an element is essential to speciation and the relative stabilities of the various oxidation state species are significantly affected by solution conditions (e.g., pH, Eh, ionic strength, complexing agents, redox reagents).

The need to understand element speciation and chemical processes (solubility, sorption, surface complexation, co-precipitation, etc.) has prompted research under simulated conditions in laboratories and in near in-situ conditions in underground facilities. A vast array of analytical methods have been used for studying chemical processes and speciation in solution, in solids, and at interfaces. However, there are few methods that allow in situ studies without prior sample preparation, separation or dissolution steps, thereby minimizing possible speciation changes. Such methods have either not been available or have not been sensitive enough.

With the advent of new XAS-methods, e.g., Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near-Edge Structure (XANES) spectroscopies, it has become possible to determine local structure around almost any atom. A serious

drawback of these methods is that the required synchrotron radiation can be produced only at synchrotron radiation facilities. These facilities represent a major capital investment. Since they require construction of a particle accelerator and a high-vacuum storage ring. In addition, expert personnel (scientists, engineers, and technicians from different disciplines) are required to run them. The number of facilities around the world is limited, and in the case of radioactive elements there are only a few beam lines available. One such beam line is the ROBL at the European Synchrotron Radiation Facility (ESRF) at Grenoble, France. This is one of the best facilities in the world, with a third generation source of great brilliance. Brilliance is a key characteristic of synchrotron radiation, which for a given energy is defined by the number of photons per second per mm^2 (source area) per mrad^2 (opening angle) and for an energy bandwidth equal to 0.1% of the energy under consideration. High brilliance is useful for studying samples that are extremely small or dilute and reactions that are very rapid.

2. XAS methods

The usefulness of the EXAFS technique may be readily understood by comparing it with diffraction methods. For crystalline materials with long-range ordering, their structures are generally determined by X-ray or neutron diffraction in which the measurements of the diffracted intensities yield a 3-D picture of atomic coordinates via a Fourier transformation. However, in studies of radionuclides such as nickel and its closest neighbours, in solutions or on solid surfaces, the nickel and its nearest neighbours exhibit only short-range order. In such cases, X-ray scattering experiments produce only 1-D radial distribution functions (RDF's) based on all the interatomic distances in the sample. EXAFS measurements, on the other hand, can provide structural information for each type of atom merely by tuning of the X-ray energy to coincide successively with an absorption edge of each type of atom in the sample. Information such as the number and kind of neighbouring atoms and their distances from the absorber are contained in the 1-D RDF.

It is clear that EXAFS is highly specific in that it can focus on the immediate environment around each absorbing species (generally out to about 6 Å, corresponding to 1–3 coordination shells). Other materials or impurities present in the sample, which either do not contain the absorber or are not directly bound to the absorber, will not interfere. The technique is highly versatile in that it can be applied with about the same degree of accuracy (0.01–0.03 Å) to matter in the solid (crystalline or amorphous), liquid, solution, and gaseous state (Teo and Joy 1981). Thus EXAFS spectroscopy is a powerful technique to characterise the structure of all forms of matter.

The two energy regions of X-ray Absorption Fine Structure (XAFS) spectra are usually referred to as EXAFS at higher energies and XANES at the lower energetic region. While EXAFS provides structural information XANES, which extends within 40 eV of the X-ray absorption edge, provides information on the chemical state and electronic properties. Recently Atomic X-ray Absorption Fine Structure (AXAFS) has been shown to form part of the total X-ray absorption spectrum. The study of AXAFS can provide valuable information about interatomic potentials (Koningsberger 1999).

EXAFS has been found to be a particularly promising tool for the identification of surface sorbed species. However, it is of limited sensitivity and is not applicable to trace concentrations. Therefore, complementary techniques having higher concentration sensitivities are needed alongside XAFS.

3. Examples of applications

X-ray absorption spectroscopy has proven to be particularly valuable in studies of sorption at the mineral-water interface. There are several reasons for this:

- 1) the absorber specificity allows study of a selected element in the presence of many elements
- 2) back-scattering atoms that differ in atomic number (Z) by more than 3 from that of the absorber atom can be distinguished and roughly identified, and their amount can be approximated,
- 3) inter-atomic distances can be determined very accurately (± 0.02 to 0.04 \AA for most back-scattering atoms)
- 4) it is a non vacuum technique (for adsorber $Z > 20$) usable at ambient temperatures and is therefore applicable to solutions and suspensions as well as solids, and
- 5) it is sensitive to relatively low concentrations of the absorbing atom.

There are many locations where XAS techniques are available (none of them in the Nordic countries, however) and a large number of widely varying applications are now appearing in the literature. OECD/NEA (1999) has published workshop proceedings containing a number of references on applications of XAS methods utilising radioactive substances. The following presents a few examples from other literature, which more or less, typify the kind of work suggested in this report.

3.1 Sorption/coprecipitation with calcite

Zavarin and Doner (1999) recently applied to the study of Ni-sorption and Ni-coprecipitation with calcite using EXAFS and XANES methods. The range of solution Ni concentrations was 5–100 ppm. Since XAS detection limits are high, approximately 50 ppm metal was required per sample; thus, all sorption samples were supersaturated with respect to $\text{Ni}(\text{OH})_2$. Coprecipitation samples were prepared using a pH-stat set-up run at 0.03% and 0.25% CO_2 with a sodium background electrolyte ($I=0.1$). In coprecipitation samples, solutions were always undersaturated with respect to all known Ni minerals. Zavarin and Doner (1999) stress that this does not eliminate the possibility of trace metal precipitation (surface precipitates have been shown to form when solution concentrations are below the solubility of the particular mineral), but it reduces the

likelihood. Zavarin and Doner (1999) collected EXAFS spectra for aqueous, sorbed, and coprecipitated Ni on calcite.

Significant change in the spectra as a function of time was not found for any sorption sample, which indicated that no significant restructuring occurred at the calcite surface during the data collection. The EXAFS and XANES spectra of the sorption samples differed significantly from the spectra of the aqueous Ni samples, which indicated inner sphere Ni sorption or formation of Ni precipitates. The EXAFS Fourier transform data for sorbed Ni contained a second neighbour feature at about 2.8 Å. This feature was much weaker than that of Ni(OH)₂, which indicates that simple Ni(OH)₂ formation did not occur. Zavarin and Doner (1999) conclude that the nickel-calcite interaction results in a Ni(OH)₂-like surface precipitate or a (Ni,Ca)CO₃ near-surface solid solution.

Although sorption EXAFS spectra were noisy, fits were attempted for all samples. In all cases, second neighbour fits were the same or better when fitting with Ni rather than Ca. This suggests that Ni multinuclear complexes were formed. Further discussion lead Zavarin and Doner (1999) to the tentative conclusion that Ni may occur as a surface precipitate that coats the calcite surface.

In the case of Ni-coprecipitation with calcite, Zavarin and Doner (1999) found that the Ni XAS data differed significantly from the corresponding data for Ni(OH)₂, aqueous Ni, or sorbed Ni. In their view, the coprecipitation data fits suggest that Ni substitutes directly for Ca in the calcite, which results in a distortion of the atom lattice positions to at least 5 Å.

3.2 Actinide sorption on cement

Ewart et al. (1990) investigated the mechanisms by which actinides sorb onto cementitious materials, the incorporation of actinides into the evolving structure of cement and the sorption of typical actinides onto several types of phases thought to be present in the long term structure of a cementitious repository.

More direct information about the sites of sorption of lanthanides, they thought, might be derived by EXAFS than X-ray diffraction study. An important advantage of EXAFS is that it can be applied equally well to crystalline and amorphous materials and if the X-rays are tuned to a fluorescent wavelength (e.g. in a synchrotron), atoms in low concentration (less than 1%) can be studied.

EXAFS spectra were recorded for La₂O₃ and LaCrO₃ as model compounds exhibiting typical coordination spheres in which La³⁺ ions are stable. In La₂O₃ the La³⁺ ion has three nearest neighbours oxygen atoms at 2.38 Å, one at 2.45 Å and three more at

2.72 Å. Similar RDF's were obtained for LaCrO₃ and La-containing test samples, which indicated that the environment of La is the same in the two cases.

The cement pastes selected for study were pastes generated in a candidate repository backfill BFS/OPC (blast furnace slag/ordinary Portland cement) and a range of calcium silicate hydrates and gels. Ewart et al. (1990) stress that cements are multi-phase. The chemistry is complex and that "there has been no adequate description of the chemical and physical processes that give rise to sorption on cement surfaces." Their results can therefore "only be interpreted by the simple mechanics of the surfaces".

EXAFS analysis was carried out on a hydrogarnet prepared with a lanthanum dopant. The sample was a reasonable analogue for the actinide-substituted cement phase of interest to Ewart et al. The analysis showed clearly that the lanthanum was seven coordinate in the hydrogarnet. EXAFS thus appears to be capable of providing a good deal of information about the coordination of ions incorporated in poorly crystalline phases. Moreover, the sensitivity is such that the analysis of much lower concentrations, such as the sorbed lanthanide, may be within reach.

Even though it was not possible fully to analyse hydrogarnet and similar compounds, because of their instability, clear evidence was found for the substitution of lanthanum for calcium in C-S-H. (C-S-H is the most significant hydration product in Portland cement. It has a variable composition which is normally expressed in terms of the CaO:SiO₂ ratio. Ewart et al. (1990) used the ratios 1.25:1, 1.5:1, and 1.7:1.)

The determination of the chemical state of the sorbed species, like the structural work, was done with use of the best available analytical tools. No XPS surface analytical method has been able to detect sorbed species, but the EXAFS technique has shown more promise: clear changes in the spectrum have been seen in the presence of relatively low concentrations of lanthanum in cement. It seems reasonable to believe that even lower levels, relevant to those of sorbed actinide, might be accessible to analysis by this method. At the present state of the science, however, it is not possible to determine the chemical state of actinides or lanthanide species sorbed onto cements (Ewart et al. 1990).

3.3 Sorption/desorption at soil mineral surfaces

Sorption and desorption are among the most important chemical processes in the environment. They determine, for example, the quantities of metals and radionuclides that are retained on various surfaces in the near-field and far-field of a repository. Experimental study of the sorption can, in principle, be done in two ways: by non-in-situ or in-situ methods (Johnston et al. 1993). The principal invasive non-in-situ techniques

for solid and aquatic systems are XPS (X-ray Photoelectron Spectroscopy), AES (Auger Electron Spectroscopy) and SIMS (Secondary Mass Spectroscopy). All three techniques yield detailed information about the structure of and bonding of minerals and the chemical species present on mineral surfaces. The disadvantage of the techniques is that they often must be performed under adverse experimental conditions, e.g., desiccation, high vacuum, heating, or particle bombardment. Such conditions may yield data that are misleading as a result of experimental artefacts (Scheidegger and Sparks 1996a, and refs. therein).

In-situ methods require little or no alteration of the samples from their natural state and they can be applied to aqueous solutions or suspensions (Johnston et al. 1993). Examples of in-situ techniques are ESR (electron spin resonance), FTIR (Fourier-transform infrared), NMR (nuclear magnetic resonance), and XAS. While ESR, FTIR, and NMR techniques are readily available, XAS provides much more information about the local structure (bond distance, number and type of near neighbours) around a sorbing element, even when the element is present at low concentration (depending on element and matrix as low as = 0.03 to 0.05% by weight, Charlet and Manceau (1993).

EXAFS studies have shown that the adsorption of heavy metals on clay and oxide surfaces results in the formation of multinuclear or polynuclear surface complexes much more frequently than previously thought (Scheidegger and Sparks 1996a). Multinuclear metal hydroxides of Pb, Ni, Co, Cu, and Cr have been observed. Such surface precipitates have been identified at metal surface loadings far below theoretical monolayer coverage and in a pH-range well below the pH where the formation of metal hydroxide precipitates would be expected according to the thermodynamic solubility product.

3.4 Kinetic studies

Observations of structural changes over time can provide valuable information about sorbed materials. Scheidegger and Sparks (1996b) used XAFS, for example, in their study where they showed that the release of Ni from Ni surface precipitates on pyrophyllite is much slower than the dissolution of crystalline Ni(OH)₂(s) reference compounds. This finding demonstrates the low solubility of mixed-cation hydroxide phases, and the potential effect of mixed-cation hydroxide formation on the bioavailability, mobility, and fate of metals in soil and water environments.

The kinetics of mixed Ni-Al hydroxide formation on clay and aluminium oxide minerals was recently studied by Scheidegger et al. (1998). The experiments were made by combining kinetic investigations with XAFS measurements over extended time periods (minutes to months). The results indicated the occurrence of three phenomena at the

mineral/liquid interface: (1) non-specific (i.e., outer-sphere complexation) and/or specific adsorption (i.e., inner-sphere complexation), (2) dissolution of Al, and (3) nucleation of a mixed Ni/Al phase. Their study emphasises the usefulness of combining time-dependent or kinetic studies with spectroscopic investigations like XAS to better understand sorption processes at the solid/solution interface. Scheidegger et al. (1998) stress that this combination can result in a detailed mechanistic understanding (e.g., distinguishing the rate of metal sorption relative to nucleation processes in sorption systems), which would never have been provided by a macroscopic approach alone.

3.5 Incorporation of Cr in alpha-Ni(OH)₂ films

The incorporation of Cr in electrodeposited alpha-Ni(OH)₂ films can be studied by investigating the site occupancy and local structure of Cr³⁺ and Cr⁶⁺ ions. Balasubramanian and Melendres (1999) found in an EXAFS study that films produced from Ni²⁺ and Cr³⁺ solutions showed Cr³⁺-incorporation into Ni lattice sites, while films produced by cathodic co-deposition of Cr⁶⁺ and Ni²⁺ resulted in CrO₄²⁻ in interlamellar sites and on surfaces.

4. Suggestions for future work

The few selected examples in the previous section demonstrate the eminent power of XAS techniques. XAS may offer superb and unique insights into both the speciation and the sorption chemistry of radionuclides. Such information is valuable in understanding the sorption mechanisms relevant to the safety of LLW and HLW repositories.

XAS methods could be applied to chemical systems that are relevant for the Finnish repository conditions. As a first approach, the study of a suitable radionuclide important in low and medium level radioactive waste is suggested. According to present concept such waste will be disposed of in a repository offering a cement environment. The groundwater in contact with the cement will be highly alkaline, with pH roughly 11–13. The main objective of such work would be to study the sorption of the radionuclide of choice onto various cementitious materials under conditions relevant to those present in the Finnish repositories for low and intermediate level waste. The study of the sorbed nuclide would be made by advanced XAS technique.

Below we outline a proposal for a possible XAS study on a suitable radionuclide in a cementitious environment.

Radionuclide

The radionuclide to be studied should be important in the sense that its activity constitutes a real problem if released to the environment. At the same time it would be advantageous if the nuclide were one with little radiological risk in the laboratory. We propose Ni as a suitable radionuclide. Nickel meets both the above requirements. According to the safety analysis of decommissioning waste from the Olkiluoto NPP, ^{59}Ni (and ^{94}Np) are dominant in the dose rates in the decommissioning waste after $6.5 \cdot 10^4$ years (Vieno et al. 1993). Experimental studies on Ni constitute no radiological problem; the element exhibits both radioactive and inactive isotopes, in contrast to the actinides, which exhibit only radioactive isotopes.

Solid

The solid material of chief interest is Portland cement, which may have been subjected to certain modifications. Sulphate-resistant cement was used in previous studies on nickel (Carlsson et al. 1999 a, b).

Cement consists of several phases – calcium silicate hydrate gels of various composition, hydrogarnet, etc. Ideally, separate sorption studies should be made for each cement component that may participate in the sorption. Batch experiments, XRD, or modelling or all of these would be required to identify the components, and the outlay of resources would be considerable. A second, less ambitious approach is to use the

cement material as such, and obtain averaged data. The results from averaged data would be more difficult to interpret and less valuable. A third possibility is to study one or two of the cement components. Other possibilities exist, but will not be discussed here.

Water phase

The water phase to be studied could be either a natural Olkiluoto groundwater, or some suitable synthetic reference water (see Vuorinen et al. 1997) to which Ni has been added.

Expected results

Advanced XAS techniques would be used as a means of determining the mechanisms behind Ni sorption on the type of cement materials to be used in the Finnish repositories for low and intermediate level radioactive waste. Similar studies have been performed elsewhere (see e.g. Ewart et al. 1990), but, to our knowledge, not under the conditions expected at a Finnish repository, nor with the same type of cement.

XAS studies of the outlined type could be expected to yield valuable and useful information about the sorption mechanisms of Ni onto various cement components. Such information should, under proper conditions, make it possible to determine the type (inner-sphere complexation, surface precipitation, etc.) of interaction prevailing between Ni and solid surfaces. Such knowledge would undoubtedly prove highly useful in the safety assessment of radioactive waste repositories.

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