

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

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 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.



	Experiment title: Determination of the speciation of Selenium and Iodine onto sulfur-containing minerals	Experiment number: 26-01-833
Beamline: BM26A	Date of experiment: from: 4 th July 2009 to: 9 th July 2009	Date of report: 27.08.2009
Shifts: 12	Local contact(s): Marika Vespa	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Dr. Marika Vespa ^{2*} , Laure Aimoz ^{1*} , Dr. Enzo Curti ^{1*} ¹ Laboratory for Waste Management Paul Scherrer Institute, CH-5232 Villigen, Switzerland ² Flemish Organization of scientific research (FWO), Dutch Belgium Beamline DUBBLE , BP 220, 38043 Cedex 9, France		

Report:

Spent Nuclear Fuel (SNF) disposed in radioactive waste repositories is liable to release long-lived nuclides including ¹²⁹Se and ⁷⁹Se. Both radionuclides are dissolved as anionic species, which are in general poorly retarded by common major minerals (clays, carbonates and sulfates) resulting in high calculated radiological doses. However, these calculations neglect the effect of minor secondary minerals such as Layered Double Hydroxides (LDH), which are able to exchange anionic species and have therefore, a high retardation potential for ¹²⁹I and ⁷⁹Se. A mechanistic understanding of the binding of I and Se to LDH phases is, therefore, essential for realistic performance assessments of radioactive waste disposal systems.

LDHs have a brucite-like structure, with positively charged octahedral sheets of edge sharing M^{II} and M^{III} hydroxides alternating with interlayers occupied by anions and water molecules ($[M_{1-x}^{II}M_x^{III}(OH)_2][A^{-n}]_{x/n}\cdot yH_2O$). In this study, the uptake of I and Se by Zn-Al LDH was investigated. The LDH phases were synthesized by coprecipitating I and Se (as I⁻, IO₃⁻ or SeO₃²⁻) with Zn^{II}-Al^{III} salts at various Zn/Al ratios at constant pH and under N₂ flux to avoid the formation of carbonate-LDH. Two further LDH-I samples were prepared with Mg or Ca as M^{II} cation. The LDH structure (R-3m) of the samples was confirmed by powder X-ray diffraction. Using the He liquid cryostat at 90 K, EXAFS spectra were recorded in transmission at the I-K edge, Se-K edge and Zn-K edge.

Fig. 1a-b presents a comparison of recorded I K-edge spectra for iodide-loaded LDH phases containing different divalent cations: **Zn**₂Al(OH)₆.I.yH₂O, **Mg**₂Al(OH)₆.I.yH₂O and **Ca**₂Al(OH)₆.I.yH₂O (). The major difference is observed for the **Ca**₂Al-doped I-LDH, which shows greater amplitudes at $k > 7 \text{ \AA}^{-1}$ (Fig. 1a) and larger magnitudes in R-space (Fig. 1b), particularly at high R+ΔR, suggesting the presence of high Z backscattering atoms in the second or third coordination shell. .

Fig. 2 shows a comparison of the spectra for the investigated Zn-LDH both at the I K-edge (Fig. 2a-b) and Zn K-edge (Fig. 2c-d) for different M^{II}/M^{III} ratios: Zn₂Al(OH)₆.I.yH₂O, Zn₃Al(OH)₈.I.yH₂O, and Zn₄Al(OH)₁₀.I.yH₂O. The spectra at the I K-edge (Fig. 2a-b) are all very similar and show consistently a threefold splitting of the first shell, in the FT, suggesting three preferred I-O distances within the range R+ΔR ~2-4 Å. This feature is emphasized at higher Zn/Al ratios (Fig. 2b). All Zn K-edge spectra show a distinctive beat pattern at $\sim 8 \text{ \AA}^{-1} < k < \sim 8.5 \text{ \AA}^{-1}$ typical for LDH phases (Fig. 2c) [1-3]. Furthermore, the shape of this beat pattern changes with the Zn-Al ratio. The corresponding FT show similar radial distribution functions (RDS, both in the magnitude and the imaginary part) for all three phases (Fig. 2d).

Fig. 3 illustrates the influence of the interlayer anion on the Zn coordination environment for $\text{Zn}_2\text{Al}(\text{OH})_6\cdot\text{NO}_3\cdot y\text{H}_2\text{O}$, $\text{Zn}_2\text{Al}(\text{OH})_6\cdot\text{I}\cdot y\text{H}_2\text{O}$, $\text{Zn}_2\text{Al}(\text{OH})_6\cdot\text{SeO}_3\cdot y\text{H}_2\text{O}$ and $\text{Zn}_2\text{Al}(\text{OH})_6\cdot\text{IO}_3\cdot y\text{H}_2\text{O}$ (Fig. 3a-b). The Zn K-edge spectra show differences at $k > 6\text{\AA}^{-1}$ (Fig. 3a) which translate in distinct RDS in R-space (Fig. 3b). Differences are observed particularly between the spectra obtained for LDH phases loaded with anions having prismatic coordination geometry (IO_3^- , SeO_3^{2-}) compared to LDHs loaded with anions having a quasi-planar (NO_3^-) or point-like (I) geometry spectra. Further data analysis is ongoing.

References

1. Jacquat *et al.* Geochim. Cosmochim. Acta, **72**, 5037-5054 (2008). 2. Scheinost, A. *et al.* J. Colloid Interface Sci., **223**, 167-178 (2000). 3. Voegelin, A. *et al.* Environ. Sci. Technol., **39**, 5311-5318 (2005).

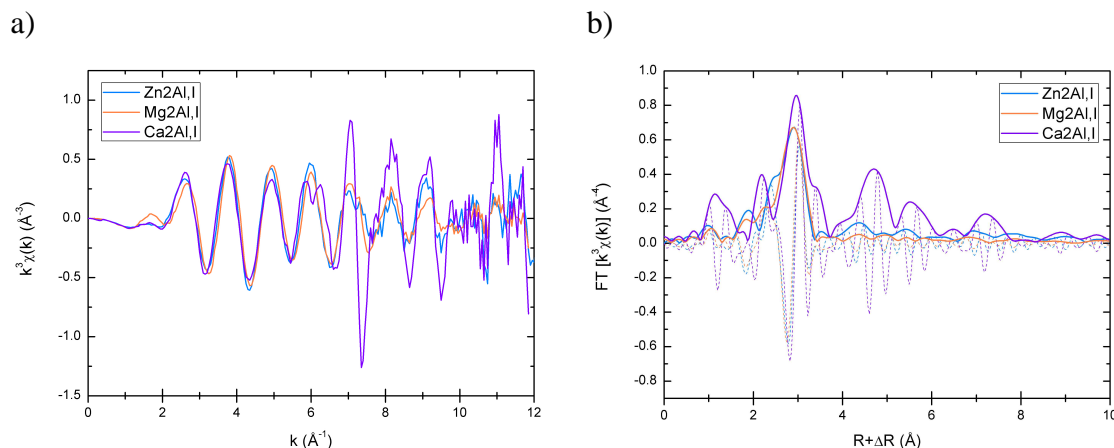


Fig. 1. Iodine K-edge spectra recorded at 90K for various $\text{M}^{\text{II}}/\text{M}^{\text{III}}$ ratios Layered Double Hydroxide phases ($\text{Zn}_2\text{Al}(\text{OH})_6\cdot\text{I}\cdot y\text{H}_2\text{O}$, $\text{Mg}_2\text{Al}(\text{OH})_6\cdot\text{I}\cdot y\text{H}_2\text{O}$ and $\text{Ca}_2\text{Al}(\text{OH})_6\cdot\text{I}\cdot y\text{H}_2\text{O}$). a) k^3 -weighted spectra; b) Fourier Transform (modulus and imaginary part).

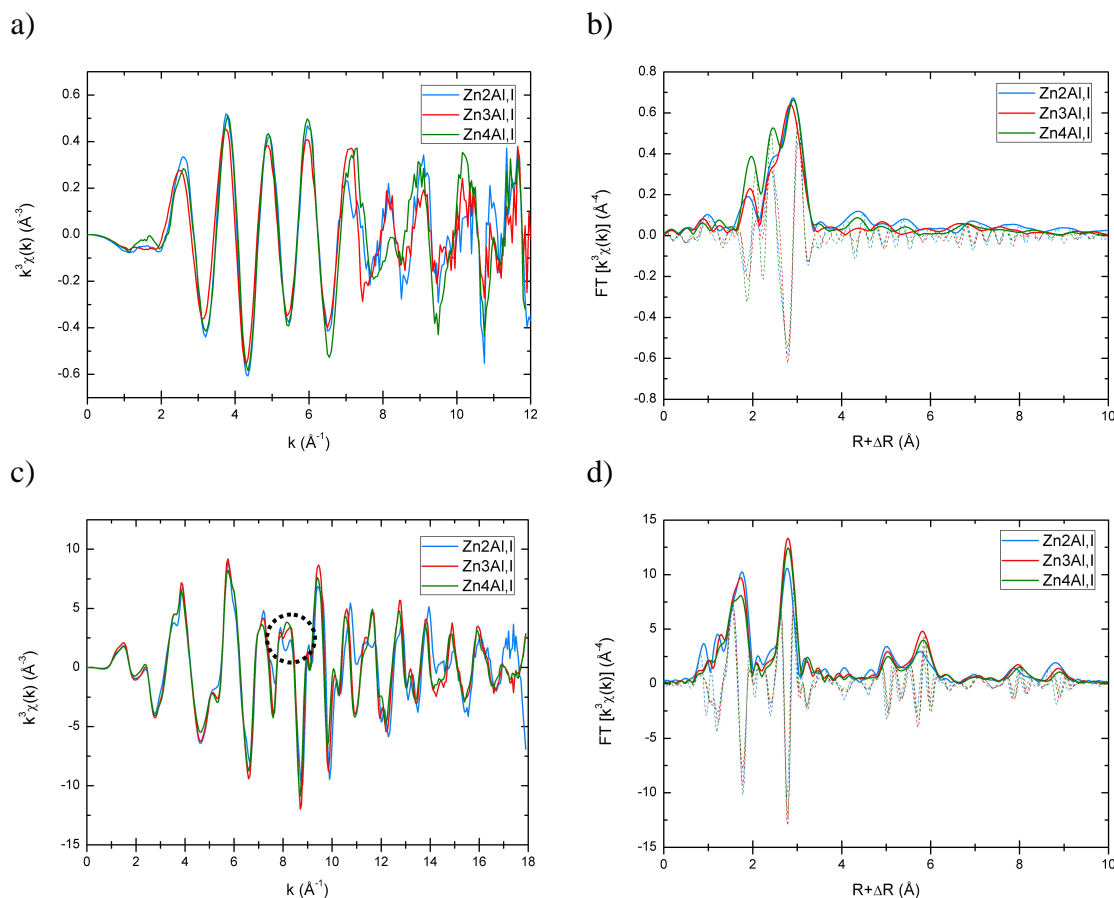
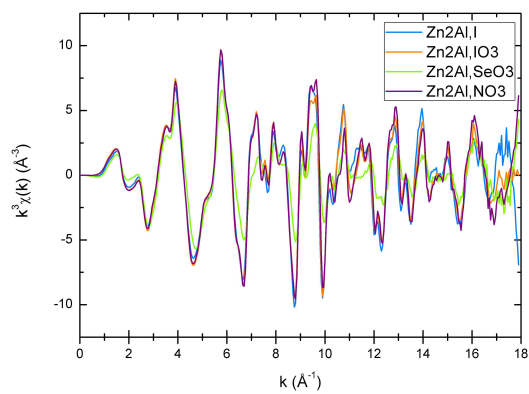


Fig. 2. Spectra of various LDH phases recorded at 90K : Zn K-edge of the a) k^3 -weighted spectra; b) Fourier Transform (modulus and imaginary part); I K-edge of the c) k^3 -weighted spectra; d) Fourier Transform (modulus and imaginary part).

a)



b)

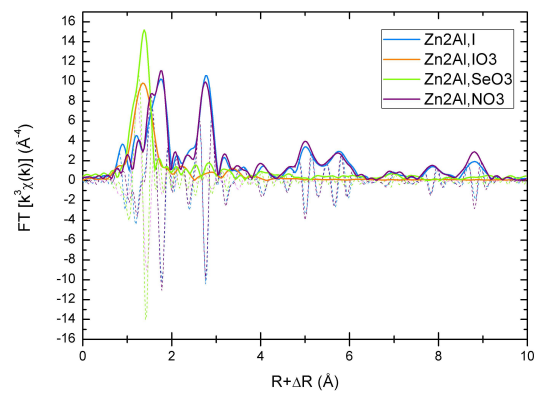


Fig. 3. Zinc K-edge spectra recorded at 90K Layered Double Hydroxide phases with varying anions ($\text{Zn}_2\text{Al}(\text{OH})_6\text{NO}_3 \cdot y\text{H}_2\text{O}$, $\text{Zn}_2\text{Al}(\text{OH})_6\text{I} \cdot y\text{H}_2\text{O}$, $\text{Zn}_2\text{Al}(\text{OH})_6\text{SeO}_3 \cdot y\text{H}_2\text{O}$ and $\text{Zn}_2\text{Al}(\text{OH})_6\text{IO}_3 \cdot y\text{H}_2\text{O}$). a) k^3 -weighted spectra; b) Fourier Transform (modulus and imaginary part).