

## 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.



	<b>Experiment title:</b> Competitive metal sorption in cementitious materials	<b>Experiment number:</b> 26-01-850
<b>Beamline:</b>	<b>Date of experiment:</b> from: 26 <sup>th</sup> February 2010 to: 3 <sup>rd</sup> March 2010	<b>Date of report:</b>
<b>Shifts:</b> 12	<b>Local contact(s):</b> Sergey Nikitenko	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists):  Dr. Marika Vespa <sup>1*</sup> , Dr. Erich Wieland <sup>2*</sup>  <sup>1</sup> Flemish Organization of scientific research (FWO), Dutch Belgium Beamline DUBBLE , BP 220, 38043 Cedex 9, France <sup>2</sup> Laboratory for Waste Management Paul Scherrer Institute, CH-5232 Villigen, Switzerland		

## Report:

Cement is an important constituent of the engineered barrier systems in underground repositories for low and intermediate level radioactive waste. Cement is used to solidify and stabilize the waste materials and, furthermore, it is used in huge amounts for the construction and backfilling of the cavern. The release of radionuclides from the cementitious near field into the underground is retarded due to their strong interaction with cement mineral phases.

In hydrated cement, calcium silicate hydrates (C-S-H),  $(\text{CaO})_x(\text{SiO}_2)_y(\text{H}_2\text{O})_z$  are quantitatively the most abundant and most important phases (C-S-H >50 wt.%, other minerals are Ca-hydroxide ~20 wt.% and calcium aluminates ~20 wt.%). They are chemically the most stable minerals in a cementitious environment (pH > 12.5) and exhibit a wide diversity of structural sites exposed for cation binding. 11 Å tobermorite is a crystalline C-S-H phase for which the structure is well known (Fig. 1) [1]. The layered structure is built up of sheets of Ca polyhedra linked through non-bridging oxygens to chains of silicate tetrahedra on both sides. The interlayer space in between the sheets may contain water and calcium. Three different modes of heavy metal interaction with 11 Å tobermorite can be envisaged: 1) surface complexation (position 1), 2) uptake in the interlayer (position 2), and 3) incorporation in the Ca sheets (position 3) (Fig. 1). Spectroscopic investigations have provided evidence that all three positions are competitive sites. For example, investigations on the uptake of Sn(IV) onto C-S-H have shown that Sn sorbs on edges of the Si chain by corner sharing between Sn octahedra and Si tetrahedral (position 1) [2]. While, XAFS investigations of Nd(III) and low concentrated Zn(II) uptake to C-S-H reveal that these metal ions tend to be incorporated in the interlayer of the C-S-H structure (position 2) [3-4]. Further studies on Nd(III) as well as Eu(III) uptake on crystalline C-S-H have shown that for long reaction times these metal can also substitute for Ca in the Ca sheets (position 3) [4-5].

In order to answer the question whether or not the competition between two metals having a similar sorption behaviour has an influence on the binding mechanism and the coordination environment of these

metals in the C-S-H structure, 11 Å tobermorite was doped at the same time with Nd and Zn. The concentrations of both elements were about 50 000 ppm. The Nd doped samples reacted over months, while the contact time with Zn varied from 1 to 6 months. EXAFS spectra were collected at the Zn K-edge and the Nd L<sub>III</sub>-edge. Fig 2 shows the Zn K-edge collected spectra together with reference samples of tobermorite doped with Zn solely for the same reaction times. The reference spectra (Fig.2a) show a shoulder forming at  $\sim 3.8 \text{ Å}^{-1}$  after 6 months reaction time, whereas a clear difference is observed between 5 and  $7 \text{ Å}^{-1}$  with ongoing reaction time. In this latter k-region the experimental spectra reveal distinct dissimilarities to the references, especially with prolonged reaction times. These differences observed between the references and the experimental spectra suggests that Nd has an influence on the incorporation of Zn in the tobermorite structure. The corresponding Fourier Transformed spectra show marked differences at higher shells between 2.5 and  $3.5 \text{ Å}$  (Fig.2b). The ongoing data analysis indicates that for all samples Zn has a tetrahedral coordination environment with Zn-O distances of  $1.96 \text{ Å}$  comparable to Ziegler et al [3]. All Nd<sub>LIII</sub> EXAFS spectra (not shown) are quite similar to each other suggesting that the Nd uptake process is comparable in all samples. Nd is octahedrally coordinated with Nd-O distances of  $2.45 \text{ Å}$  in accordance with Mandaliev et al [4]. Development of a structural model of metal competition is ongoing.

## References

- [1] Merlino, S., Bonaccorsi, E., Armbruster, T. 2001 *Eur. J. Mineral.* **13**, 577.
- [2] Bonhoure, I., Wieland, E., Scheidegger, A. M., Ochs, M., Kunz, D. 2003. *Environ. Sci. Technol.* **37**, 2184.
- [3] Ziegler, F., Scheidegger, A. M., Johnson, C. A., Dähn, R., Wieland, E. 2001. *Environ. Sci. Technol.* **35**, 1550.
- [4] Mandaliev, P., Wieland, E., Dähn, R., Tits, J., Churakov, S.V., Zaharko, O. 2010. *App. Geochemistry* **25**, 763-777.
- [5] Mandaliev, P., Stumpf, T., Tits, J., Dähn, R., Walter, C. Wieland, E., 2010. *Geochim. Cosmochim. Acta* (accepted).

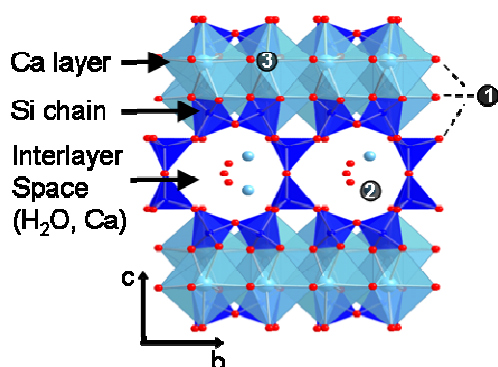


Fig 1. The crystal structure of 11 Å tobermorite with possible positions of Ca in the Ca layers and interlayer Ca (●) as well as positions of structural oxygens and water molecules in the interlayer (●). Potential sites for metal sorption and structural incorporation (●) are labelled 1, 2 and 3.

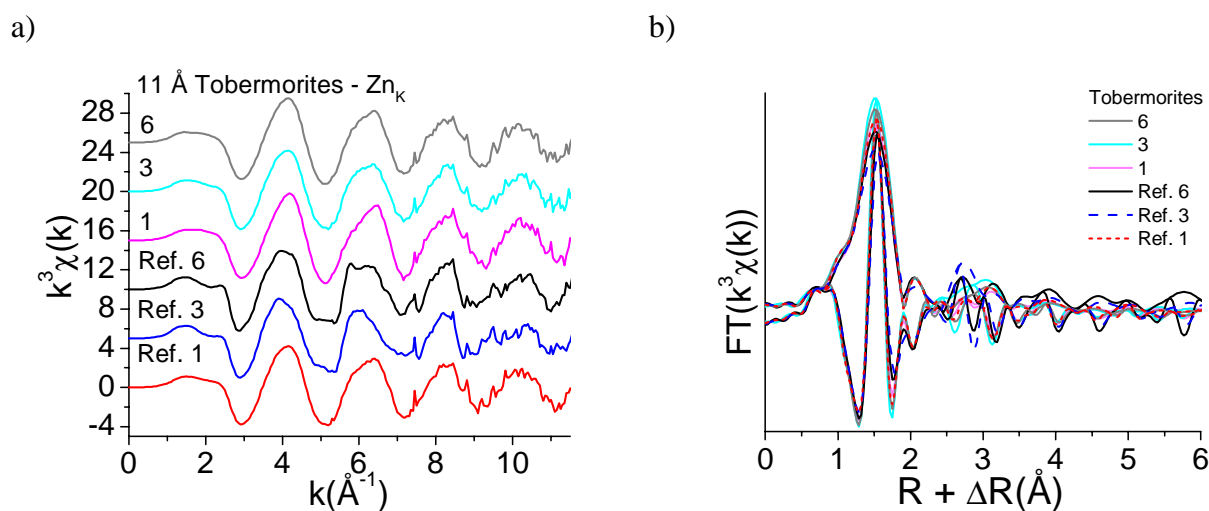


Fig. 2. Zn K-edge EXAFS (a) and the corresponding Fourier Transformed spectra (b) of 11 Å tobermorites samples doped with 50 000 ppm Nd and Zn and 11 Å tobermorite references only doped with 50 000 ppm Zn. The numbers 1/3/6 labelling the spectra indicate reaction times of 1, 3 and 6 months.