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ESRF

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 via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can 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: **X-ray micro-diffraction study of cement/claystone interfaces**	**Experiment number:** 01-02 1120
Beamline: BM01	**Date of experiment:** from: 9. March 2017 to: 12. March 2017	**Date of report:** 12. March 2017 *Received at ESRF:*
Shifts: 9	**Local contact(s):** Dmitry Chernyshov	

Names and affiliations of applicants (* indicates experimentalists):

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Report:

(A) Overview

Deep geological waste repositories require cementitious structural elements. The material contrast between concrete and host rock leads to chemical and mineralogical interactions. These interactions are driven by chemical gradients in the porewaters, and might influence host rock properties like permeability, swelling pressure, or specific retention in case of clay rocks or compacted bentonite.

Cement-Opalinus Clay (OPA) interface samples from the Cement-Clay Interaction (CI) experiment at the Mont Terri rock laboratory (St. Ursanne, Switzerland) have been extensively characterised and modelled after different reaction times [1–4]. The investigations revealed significant alteration in cements within several millimetres from the interface, and less prominent changes in OPA. The analysis of thin interaction layers in cement and OPA, containing small-scale phase assemblages and poorly crystalline and/or solid-solution phases, required a comprehensive suite of spatially resolved techniques, that revealed major chemical disturbances including depletions/enrichments in Ca, Mg, S, and C, as well as alterations of the cation occupancy of the clay. Precipitation of calcium carbonate, magnesium silicate hydrate (M-S-H), and gypsum, and dissolution or hindered formation of portlandite, ettringite, and calcium silicate hydrate (C-S-H) are the main interaction-related phase reactions inferred from several investigations. The exact phase identities remained, however, unclear due to small reaction volumes, sub-micron grain sizes, amorphous nature of neoformations, and solid solutions.

Identification of phases involved in reactions improves the understanding of the interaction mechanisms and enables the verification of reactive transport models used to simulate such processes. A spatially resolved phase identification is therefore essential for a detailed interpretation of the observed chemical zonation.

This study employed spatially resolved synchrotron X-ray diffraction. Previously characterised (SEM-EDX, etc.) ordinary Portland cement mortar (OPC)/OPA and low-pH cement mortar (ESDRED)/OPA interfaces (three years old) originating from the CI experiment were investigated.

(B) Quality of measurement/data

We have used a focused 100 by 100 um large X-ray beam at BM01 in order to map areas on a point-by-point basis around the mortar - OPA interface. The collected diffraction data are of very high quality and due to the

high efficiency of the beamline, we were able to investigate large areas of our samples in the available time. Compared to previous experiments, data quality has also been much improved by our new sample preparation method, which has much thinner glass supports for the thin-sections (Fig. 1).
The capability of directly using Pilatus data in the software package XRDua (http://xrdua.ua.ac.be) will allow plotting d-values vs. intensity on 2D maps, which again can be overlaid with e.g. microscopy photographs of the samples. Together with previously collected XRF data, this allows an unambiguous, spatially resolved phase identification.

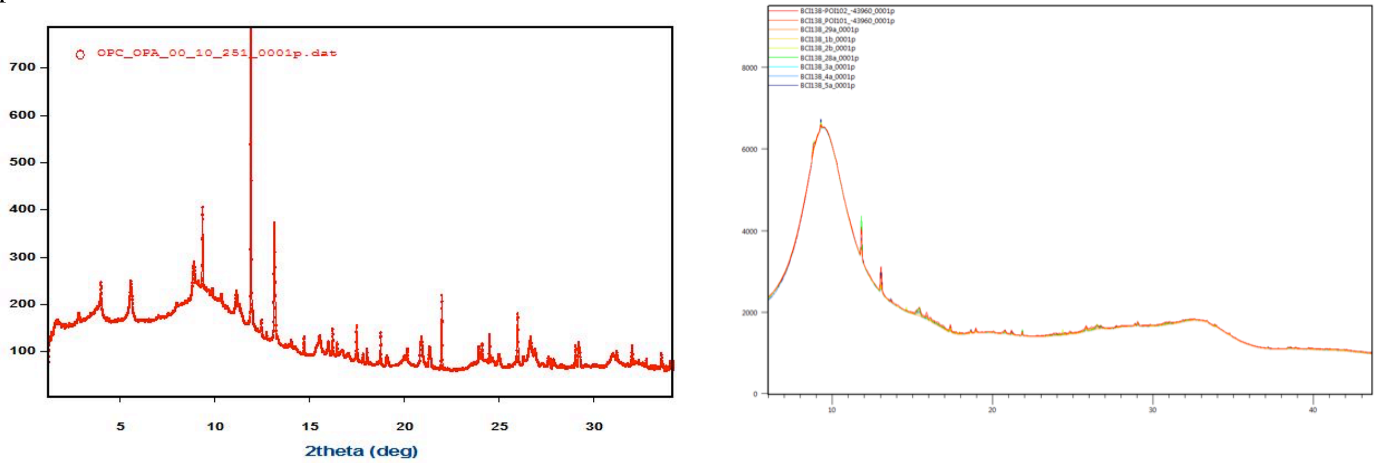

Fig. 1. Diffraction data of the clay part of the sample from this study (left) and of a previous study performed at BM01 (Dähn, Wieland, Jenni, 2012 at SNBL).

(C) Status and progress of the evaluation

Raw data are post-processed. Diffraction data will be processed with the software package XRDua and conventional batch-processed Rietveld analysis tools for relative phase quantification across the measured area.

(D) Preliminary Results

Previous SEM/EDX fluorescence maps reveal chemical information and allow for exact correlations of the XRD map with elemental concentrations. As a preliminary example, a Ca map of the cement mortar and clay (Fig. 2, left) with bright areas representing high content, is correlated with the calcite 104 reflection (Fig. 2, right). Calcite may be locally present in the cement, which would be in agreement with reactive transport modelling of a similar interface suggesting cement carbonation.

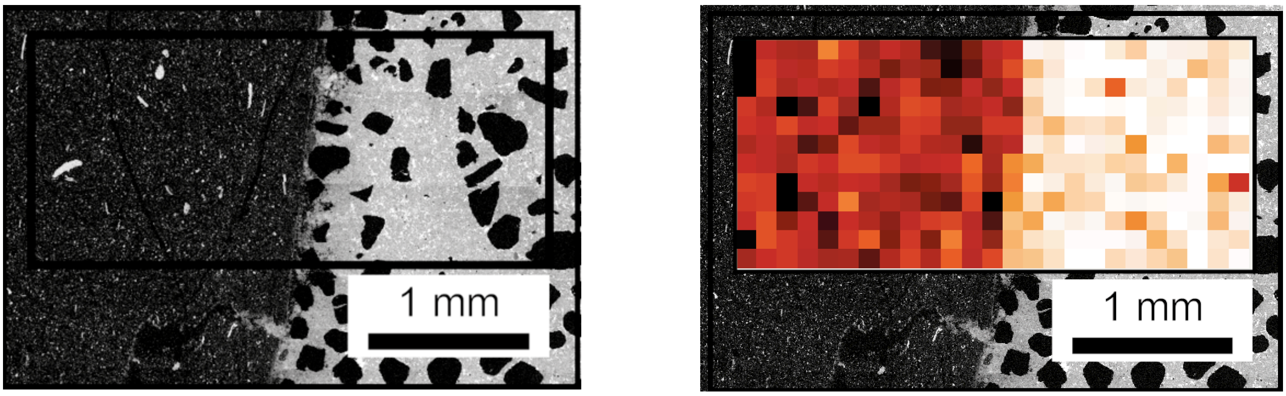

Fig. 2. Left: SEM/EDX Ca-map of the clay (left, dark zone) - OPC mortar (right, bright zone) interface. Right: the same area but the intensity distribution of the calcite 104 reflection is shown.

References

[1] Dauzères et al. (2016). Cement and Concrete Research 79, 137-150.
[2] Jenniet al. Physics and Chemistry of the Earth, Parts A/B/C, http://dx.doi.org/10.1016/j.pce.2017.01.004.
[3] Jenni et al. (2014) Physics and Chemistry of the Earth, Parts A/B/C 70–71, 71-83.
[4] Lerouge et al. (2017) Physics and Chemistry of the Earth, Parts A/B/C, http://dx.doi.org/10.1016/j.pce.2017.01.005.