

Characterization of initial ASR products by SEM, FIB and STEM-EDX

Solène Barbotin, Laboratory of construction materials (LMC), EPFL-STI-IMX-LMC, Station 12, CH-1015 Lausanne, Switzerland, solene.barbotin@epfl.ch

Emmanuelle Boehm-Courjault, LMC, EPFL-STI-IMX-LMC, Station 12, CH-1015 Lausanne, Switzerland, emmanuelle.boehm@epfl.ch

Andreas Leemann, Laboratory of concrete / construction chemistry, Empa, 8600 Dübendorf, Switzerland, andreas.leemann@empa.ch

Karen Scrivener, LMC, EPFL-STI-IMX-LMC, Station 12, CH-1015 Lausanne, Switzerland, karen.scrivener@epfl.ch

INTRODUCTION

In Switzerland, several hundreds of structures are affected by alkali-silica reaction (ASR) [1,2]. This is a major concern in the field, especially for structures where mechanical properties and dimensions must be stable over time, like bridges and dams. Most structures in Switzerland were presumably built with non-reactive aggregates, but as they grew older, expansion and cracking were noticed. It is estimated that 20-30% of Swiss dams are affected nowadays [2]. There is no possibility to stop the expansion and repair of such massive structures is very expensive like cutting slots across the dam to release stress.

There is thus a great need of improving our knowledge about ASR occurrence in order to prevent it. Even though the basics of mechanisms seem to be addressed, there are still many open questions regarding the swelling of the ASR products, its ageing behaviour, as well as the reactivity of various silicates. It is difficult to determine if a given aggregate combination will be reactive or not due to the very slow nature of the reaction.

ASR products have been analysed once they are present in relatively large quantities in cracks $> 10 \mu\text{m}$ product [3-6]. However, results about the early stage formation are needed for a better understanding of the mechanism of cracking.

MATERIALS AND METHODS

Field Samples

Samples were collected in Switzerland on dam and on a containing wall at the Brünigpass in Meiringen (Bern Canton), both severely affected by ASR. The dam is a weight dam built in 1950, at 1850m of altitude. The Brünigpass wall is about 40 years old, at around 1000m of altitude.

SEM analysis and FIB cutting

The samples region of interest was located first by SEM imaging and confirmed by energy-dispersive X-ray spectroscopy (EDX). A line scan across the crack is done and an increase of calcium and alkalis content of a few atomic percent (mostly from 1 to 5 percent) is looked for to confirm the presence of ASR in the thin crack ($< 2 \mu\text{m}$). Once localized, the region of interest is cut perpendicular to the crack, using a focused ion beam (FIB). Thinning of the lamella is done at progressively decreasing voltages and currents, ranging from 30kV-27nA down to 5kV-80pA, in order to optimize the time spent and to prevent beam damage. A thin lamella of approximate dimensions $10 \times 12 \mu\text{m}$ and thickness 200nm is obtained and welded to a TEM grid for further analysis regarding composition and structure.

STEM analysis

The product is studied in STEM mode (scanning TEM mode) to perform EDX measurements. Selecting a specific area of the sample with selected area electron diffraction (SAED), specific diffraction patterns have been obtained, as shown in Figure 5. The parameters used for analysis with STEM are also important to preserve the product, and thus analysis is performed at a rather low voltage, 80kV instead of the usual 200kV. For EDX measurements, the sample is tilted by 20° to improve X-rays collection efficiency and a defocusing of approximately 200nm is done to avoid beam damage. The analysis is then done after selecting the region of interest.

RESULTS AND DISCUSSION

Two lamellae have been prepared from the dam sample and two from the Brünigpass wall sample, all prepared from crystalline SiO_2 mineral phases, where a region of interest as described in *SEM analysis* section has been identified. Due to the sample sizes and product quantities, between three to six areas per sample were measured. An example of a chosen area is given in the STEM image in Figure 1, delimited in green.

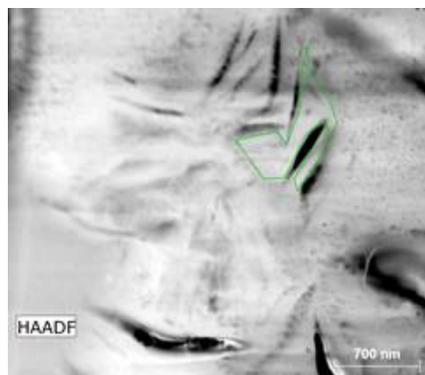


Figure 1: Brünigpass wall sample. Area of composition calculation is delimited in green

Morphology

Two different morphologies of the ASR product can be observed (Figure 2). One has a net-like or globular morphology and is sparse, the other has a platelet-like morphology and seems to be dense. Both products are also co-existing in the same crack, as in Figure 2 (a). In the dam sample the morphology of the products is similar. In Figure 3, the product has a fibril-like or platelet-like morphology, and seems to be dense. It looks similar to the product in Figure 2 (a & b). In Figure 3 right, it is less obvious but the product also looks dense.

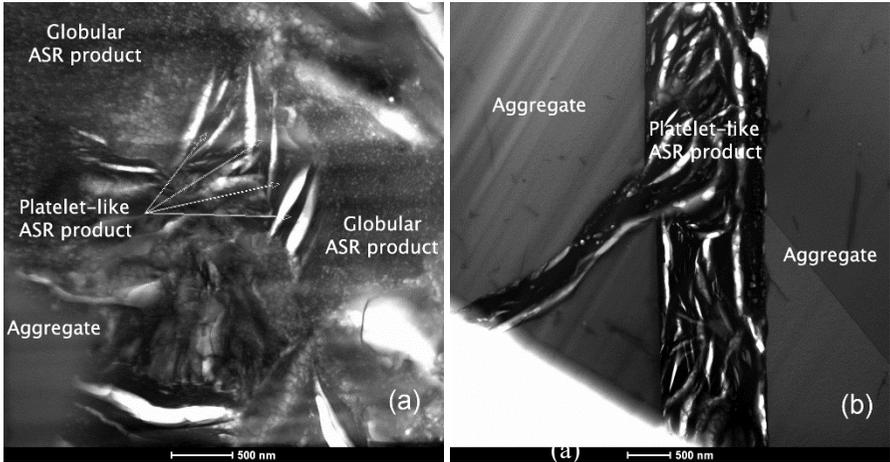


Figure 2: Brünigpass wall L1 (a) and L2 (b) samples STEM image

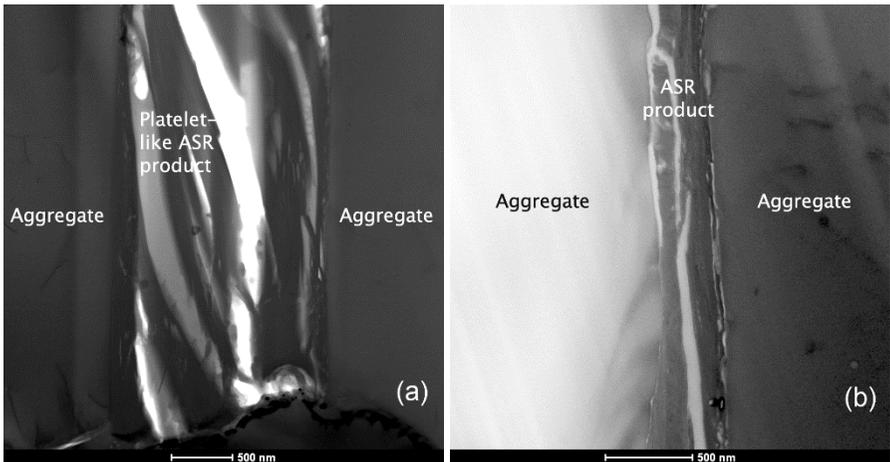


Figure 3: Dam L1 (a) and L2 (b) sample STEM image

Composition

The results in atomic percentages are normalized to represent silicon, potassium, sodium and calcium and presented in the ternary diagram in Figure 4. For Brünig L2 sample, a difference in the analysed area has been made between the products with differing morphology to see an eventual change of composition. From the results, the composition is similar for the four different lamellae, independently of their morphology. Only an increase of alkalis in one region of Brünig L2 (net-like product) indicates that there might be a variation in composition. Generally, there seems to be slightly more calcium and less alkalis in the dam samples (Figure 4). But the variations are too subtle and more data would be needed to confirm a difference. The ASR products contains between 15-25 atomic% of alkalis, 15-25 atomic% of calcium and 50-70 atomic% of silicon.

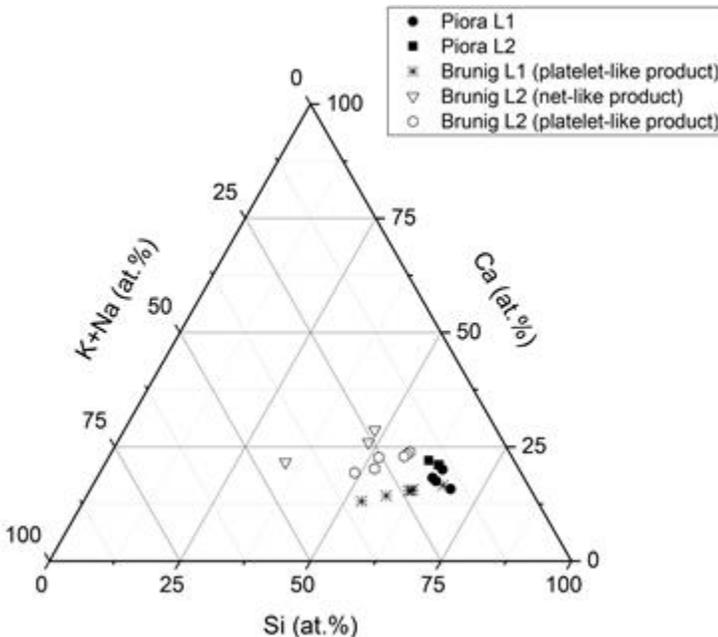


Figure 4: Ternary diagram showing ASR products normalized composition in atomic%

Structure

Analysing the electron diffraction patterns with SAED, the products present in the dam sample and the net-like product in Brünig wall were found to be amorphous. However, SAED performed on the platelet-like product in Brünig sample L2 showed a diffraction pattern with two weak diffracting spots as seen in Figure 5.

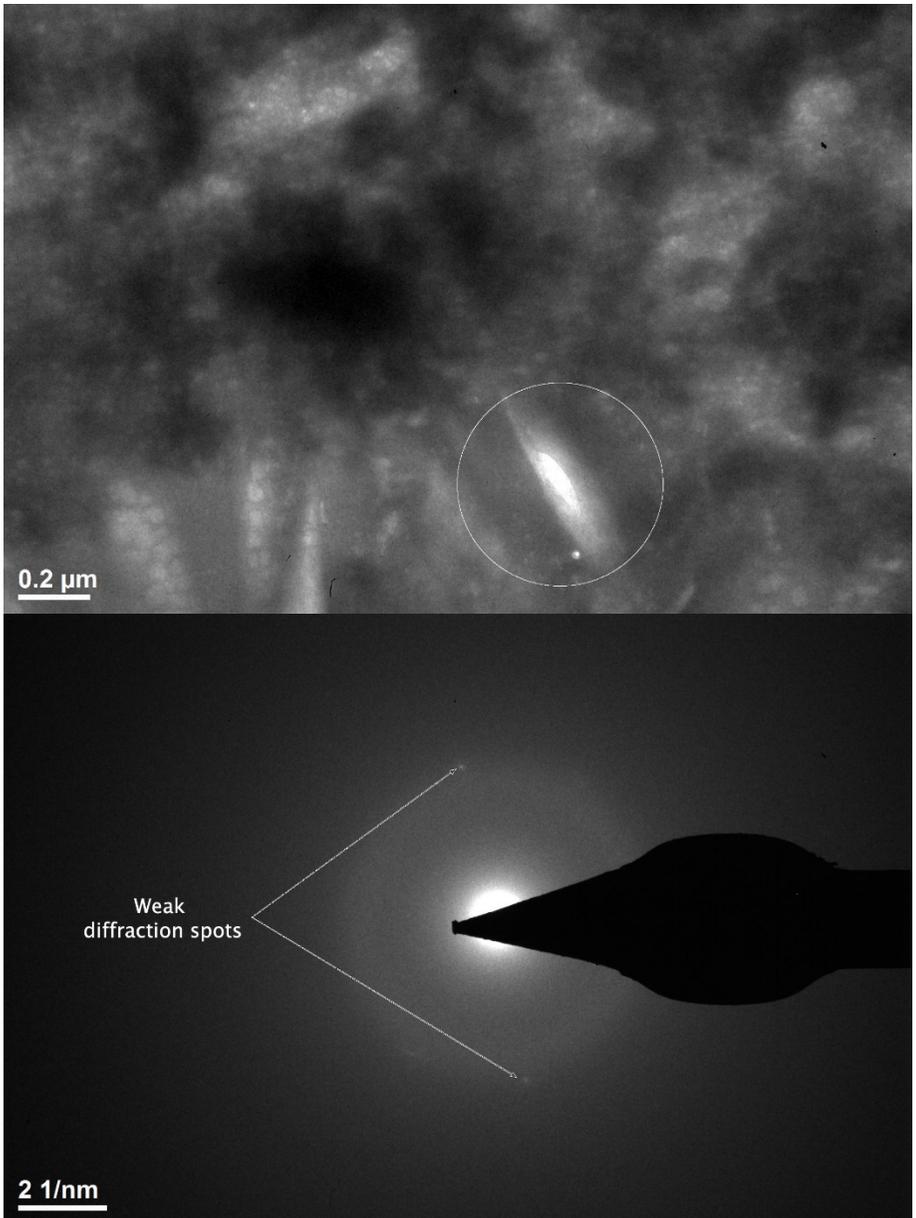


Figure 5: Selected Area Electron Diffraction of platelet-like product in Brünig L2 sample (top) and its associated diffraction pattern (bottom)

The weakness of the diffraction spots indicates there is a low amount of ordered material in the analysed zone and it can be due to two reasons

- The product is only partially crystalline inducing very few diffracted electrons and thus a weak intensity.
- The ASR crystalline product is amorphized by the electron beam during the measurement.

Indeed, the ASR product appeared to be beam sensitive, and in a parallel on-going study, the author could demonstrate that after 1 to 5 minutes, the diffraction spots becomes very weak, in a similar way as what is seen in Figure 5. Further investigations are needed to conclude in favour of one or the other hypotheses.

CONCLUSIONS AND OUTLOOK

Preparation of thin lamella of concrete to study the composition and structure of very small product quantities proved to be feasible and is a novel technique in the field of concrete. It is an accurate and efficient method to analyse the early stage product and reveals the morphologies of ASR products. As such, it may lead to a better understanding of the cracking mechanisms.

The analysis of ASR products with STEM confirmed the existence of two distinct products in terms of morphology, namely globular and “platelet-like” product. Their composition is quite similar with 15 to 25 atomic% of calcium, alkalis and 50 to 70 atomic % of silicon (normalized composition). No significant compositional change is observed based on the morphology. Concerning the structure, the globular product shows a diffuse ring diffraction pattern indicating that it is amorphous. The platelet-like product shows a weakly developed crystallinity in some areas; This is either a distinct property of the product or an effect of beam damage.

In the next steps, samples placed in accelerated laboratory conditions according to the Swiss standard SIA 2042 [7] or with a different temperature will be studied. Thus, the effect of boundary conditions (time exposure, environment...) on ASR product morphology, composition and structure will be investigated.

ACKNOWLEDGEMENTS

The authors sincerely thank the Swiss National Science Foundation SNSF for its funding in the framework of a Sinergia grant (CRSII5_171018). They also thank the CIME team in EPFL for their support with the electron microscopy equipment.

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