

## THE ROLE OF THE MICRON-SCALE IN REACTIVE TRANSPORT PROCESSES

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### Abstract

Quantitative predictions for durability issues are necessary to adapt the formulations of cement blends with novel supplementary cementitious materials. These predictions are usually carried out with reactive transport models which are solved at the macroscopic scale. Upscaling laws are necessary to ensure that effective transport properties represent the lower scales properties. Therefore, to define reasonable laws, we need to understand the mechanisms at lower scales.

In this work, we focus on the impact of the micron-scale on reactive transport models. We employ the *edxia* framework to investigate chemical mappings of samples subjected to macroscopic durability tests (obtained with energy dispersive spectroscopy in a scanning electron microscope). The samples investigated are (1) a carbonating cement paste sample, (2) a specimen of 16-year old concrete exposed to sea water, and a cement paste subjected to chloride electro-migration. We demonstrate that both profiles and quantitative chemistry of phases can be readily obtained to characterize reactive transport processes at the micron scale. The results are used to discuss the definition of the representative elementary volume in the case of carbonation and chloride ingress. In addition, we demonstrate that we can quantify the AFm solid solution along the depth of the sample.

Keywords: Durability, Carbonation, Chloride Ingress, SEM-EDX, edxia

### 1. INTRODUCTION

To improve the sustainability of cementitious material, the best compromise must be found between the environmental footprint of the initial materials and the durability of the concrete. Modeling and simulations are promising methods to accelerate the discovery and the standardization of new formulations, but they need to be fully validated before quantitative predictions can be claimed. This is a difficult challenge as it necessitates to decouple the transport and chemical driving forces. Most experimental protocol only provides macroscopic profiles. However most simulations lacks both the effective diffusion properties and precise information about the phase assemblage. Therefore, fitting these profiles to obtain the properties depends on many assumptions. It was recently shown that many of these assumptions often breaks when many systems are compared together [1].

More advanced characterization techniques can be used. For example Morandea et al. [2], used gamma-densimetry, TGA and XRD to analyse the change in phase assemblage during carbonation. However, their measure average over a large volume (5mm in depth) and their analysis depends on strong assumptions (e.g., no density changes due to drying). Maltais et al. [3] presented microprobes analysis and qualitative SEM-EDX analysis to study chloride ingress and sulfate attack. Although it was shown that it can improve the validation of models, the lack of quantification and phase identification means that the mechanisms cannot be independently validated.

In this paper we present practical examples of advanced microstructure characterization of carbonation and chloride ingress experiments initially performed at the macroscopic scale. Chemical mappings are analysed using the *edxia* framework to identify phases, quantify their chemistry and determine profiles of elemental concentrations and phase chemistry.

## **2. MATERIALS AND METHODS**

### **2.1 Carbonation sample**

Cement pastes were prepared from an ordinary Portland cement at  $w/b=0.4$  using a vacuum mixer and cast in plastic cylindrical moulds (diameter 32mm). After one day of sealed curing, the pastes were demolded and exposed at the relative humidity (RH) of 95 % until the age of 28 days. Cylinders were cut with a slow speed saw allowing to obtain thin slices with a thickness of 1mm. The slices were exposed to natural carbonation environment at 400ppm of  $CO_2$  and 70% RH. Moreover, reference samples were exposed to  $CO_2$ -free atmosphere and 70% RH [7].

### **2.2 Bulk diffusion sample**

Concrete samples were prepared with an OPC cement blended with 30% Fly Ash. In a 10x10x10 cm molds. The samples were demolded at 1 day and cured for 28 days. They were then exposed in an industrial facility for 16 years in the tidal zone. The total chloride profile was obtained by grinding the samples layer by layer and titrating the chloride content following the ASTM C1152 [11].

### **2.3 Electro-migration sample**

ement pastes were prepared from an ordinary Portland cement at  $w/b=0.4$  using a vacuum mixer and cast in plastic cylindrical moulds (diameter 32mm). After one day of sealed curing, the pastes were demolded and cured in small amount of water with crushed samples to avoid leaching. Cylinders were cut with a slow speed saw allowing to obtain thin slices with a thickness of 10mm. The samples were subjected to an electro-migration test as described in Wilson et al. [12].

### **2.4 SEM-EDS sample preparation and acquisition**

After the analysis, the samples were dried using the solvent exchange method: isopropanol was changed two times during the first 24 hr, then the sample was removed after 5–7 days of immersion and placed in a desiccator for at least 48 hr. A piece of the sample was then impregnated using a low viscosity epoxy resin. The sample's surface was polished using diamond suspensions (9  $\mu m$ , 3  $\mu m$  and 1  $\mu m$ ) [13].

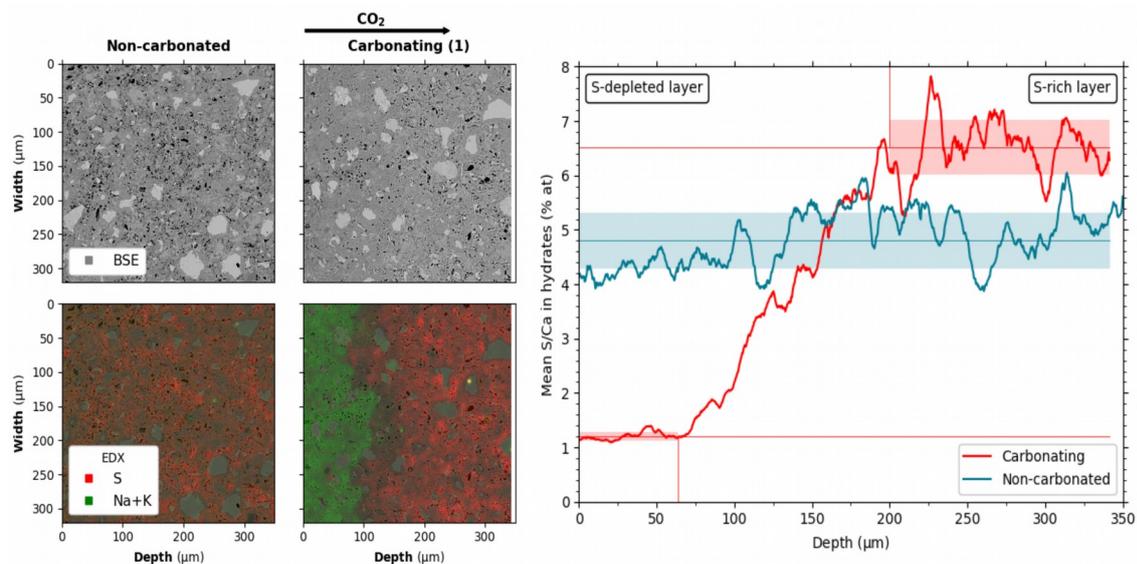
SEM-EDS for the carbonation and the bulk diffusion samples were carried out with a Quanta 200 scanning electron microscope equipped with a tungsten filament and operated at an accelerating voltage of 15 kV, the working distance was 12.5 mm. A Bruker AXS Microanalysis XFlash 4030 silicon drift detector was used as the EDS detector. The electron migration sample was studied using a Zeiss Cross Beam FEI equipped with an Oxford Ultim Max 170 energy-dispersive spectrometer. The EDS analyses were calibrated with standard reference materials (CaCO<sub>3</sub> for C, CaSiO<sub>3</sub> for O & Ca, Jadeite for Na, MgO for Mg, Al<sub>2</sub>O<sub>3</sub> for Al, SiO<sub>2</sub> for Si, CaSO<sub>4</sub> for S, KCl for Cl & K, TiO<sub>2</sub> for Ti, and Fe<sub>2</sub>O<sub>3</sub> for Fe).

## 2.5 SEM-EDS maps analysis

The maps were analyzed with the *edxia* framework [10,14]. Quantitative maps are used as input. Representative points are extracted from the maps using a SLIC segmentation of a Si-Al-Ca composite image. These points are then analyzed using ratios plots similar to the EDS point analysis workflow[13]. The composition of the AFm was found by using the Cl/Ca vs. Al/Ca ratio plots as described by Sui et al. [6], i.e. the composition of the pure AFm is given by the extrapolation of the mixture line between the C-S-H and the AFm to Al/Ca=0.5. The C-S-H were found by plotting the points in the Al/Ca vs Si/Ca. The Cl/Ca were found by averaging the Cl/Ca of the points identified as C-S-H.

## 3. RESULTS

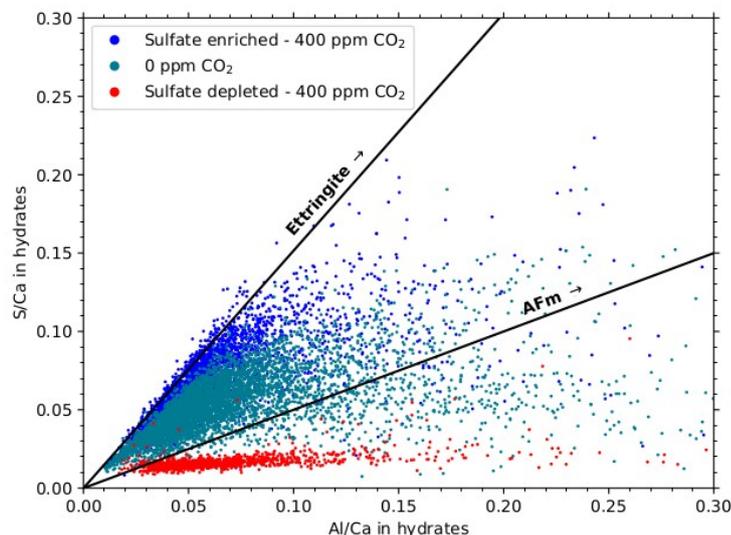
### 3.1 Characterization of the carbonation front



**Figure 1: Identification of the carbonation front by SEM-EDX: sulfur concentration across the carbonation front**

Figure 1 presents the BSE and an EDS composite map as well as the mean S/Ca in the hydrates in a carbonated sample and a similar sample subjected to a carbon-free atmosphere. In the non-carbonated sample, the S/Ca is mostly constant across the sample. But the

carbonated sample present a clear gradient with a sulfate-depleted layer at the surface and a sulfate enrichment in the core. This sulfate diffusion was hypothesized by Georget et al. [4] and verified experimentally by De Weerd et al. [5]. This is an independent validation of this intrinsic mechanisms of carbonation. It should be noted that few models consider this effect that may have drastic effect on the porosity [4].



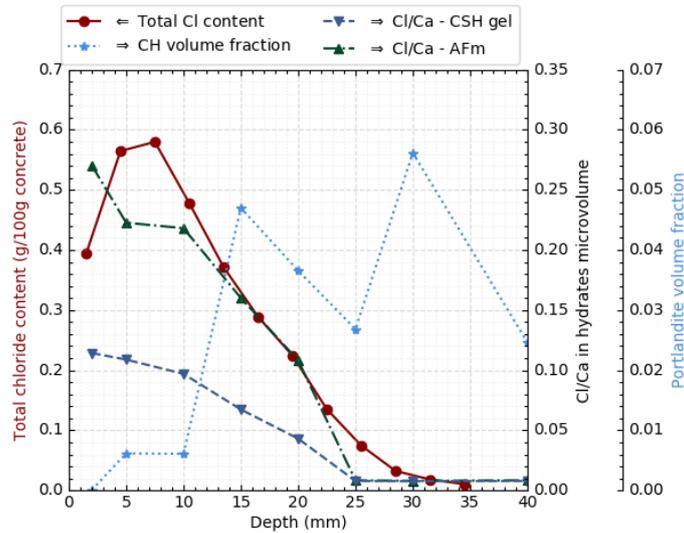
**Figure 2: Phase identification across the carbonation front: the higher sulfate concentration in the non-carbonated layer is due to the precipitation of ettringite.**

Using thermodynamic arguments, it can be hypothesized that the sulfate enrichment is due to the precipitation of ettringite. Our methods can demonstrate it. Figure 2 shows the S/Ca ratio versus the Al/Ca ratio in sampling points situated in the hydrates. The points from the non-carbonated samples shows the typical profile where the C-S-H point are mixed in-between the ettringite and the AFm mixture lines. In the sulfate-depleted layer, the S/Ca is greatly decreased without significant change to the Al/Ca. This indicates that the other main elements do not diffuse with sulfur. On the opposite side of the sample, the S/Ca is significantly increased and the points align better with the portlandite-ettringite mixture line. This is a demonstration of the higher content of ettringite in the non-carbonated layer of the carbonated sample.

### 3.2 Characterization of bulk diffusion profiles

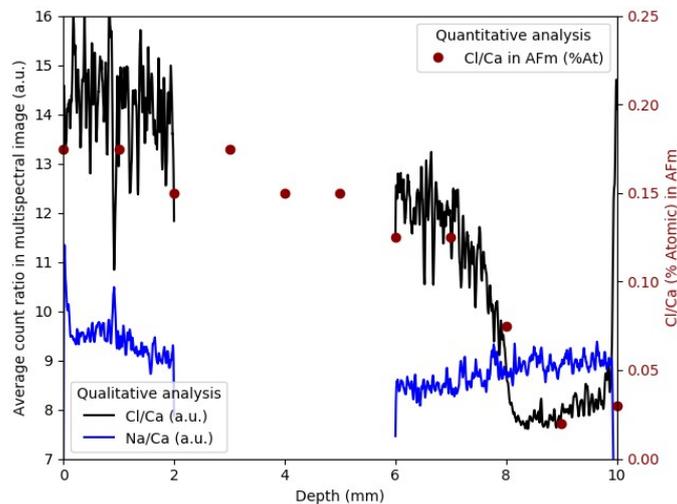
A similar chemical characterization can be performed for chloride bulk diffusion sample. Figure 3 presents the total chloride content profile for a fly ash concrete. These type of profile is hard to validate because it mixes many mechanisms: diffusion of chloride, leaching, chemical binding in AFm and chemical binding in C-S-H. Using quantitative SEM-EDS maps acquired along the depth of the sample, it is possible to separate these effects. Thus, Figure 3 also present the Cl/Ca ratio in the C-S-H gel and in the Afm, as well as the portlandite volume

fraction. The Cl/Ca ratio provides the binding affinity for these phases. With the quantification of these phases, it is possible to quantify the total binding capacity provided by these phases [6]. The portlandite volume fraction provides an indication of the leaching. Although the signal-to-noise ratio is high, there is a clear indication of leaching in the first 10mm of the sample.



**Figure 3: Characterization of the bulk diffusion profile in fly ash concrete samples: Cl/Ca in AFm and C-S-H gel microvolume and the portlandite volume fraction.**

### 3.3 Characterization of electro-migration profile



**Figure 4: Characterization of the electro-migration front: Cl/Ca in AFms and sodium gradient**

Figure 4 presents the chloride front as seen by the Cl/Ca ratio in counts, as observed in qualitative EDS maps, at day 6 of the experiment. A clear drop is observed around 8mm. On the opposite, the Na/Ca is flatter, with a small increase on the side of the samples. On the upstream side, the Cl/Ca profile is relatively flat even the chloride content is slightly higher at the surface. To complement this analysis, quantitative EDS maps were acquired along the depth of the sample.

## 4. DISCUSSION

### 4.1 The representative elementary volume

The resolution of SEM-EDS maps is typically around the micrometer. This size is limited by the interaction of the electron beam with the sample [8]. It is however smaller than most other methods available such as XRD and TGA. It is also smaller than the characteristic length of transport as seen in our profiles. As such it allows us to investigate the details of the front.

These analysis can be used to define a representative elementary volume characteristic for the durability problem. This can be used to identify the main mechanisms at play. For example, in the case of carbonation the advancement at 6 months is limited to the first hundreds of micrometers. However, the apparent carbonation front is also a hundred micrometers. This is only an apparent carbonation front, because the front is narrower if it is observed directly on the EDS composite maps (figure 1). Locally it can be seen that the front is at most 50 micrometer. However, the front is non-sharp and tortuous. This micrometer scale tortuosity creates a wider apparent diffusion coefficient. This tortuosity should be considered when identifying the representative elementary volume.

However, Figure 1 shows that no clean representative elementary volume can be defined for this experiment since the scale of the heterogeneities is close to the scale of the front. It means that no single effective diffusion coefficient can be defined, instead a distribution of diffusion coefficient needs to be defined. This distribution of diffusion coefficient will widen the front even if local thermodynamic equilibrium is assumed [7].

The same problem does not impact as strongly the chloride diffusion. The diffusion profiles are wider (a few millimeters) and the microstructure is more homogeneous at the millimeter scale. Therefore, a correct representative volume can be defined, as well as a unique chloride diffusion coefficient in the cement paste. However, it should be noted that the aggregates still create large scale heterogeneities. For example, it can be seen on figure 3 that the Cl/Ca ratio in AFm and in CSH is null at 25mm. However, the total chloride content is not 0. The total chloride content is measured over a much larger volume than the EDS maps. This higher content is probably due to the heterogeneities caused by the aggregates which widen the apparent diffusion profile.

### 4.2 The chloride solid solution

The wide front of the bulk diffusion problem is assumed to be due to the solid solution between the AFm and the Friedel's salt, where the total content of chloride in AFm is

increasing with the chloride concentration in solution. Most chloride ingress models assume a monosulfate based solid solution. However, most OPC contains at least 2 % limestone which is sufficient to transform all sulfate-AFm into carbonate-AFm [8]. However, this solid solution is less known and the necessary data for proper validation is lacking [6]. Our method provides the amount of chloride in the solid solution along with the bulk diffusion profiles, or the electromigration front. This is an important information as it allows to decouple the chemical and the transport mechanisms when validating reactive transport models. In particular it can be noted in figure 5 that only a fraction of the maximum binding capacity in AFm is reached in this electro-migration experiment ( $Cl/Ca = 0.15 < 0.5$ ). In the bulk diffusion profile, higher values are reached however they are still half of the maximum value.

## 5. CONCLUSIONS

Validating reactive transport models on profiles of macroscopic experiments is challenging for cementitious materials due to the different mechanisms occurring simultaneously. The use of the *edxia* framework for quantitative image analysis of SEM-EDS maps provides comprehensive and complementary information on the microstructure:

- The phases formed can be identified;
- The composition of these phases can be measured;
- The analysis can be done along the depth of the sample and compared to standardized macro-scale measurements.

For example, the fate of sulfur was studied in carbonating sample. In addition to validating mechanisms seen in simulations [4], this study provided some insight on the representative elementary volume necessary to define the effective transport properties. Large heterogeneities exist at the scale of the front and creates a sharp but tortuous front which could be misinterpreted as kinetically-controlled reaction. For chloride ingress, we demonstrated that we can obtain crucial information on the chloride binding (usually neglected in assumptions). This information is key to decouple the transport and chemical mechanisms.

Future studies will focus on coupling this method with complementary methods to study the microstructure, and on applying these results to validate reactive transport modelling of chloride ingress.

## ACKNOWLEDGEMENTS

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