

Experiment Report Form



	Experiment title: Understanding the interactions between CO ₂ and novel cement materials via advanced XRD-CT	Experiment number: MA5424
Beamline:	Date of experiment: from: 19-09-2022 to: 24-09-2022	Date of report: 07.09.2023
Shifts:	Local contact(s): Dr Partha Paul Dr Marco Di Michiel	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):
 Prof. Susan Bernal Lopez, University of Leeds, UK (Main proposer)
 Prof. Phillip Withers, University of Manchester, UK
 *Prof. John L. Provis, PSI, Switzerland (previously at the University of Sheffield, UK)
 *Dr. Alastair Marsh, EPFL, Switzerland (previously at the University of Leeds, UK)
 *Mr Zengliang Yue, University of Leeds, UK
 *Mr Zixian Su, University of Manchester, UK

Preliminary report:

In this document, only results derived from the analysis of sodium sulfate-activated slag cements are presented. Analysis of data collected for alkali-activated cements produced with other activators is also progressing. A workflow for data analysis has now been created, and there is confidence that the results are highly representative of the systems analysed. Fig 1A shows a schematic of the assumed layered carbonation progress once a hardened cement paste sample is exposed to CO₂. For analysis of the XRD-CT results, every 10-pixel (0.1 mm) thick layer was cropped from the outside to the core of the specimen to determine changes in the crystalline phases forming upon carbonation. Fig 1B presents the averaged XRD patterns of each cropped layer. As CO₂ tends to transport from the surface to the core, the bound amount of CO₂ decreases. Correspondingly, a marked increase is observed in the crystalline ettringite phase (peak at 2θ ~9°). Besides, a highly amorphous sulfate-intercalated layer double hydroxide (marked by the broad peak at ~12°) was found, whose formation has been hypothesised but never experimentally observed in these cements. A subtle decrease in the gypsum and vaterite phases from the surface to the core of the specimen was observed.

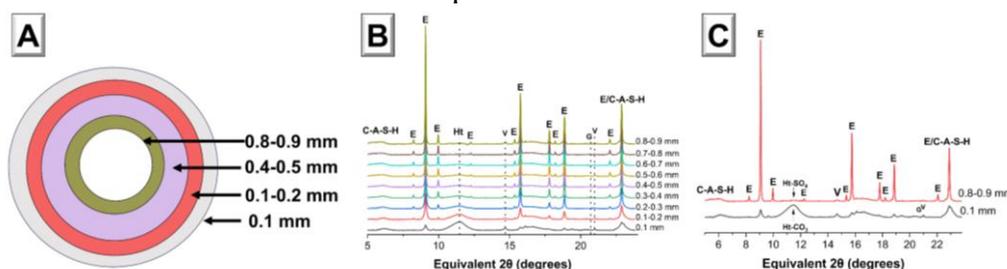


Figure 1. (A) Illustration showing the cropped layer of carbonation material assumed in cylindrical sulfate-activated slag cements for analysis of XRD-CT results; (B) Cu-Kα equivalent XRD pattern of the cropped layer from outside to inside of the specimen after two cycles of carbonation; (C) the comparison of XRD patterns between 0.1 mm of side layer and 0.8-0.9 mm of the core layer. Values indicate the distance (unit: mm) of the

cropped layer from the surface of the specimen. Phases indicated in the XRD patterns correspond to C-A-S-H-calcium aluminium silicate hydrate; E-ettringite; Ht-CO₂-layered double hydroxide (hydrotalcite); G-gypsum; V-vaterite.

Figure 2 (A-C) shows the spatial distribution of ettringite, one of the main secondary crystalline phases typically forming in sulfate-activated slag cements. This mineral gradually disappears under carbonation in the layer close to the surface, evidenced by the reduced intensity of its (100) peak at 9.138°(2θ). These results suggest that ettringite is one of the phases governing the carbonation in sodium sulfate-activated slag cements. This observation is consistent with lab-based results where a reduction in the quantity of ettringite was observed in samples exposed to 1 % CO₂ [1]. Fig 2 (E and F) shows the spatial distribution of MgAl-CO₃-LDH upon carbonation. This phase is precipitated in the surface regions exposed to CO₂; the SO₄²⁻ analogue group has a highly crystalline amorphous structure in uncarbonated samples. A similar phenomenon was observed in carbonated sodium carbonate-activated slag [2]. This LDH phase absorbs CO₂ from the environment without leading to the degradation of mechanical properties in alkali-activated cements [2]. The observation of SO₄²⁻ intercalated MgAl-LDH reveals that sulfate tends to bind into the ettringite and MgAl-LDH phases during the sodium sulfate-activation of slag. When the sulfate is consumed in the pore solution, the chemical reaction proceeds similarly to a NaOH-activated slag cement system. The higher carbonation resistance of activated slag cements with rich Mg content is related not just to an increased degree of slag reaction but potentially to the formation of a higher amount of LDH phases in this system. These results have significant implications for the selection of the raw materials (e.g. slag) for the production of carbonation-resistant alkali-activated cements.

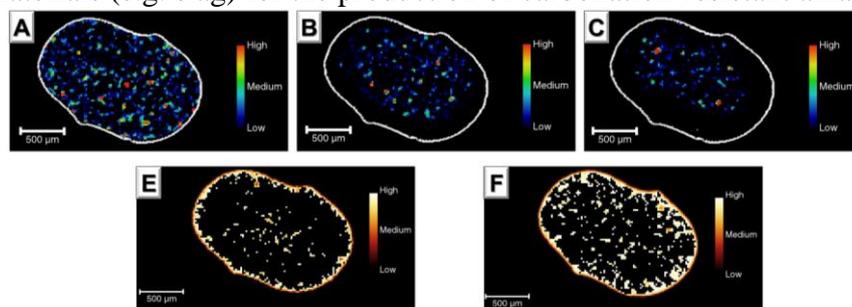


Figure 2. Ettringite spatial distribution in one slice in Na₂SO₄-activated slag cements for uncarbonated (A), one cycle (B) and two cycles (C) of carbonation; MgAl-CO₃-LDH spatial distribution in Na₂SO₄-activated slag cements after one cycle (E) and two cycles (F) The white line (A, B and C) have 1 pixel thick delineating the specimen boundary.

Follow up studies required

These experiments demonstrate the applicability of XRD-CT to understand complex degradation processes of cement materials upon CO₂ exposure. The results derived from this study are providing unique and new insights into the role of secondary reaction products in the carbonation process of these cements. However, when conducting experiments in the previously allocated beamtime, it was not possible to collect data to elucidate how different calcium carbonate polymorphs and how such formation might be linked to the degradation of the main reaction products a calcium aluminosilicate type gel with a tobermorite structure. Since completing these experiments, the applicants have been working on developing strategies to overcome the issues encountered in the first experiments, preventing the collection of data at higher XRD 2-theta values, so that analysis of calcium carbonate polymorphs and degradation of the main reaction product forming in cements can be conducted.

Understanding the type and amount of calcium carbonate polymorphs forming as a function of carbonation of different Ca-bearing phases present in hardened alkali-activated cements, will provide a new understanding about the carbonation mechanism of these cements, and enabling determining the potential ability of carbonation reaction products to precipitate in the pore structure to compensate changes in porosity linked to carbonation. A phenomenon observed in conventional cements, but never evaluated for low carbon cements, such as the ones evaluated in this study.

References

1. Yue, Z., et al. *Influence of Slag Chemistry on the Carbonation of Sodium Sulfate-Activated Slag Cements*. in *International RILEM Conference on Synergising expertise towards sustainability and robustness of CBMs and concrete structures*. 2023. Springer.
2. Ke, X., et al., *Slag-based cements that resist damage induced by carbon dioxide*. *ACS Sustainable Chemistry & Engineering*, 2018. **6**(4): p. 5067-5075.