

SEM-EDS analysis of products formed under natural and accelerated carbonation of concrete with CEM I, CEM II/B-M and CEM II/B-V



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ABSTRACT

Carbonation resistance of concrete is usually tested under accelerated conditions, i.e. by elevating the CO₂ concentration compared to natural conditions and keeping the RH close to 60%. However, it is not clear if these conditions mirror the natural process. Using SEM-EDS we investigated the composition of the reaction products of carbonated and non-carbonated concrete containing 0, 18 and 30% fly ash exposed to three different carbonation conditions. In non-carbonated concrete the reaction products depended on the binder. However, in carbonated concrete the reaction products were similar in composition in all the concretes and exposure conditions tested.

Key words: Carbonation, Supplementary Cementitious Materials (SCM), Testing

1. INTRODUCTION

Carbonation is a spontaneous reaction of the cement paste with the CO₂ present in the atmosphere. It is a slow process under natural conditions (0.03% CO₂) and is therefore accelerated for testing purposes by controlling the relative humidity (50-65%) and using increased CO₂ concentration (e.g. 1 to 50%, see summary in [1]). Carbonation causes changes in microstructure, phase composition and pH of the pore solution in the cement paste [2]. It is, however, not clear if the accelerated exposure conditions cause similar changes compared to natural carbonation.

The investigation is part of a PhD study on carbonation-induced corrosion in fly ash concrete. In the project two different accelerated conditions were used in addition to natural conditions: one to accelerate carbonation (60% RH and 1% CO₂) and one where also corrosion in carbonated concrete is facilitated (90% RH and 5% CO₂). The aim of the investigation is to check if the tested accelerated conditions mirror the natural carbonation process. The phase composition, pore solution and other microstructural features in the carbonated concrete, especially in the vicinity of the reinforcement, will influence reinforcement corrosion. In this paper, we focus on the composition of the reaction products.

2 EXPERIMENTAL

Concretes containing three different cements water-to-binder ratio 0.54-0.56 and 370 kg/m³ cement were prepared. The cements contained limestone addition (4%) and different amounts of fly ash CEM I (0%), CEM II/B-M (18%) and CEM II/B-V (30%), see Table 1. The concrete samples were kept in the mould for three days and when demoulded wrapped in plastic for 11 days. After this period, they were carbonated for 20 weeks. Three exposure conditions were used: "N": natural carbonation sheltered from rain, "1-60": 60% RH and 1% CO₂, and "5-90": 90% RH and 5% CO₂. The temperature was in all cases close to 20°C. Polished epoxy impregnated sections were prepared at the Danish Technological Institute (DTI). All polished sections were carbon coated before testing. A scanning electron microscope Quanta 400 ESEM from FEI operated at high vacuum mode, accelerating voltage of 15 kV, spot size 5 and working distance of around 10 mm was used. The data was Proza corrected. 50 points were manually taken selecting the outer reaction products in carbonated ("Carb") and non-carbonated ("Non") areas of each sample.

3 RESULTS AND DISCUSSION

Figure 1 presents the data obtained by SEM-EDS point analysis. The horizontal axis shows the Si/Ca molar ratio and the vertical the Al/Ca molar ratio. The ideal stoichiometry of the following phases is indicated: calcium hydroxide (CH) and calcium carbonate (CC) in the origin, and on the vertical axes ettringite (AFt) and monosulphate (AFm). The estimated composition of the C-S-H for the tested non-carbonated concretes is marked with large black squares. During the SEM-EDS point analysis a certain volume is analysed, which generally includes a mixture of phases and the resulting point lies in between the ideal stoichiometry of the phases in the mixture. The points taken in the non-carbonated areas indicate the presence of AFm, AFt, CH/CC and C-S-H. In the carbonated areas less AFm and AFt phases seem to be present as fewer points are found between the C-S-H and AFt or AFm compositions. The points associated with C-S-H in the carbonated concrete seem to gather mainly around a Si/Ca ratio from 0.15-0.35. This is opposite of what one would expect. Upon carbonation C-S-H decalcifies [3] and one would expect the data point to move to higher Si/Ca ratios. A possible reason for the observation is that during SEM-EDS point analysis a volume comprising several phases is analysed. The lower Si/Ca ratio may originate from fine intermixing of decalcified C-S-H and CC. This is in line with recent TEM observations indicating the formation of finely dispersed CC crystals in C-S-H upon carbonation [4].

Table 1 – Chemical composition of the cements determined by XRF [% by mass]

Cement	Label	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	P ₂ O ₅	K ₂ O	Na ₂ O
CEM I	A	20.4	4.8	3.4	61.7	2.2	3.5	0.2	0.9	0.5
CEM II/B-M	B	27.5	8.4	3.9	52.7	1.6	2.6	0.2	0.6	0.5
CEM II/B-V	C	29.5	10.8	4.5	44.6	2	3.2	0.4	1.1	0.5

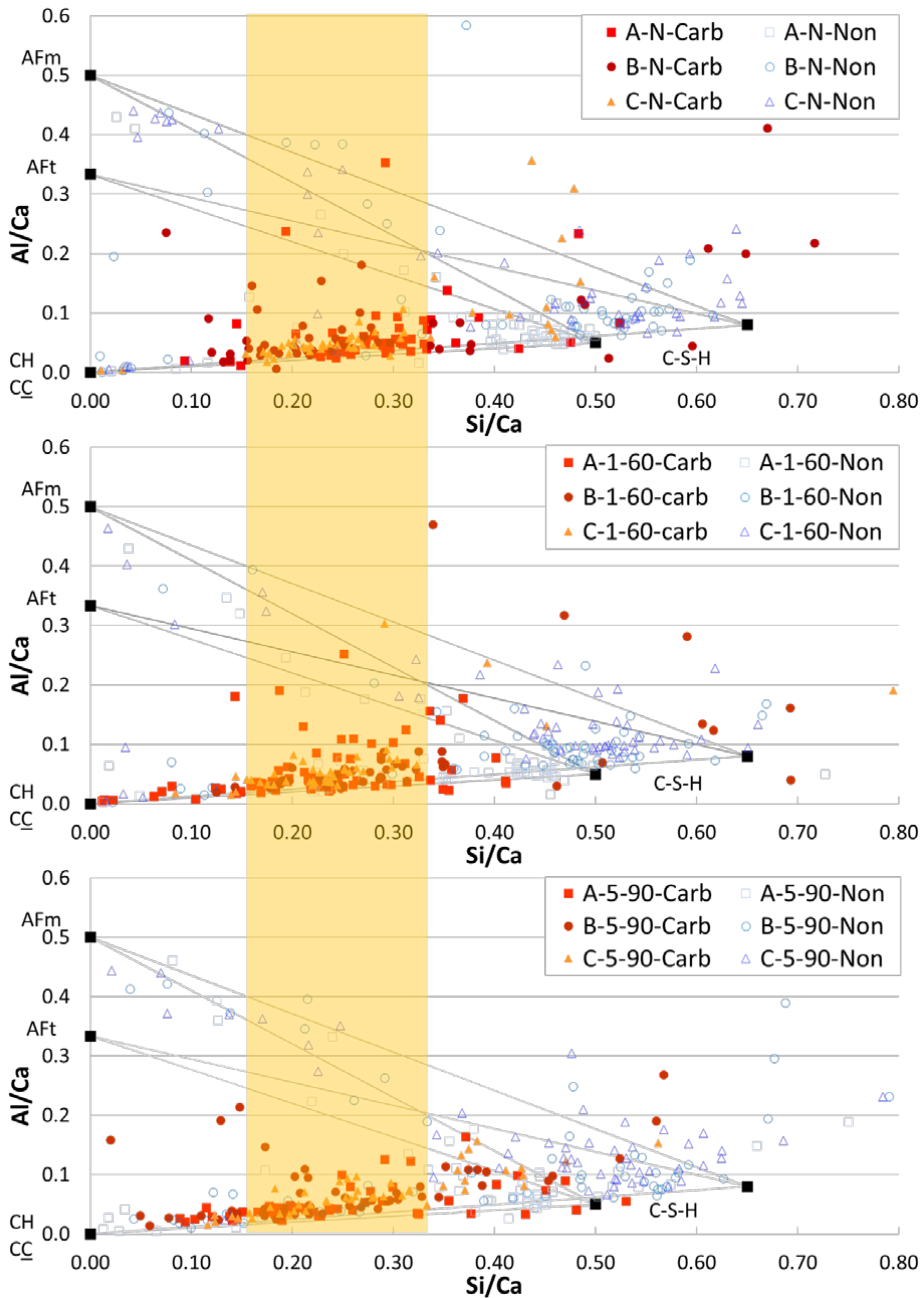


Figure 1 – SEM-EDS point analysis, Si/Ca versus Al/Ca ratios. The ideal composition of ettringite (AFt), monosulphate (AFm), portlandite (CH) and calcium carbonate (CC), as well as the estimated compositions of C-S-H in the non-carbonated concretes with fly ash (Si/Ca=0.65) and without fly ash (Si/Ca=0.5) are marked. The shaded area indicates the data points in carbonated concrete (0.15-0.35 Si/Ca) where decalcified C-S-H is finely intermixed with CC.

The lowering of the Si/Ca ratio of C-S-H related points upon carbonation indicates that Ca redistributes in the system. For example, Ca originating from portlandite will dissolve and precipitate as very small CC crystals finely intermixed with the decalcified C-S-H. Note that a mass balance of the Ca cannot be performed as only few manually selected points were analysed. Similar observations using SEM-EDS point analysis on mortars containing similar binders exposed to 60% RH and 1% CO₂ were reported earlier [5]. The results presented in this paper show that upon carbonation decalcified C-S-H is finely intermixed with CC independently of the binder as well as the exposure conditions. As the reaction products are in equilibrium with the pore solution, the results indicate that the composition of the pore solutions upon carbonation might not be that different either. Assuming similar pore structure, it could lead to comparable concrete resistivity in carbonated concrete. Further research is needed to confirm this.

5 CONCLUSION

Concretes with varying fly ash content were exposed to natural and accelerated carbonation and the reaction products were investigated using SEM-EDS. The data shows that the reaction products upon carbonation are similar for the tested concretes and exposures conditions even if the initial hydration products were different.

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REFERENCES

- [1] Harrison, T., Jones, M., Newland, M. Kandasami, S. and Khanna, G. "Experience of Using the prTS 12390-12 Accelerated Carbonation Test to Assess the Relative Performance of Concrete." *Magazine of Concrete Research* 64 (8): 737-47 (2012)
- [2] Bertolini, L., Elsener, B., Pedferri, P., Redaelli, E. and Polder, R.: "Corrosion of Steel in Concrete", Wiley-VCH Verlag GmbH & Co, Weinheim, Germany, pp. 79-91 (2013)
- [3] Sevelsted, T. F. and Skibsted, J.: "Carbonation of C-S-H and C-A-S-H samples studied by ¹³C, ²⁷Al and ²⁹Si MAS NMR spectroscopy", *Cement and Concrete Research*, Vol. 71, pp. 56-65 (2015)
- [4] Herterich, J., Black, L. and Richardson, I.: "Microstructure and phase assemblage of low-clinker cements during early stages of carbonation", 14th International Congress on the Chemistry of Cement, Beijing, China (2015)
- [5] Revert, A. B., De Weerd, K., Hornbostel, K. and Geiker, M.R.: "Investigation of the effect of partial replacement of Portland cement by fly ash on carbonation using TGA and SEM-EDS", International RILEM Conference on Materials, Systems and Structures in Civil Engineering, Lyngby, Denmark, pp. 413-422 (2016)