

CARBONATION RESISTANCE OF IRON-RICH INORGANIC POLYMERS

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Introduction

The production of Ordinary Portland cement is energy-intensive and linked to the use of limestone, thus emits large quantities of CO₂ (8% of anthropogenic emissions worldwide¹). The cement industry is taking action to address this challenge, yet, current practice seems not very promising and is doubtful if the global temperature rise will be limited below 1.5°C during this century, which is one the global goals set on the Paris climate conference.² Newly emerging eco-friendly alternative binders, like alkali-activated materials and inorganic polymers can be part of the solution.³

When concrete is in contact with CO₂, a carbonation process initiates which neutralises part of the alkaline components of the binder. This process lowers the ductility of Portland cement binders and the pH of their pore solution, which lowers the protection of steel reinforcement by passivation. To that extent, the study of carbonation is important also for the newly emerging eco-friendly alternative binders, such as alkali-activated materials and inorganic polymers.^{4,5}

In this paper, the influence of carbonation on the mechanical properties of an inorganic polymer (FeO_x-SiO₂-CaO slag with a sodium silicate activator) is tested for different curing times, curing temperatures and curing atmospheres (ambient air and a 2% CO₂ atmosphere). The results are compared with CEM-II samples which are processed under identical conditions. The effect on steel reinforcement is not considered, but is the subject of future work.

Experimental

Synthetic FeO_x-SiO₂-CaO slag was produced with the same procedure as in a previous work⁶, by melting analytical grade oxides and casting the molten slag into a container filled with water. The chemical composition was determined by X-ray fluorescence (XRF) using a Philips PW2400. The mineralogy was studied with X-ray diffraction (XRD) using a Bruker D2 Phaser.

Mortars were made by mixing 526 g of slag with 1350 g of CEN standard quartz sand and 206 g of sodium silicate solution with molar ratios $\text{SiO}_2/\text{Na}_2\text{O} = 1.8$ and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 20$. The mixing procedure described in EN196-1 was followed and mortar bars of $40 \times 40 \times 160 \text{ mm}^3$ were cast. The samples were cured at 20°C or 40°C , a relative humidity of 60% and a 0.04 vol% (= ambient) or 2 vol% CO_2 atmosphere. The compressive strength measurements were carried out after 7, 14 or 28 days with an Instron 5985 (load cell 250 kN and crosshead speed of 1 mm/min) and compared with a CEM-II mortar (450 g CEM II, 1350 g sand, 200 g water) cured for the same time and in the same conditions. The same preparation procedures and Instron 5985 were used for three point bending tests (but with crosshead speed: 0.5 mm/min). Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was performed on a Bruker Alpha-P using 32 scans/measurement with a resolution of 4 cm^{-1} . The presented spectra are the average of 2 measurements.

Results and discussion

The chemical composition (XRF) is presented in Table 1. No diffraction peaks were observed in XRD with the settings: 30 kV, 10 mA, $0.02^\circ 2\theta/\text{step}$, 0.6 s/step. The amorphous fraction should thus be at least 95 wt% (Table 1).

Table 1: Slag characteristics; the chemical composition from XRF and amorphous fraction from XRD

Chemical composition (wt%)				Amorphous (wt%)
FeO	SiO_2	CaO	Al_2O_3	
54%	31%	14%	1%	> 95%

The compressive strength of the inorganic polymer mortar and the CEM-II mortar at ambient CO_2 concentrations are equivalent at room temperature and 40°C (Figure 1), reaching approximately 40 MPa after 7 days and 50 MPa after 28 days. The exposure to 2 vol% CO_2 drastically increases the compressive strength of the inorganic polymer samples, going to $91 \pm 4 \text{ MPa}$ and $101 \pm 4 \text{ MPa}$ at 28 days at room temperature and 40°C , respectively. The OPC samples show a 20% increase in strength.

After exposure of the OPC samples to a 2 vol% CO_2 environment, multiple cracks could be observed. This caused immediate fracture during three-point bending tests which indicates a reduction in ductility during carbonation. The inorganic polymers had no sign of any cracks and no reduction in bending strength after exposure to a higher CO_2 concentration, indicating a potentially interesting benefit of inorganic polymer concrete over OPC.

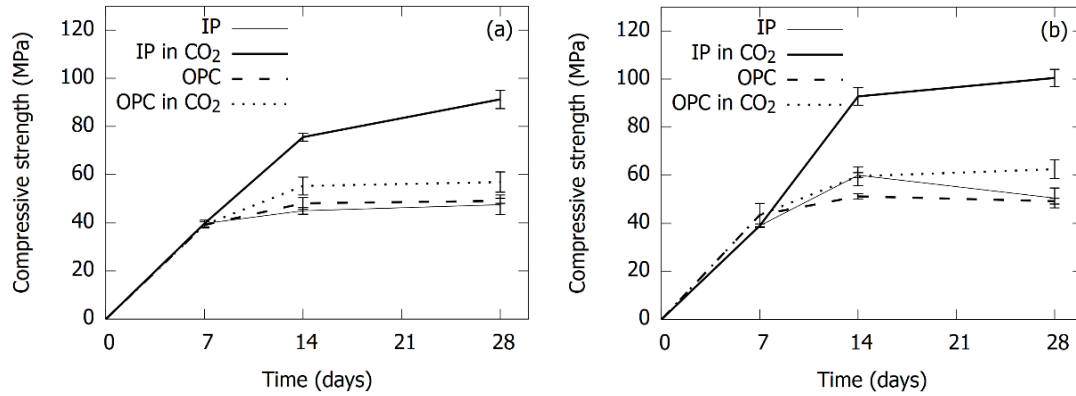


Figure 1: Compressive strength evolution of samples cured at (a) room temperature and (b) 40°C

No peaks are observed in XRD after the accelerated carbonation, the present carbonates are amorphous. Additionally, the polymerisation degree (*i.e.* the position of the Si-O stretching band in Figure 2) was not affected, as opposed to results for alkali-activated blast furnace slag.⁵ A more detailed characterisation of the carbonation products was performed by comparing the results before and after a washing step. During this step, the samples (mortars for compressive testing, powders for FTIR spectroscopy) were immersed in water for 7 days to dissolve water soluble carbonates, *i.e.* sodium carbonates. FTIR spectroscopy shows bands at 1450 cm⁻¹ before and after washing in Figure 2. The intensity seems to have declined after washing, indicating that at least part of the carbonates are water soluble Na-carbonates. The compressive strength results in Figure 3 do not show a statistically significant effect of the washing. The reinforcing effect is thus caused by water insoluble carbonates (Ca- or Fe-carbonates). The studied system thus develops a combination of Na- and water insoluble carbonates when exposed to 2% CO₂, where the effect on the compressive strength gain is caused by the formation of the water insoluble carbonates.

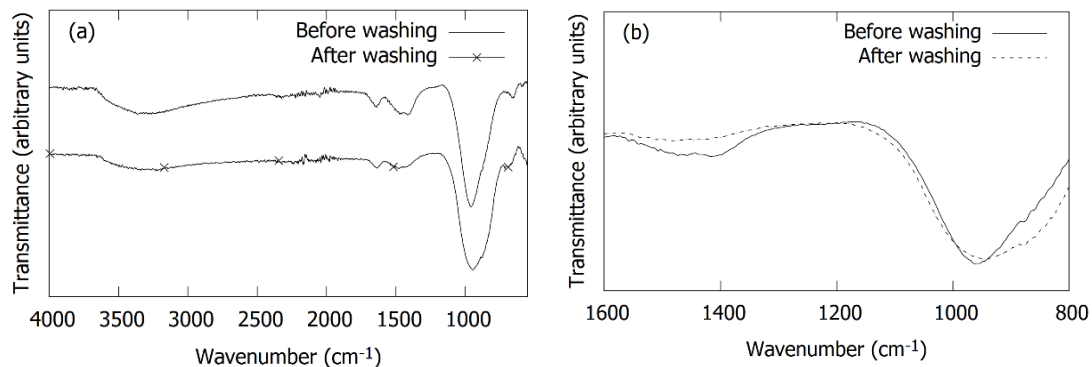


Figure 2: ATR-FTIR after 28 days at 40°C and 2% CO₂, compared before and after washing the samples for 7 days in water; (b) is a zoomed and not stacked version of (a), in the range 1600-800 cm⁻¹

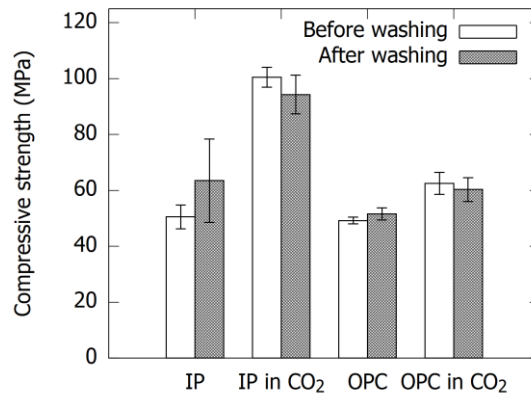


Figure 3: Compressive strength after 28 days at 40°C and 2% CO₂, compared before and after washing the samples for 7 days in water

Conclusion

After curing in a CO₂-rich environment, the compressive strength of Fe-silicate inorganic polymer rises significantly; after 28 days the inorganic polymer reached 91 ± 4 MPa at room temperature, 101 ± 4 MPa at 40°C. The increased compressive strengths are due to the formation of water insoluble carbonates during the carbonation process in the inorganic polymer, filling the pores of the material. No crack formation is observed, which was observed to be a problem in the tested CEM-II formulation.

Acknowledgements

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