

Effect of Carbonation on the Microstructure and Phase Development of High-Slag Binders



M. J. Tapas, A. Yan, P. Thomas, C. Holt, and V. Sirivivatnanon

Abstract The drive for sustainable concrete production favors the use of high replacement levels of supplementary cementitious materials (SCMs) in the concrete mix. The use of SCMs such as fly ash and slag, however, although they improve the sustainability of concrete production as well as most concrete durability properties, increases the carbonation rate. Carbonation decreases the pH of the concrete pore solution, making the steel reinforcement susceptible to corrosion. The effect of carbonation is, however, not confined to the change in pH of the pore solution. We investigated changes in the microstructure and phases of high-slag binders due to carbonation. The carbonation resistance of mortars with 50 and 70% slag replacement were investigated at exposure conditions of 2%CO₂, 50%RH, 23 °C. The carbonated and non-carbonated parts of the mortars were subjected to various characterization techniques to investigate the effect of carbonation on microstructure and phase development. Results confirmed the absence of portlandite in all the carbonated regions (“colorless” by phenolphthalein test, which indicated that the change in color of the phenolphthalein solution was due to the absence of portlandite to buffer the pH). Significant reduction in the amount of C-S-H, as well as increase in the amount of calcium carbonate, were been observed in the carbonated regions. Aragonite, a polymorph of CaCO₃, was very prominent in all the carbonated mortars.

Keywords Carbonation · Microstructure · Slag

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1 Introduction

Concrete, the most utilized construction material and the second most used substance on earth after water, creates significant amount of CO₂ emissions during production [1]. The CO₂ emissions primarily originate from the calcination of limestone (CaCO₃) to produce cement (main binder material in concrete), releasing CO₂ in the process. As CO₂ contributes to global warming, there has been a strong focus on the decarbonation of concrete, and reducing the amount of cement per cubic meter of concrete is a proven approach to deliver on the target CO₂ reduction. Reducing the cement content can be achieved through partial cement substitution with supplementary cementitious materials (SCMs) such as slag or fly ash. Slag, being hydraulic in nature like cement, can be used at higher substitution rates than other SCMs (usually $\geq 50\%$), translating to better CO₂ reduction. However, although slag notably improves the later-age strength as well as most concrete durability properties, including chloride ingress [2], the alkali–silica reaction [3–5], sulfate resistance [6, 7], and delayed ettringite formation [8], its use results in increased susceptibility of the concrete to carbonation [9–11].

Carbonation refers to the ingress of CO₂ into the binder system, which results in the formation of carbonic acid (H₂CO₃) that further dissociates into H⁺ and CO₃²⁻ and reacts with calcium ions in the pore solution, resulting in the precipitation of calcium carbonate (CaCO₃) and a decrease in the pH of the pore solution. Low concrete pH (≤ 9.5) resulting from carbonation is detrimental to steel-reinforced concrete because steel begins to lose its passivation layer at low pH, making it susceptible to corrosion [10]. Thus, carbonation is a serious durability concern, particularly for steel-reinforced concrete [12].

Phenolphthalein is an indicator used to assess the depth of carbonation. It is colorless at lower pH values (≤ 9), whereas at pH > 10.5, it presents a characteristic purple or magenta. Because mortar or concrete that has been carbonated has pH ≤ 9 , phenolphthalein is used to visually confirm the drop in pH due to carbonation [13]. The effect of carbonation is, however, not confined to the change in pH of the pore solution. Although it has been reported that carbonation in general is beneficial and results in an increase in compressive strength due to the conversion of Ca(OH)₂ to CaCO₃, which increases the volume of the binder and reduces porosity [10], it appears that this may not be true for all binder systems. It has been reported that although moderate carbonation can improve the mechanical properties of the concrete, excessive carbonation impairs mechanical strength due to the decalcification of the C-S-H [14]. High-slag concrete is also particularly susceptible to carbonation shrinkage [9]. Therefore, due to variability in the reported effect of carbonation and considering the increasing levels of slag being used in concrete production, a better understanding of the effect of carbonation on microstructure and phase development is required.

We investigated the effect of carbonation on the microstructure and phase development of high-slag mortars (50% and 70% slag replacement). The mortars were characterized after being subjected to accelerated carbonation conditions (2%CO₂, 23 °C, and 50% relative humidity (RH) for 112 days.

Table 1 Mortar mixes

Mix details	Normen sand (g)	Cement (g)	Slag (g)	Total binder (g)	Water (g)
OPC	1350	450.0	0.0	450.0	171.0
OPC + 50% slag	1350	225.0	225.0	450.0	171.0
OPC + 70% slag	1350	135.0	315.0	450.0	171.0

OPC, ordinary Portland cement

2 Methods

2.1 Raw Materials

We used General Purpose cement and slag that complied with AS3972 and AS3582.2 respectively. Normen sand (CEN Standard Normsand according to EN196-1) was used as fine aggregate. The maximum moisture content of sand was 0.2%.

2.2 Carbonation Test

The $40 \times 40 \times 160$ mm mortars were prepared using Normen sand in combination with ordinary Portland cement (OPC) and OPC + slag binders (slag at 50% and 70% replacement) at 0.45 water to cement ratio. Table 1 shows the mortar mixes investigated in this study.

The mortars were demolded after 1 day, cured for 28 days inside a sealed moisture bag and then transferred into the shrinkage room (50%RH, 23 °C) to air cure for 7 days in preparation for the accelerated carbonation test. At age 35 days (28 + 7 days), the mortars were transferred into the carbonation chamber running at 2%CO₂, 50%RH and 23 °C for the accelerated carbonation test. Carbonation depth measurements using phenolphthalein (1% solution) were carried out after 1 week (7 days), 4 weeks (28 days), 9 weeks (63 days), and 16 weeks (112 days) exposure of the mortars in the carbonation chamber.

2.3 Characterization of the Mortars

After 112 days carbonation, the “colorless” and “pink regions” of the mortars were subjected to thermogravimetric analysis (TG; SDT-Q600 Simultaneous TGA/DSC equipment, TA Instruments) and scanning electron microscopy (SEM). The mortar specimens were ground and 50-mg samples of the ground material were transferred to a platinum crucible, which was placed inside the TG instrument. The thermal

analysis was performed in a nitrogen gas atmosphere, within a temperature range of 23–900 °C and at a heating rate of 10 °C/min.

All imaging and elemental analyses of the fractured mortars were performed using a Zeiss Supra 55VP SEM fitted with a Bruker SDD EDS Quantax 400 system and FEI Quanta 200 with Bruker XFlash 4030 EDS detector. The microscopes were operated at 15 kV accelerating voltage and 12.5 mm working distance.

3 Results and Discussion

Figure 1 shows the carbonation depths at 16 weeks (112 days). As expected, the plain OPC mortar showed the best resistance to carbonation (largest pink region) while mortars with slag exhibited poorer resistance. The higher the slag replacement, the poorer the carbonation performance.

Figure 2 shows the increase in carbonation depth over time, with the mortar with 70% slag consistently having the highest carbonation depth and fully carbonated at 63 days.

Figure 3 shows the TG curves of the non-carbonated (pink) and carbonated parts (colorless) of the plain OPC mortar, mortar with 50% slag and the mortar with 70% slag. Mass loss in the range of calcium hydroxide (CH) decomposition at ≈ 400 – 500 °C corresponds to the dehydroxylation of CH, ($\text{Ca}(\text{OH})_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$) [15]. Therefore, the area under the curve at ≈ 400 – 500 °C corresponds to the amount of CH, and thus a larger area means more CH. Comparing the CH content of plain OPC mortar and the 50% slag mortar (pink regions), OPC notably has more CH, as may be expected, which explains its better carbonation resistance. During carbonation, portlandite, which is the most soluble source of calcium in the binder, serves as a buffer and maintains the pH of the pore solution by dissolving and releasing OH^- and Ca^{2+} ions. The OH^- neutralizes the H^+ while Ca^{2+} binds CO_3^{2-} , precipitating CaCO_3 [11]. Therefore, due to the lower amount of portlandite, high-slag binders carbonate much faster (i.e. pH drops faster) than pure cement. Absence of portlandite in the

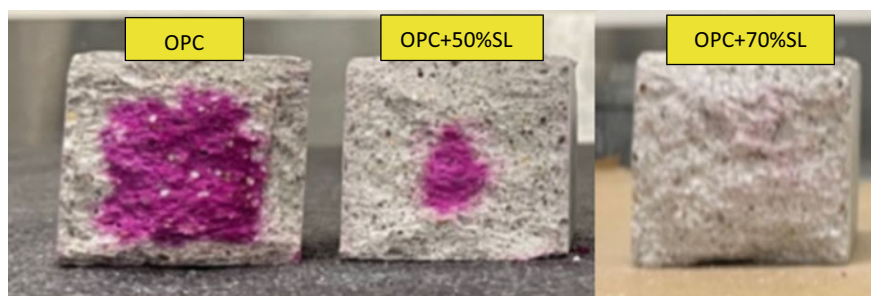


Fig. 1 Photos of the mortars (OPC, OPC + 50% slag and OPC + 70% slag) at 112 days exposure in the carbonation chamber showing the carbonation depth determined using phenolphthalein

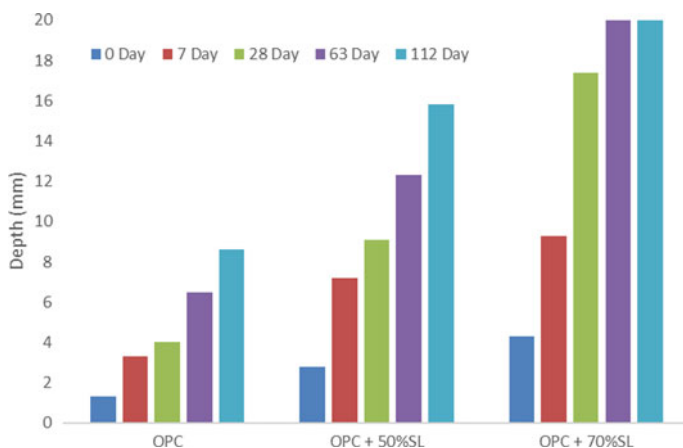


Fig. 2 Carbonation depth measurements before carbonation (Day 0) and after 7, 28, 63 and 112 days exposure to 2%CO₂ at 23 °C and 50% relative humidity. OPC, ordinary Portland cement; SL, slag

“colorless regions” of the plain OPC and 50% slag mortars are notable indicating the full consumption of portlandite in the carbonated regions. There is also no portlandite remaining in the 70% slag mortar, consistent with it being fully carbonated (top and middle areas of the mortar were tested). Moreover, consequent to the full consumption of portlandite in the “colorless regions” of all mortars (i.e., fully carbonated regions), there was a drastic increase in the amount of CaCO₃. A notable decrease in the amount of C-S-H, carboaluminates, and ettringite (TG region 0–300 °C) can also be seen, because once portlandite has been fully consumed, the other calcium-bearing phases start to react with CO₂ and carbonate as well [10]. Decalcification of the C-S-H can occur, resulting in carbonation shrinkage [12].

Figure 4 shows the amount of CaCO₃ in the different binder systems (carbonated regions) calculated from the decarbonation region (CaCO₃ → CaO + CO₂). The higher the amount of CaCO₃ formed, the higher the CO₂ binding capacity. CO₂ binding capacity is related to the amount of CaO in the binder and because the higher the slag replacement, the lower the CaO available, the CO₂ binding capacity also decreases.

SEM images of the fractured “carbonated” 50% and 70% slag mortars are shown in Figs. 5 and 6 respectively. The presence of aragonite (a CaCO₃ polymorph) is very prominent in both systems. The microstructure also appears to be porous, although the change in porosity due to carbonation should be quantified.

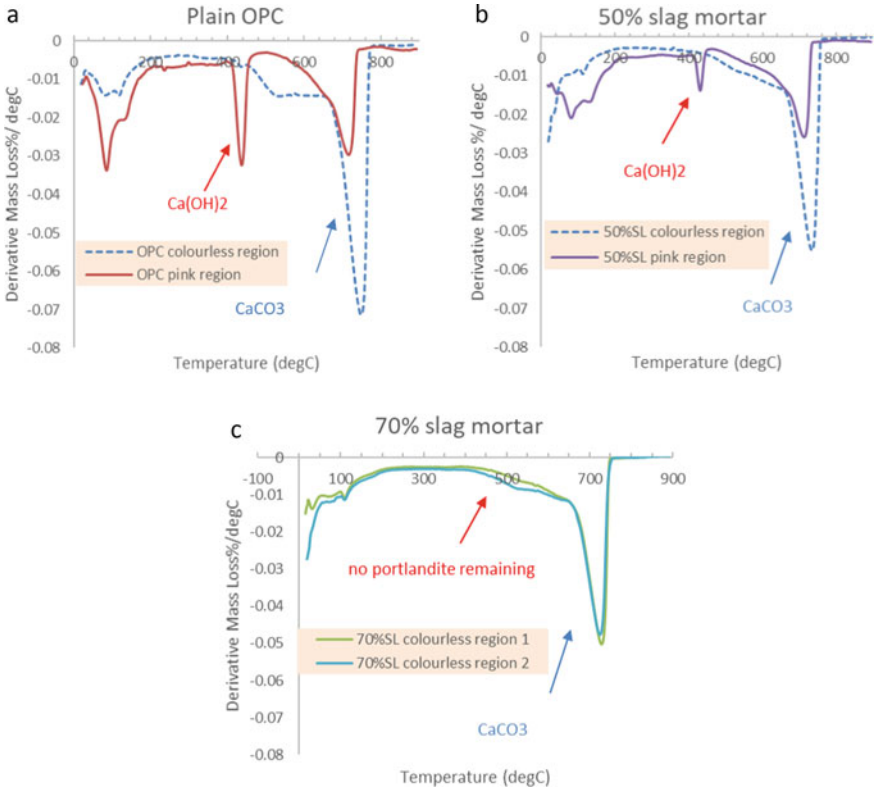


Fig. 3 Derivative thermogravimetric curves of the carbonated and non-carbonated part of plain OPC, 50%SL mortar and 70%SL mortar. OPC, ordinary Portland cement; SL, slag

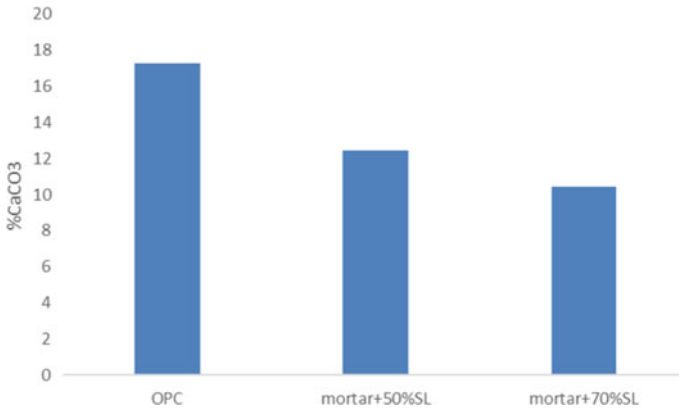


Fig. 4 Percentage CaCO₃ in the plain OPC, 50%SL mortar and 70%SL mortar determined from the thermogravimetric mass loss measurements. OPC, ordinary Portland cement; SL, slag

5. SEM images confirmed the prominent presence of aragonite (a CaCO_3 polymorph) in the carbonated mortars.

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