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Effect of silicate modulus and metakaolin incorporation on the carbonation of alkali silicate-activated slags

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ABSTRACT

Accelerated carbonation is induced in pastes and mortars produced from alkali silicate-activated granulated blast furnace slag (GBFS)–metakaolin (MK) blends, by exposure to CO_2-rich gas atmospheres. Uncarbonated specimens show compressive strengths of up to 63 MPa after 28 days of curing when GBFS is used as the sole binder, and this decreases by 40–50% upon complete carbonation. The final strength of carbonated samples is largely independent of the extent of metakaolin incorporation up to 20%. Increasing the metakaolin content of the binder leads to a reduction in mechanical strength, more rapid carbonation, and an increase in capillary sorptivity. A higher susceptibility to carbonation is identified when activation is carried out with a lower solution modulus (SiO_2/Na_2O ratio) in metakaolin-free samples, but this trend is reversed when metakaolin is added due to the formation of secondary aluminosilicate phases. High-energy synchrotron X-ray diffractometry of uncarbonated paste samples shows that the main reaction products in alkali-activated GBFS/MK blends are C–S–H gels, and aluminosilicates with a zeolitic (gismondine) structure. The main crystalline carbonation products are calcite in all samples and trona only in samples containing no metakaolin, with carbonation taking place in the C–S–H gels of all samples, and involving the free Na^+ present in the pore solution of the metakaolin-free samples. Samples containing metakaolin do not appear to have the same availability of Na^+ for carbonation, indicating that this is more effectively bound in the presence of a secondary aluminosilicate gel phase. It is clear that claims of exceptional carbonation resistance in alkali-activated binders are not universally true, but by developing a fuller mechanistic understanding of this process, it will certainly be possible to improve performance in this area.

1. Introduction

Durability is one of most important properties of cementitious materials because it is associated with the life service of civil structures, and is modified by the interaction of the material with the environment. The presence of CO_2 in the atmosphere, including the higher levels now being induced by human-derived CO_2 emissions, affects the long-term durability of built structures through the sequence of degradation phenomena that are jointly referred to as carbonation [1–4]. The mechanism of carbonation consists of diffusion through gas, aqueous and solid/gel binder phases, as well as chemical reaction processes. The overall rate of carbonation is controlled by the physical properties of the solid binder, in particular the porosity and pore size distribution of the material and the CO_2 permeability through the porous network. Gas diffusion is in many situations the slowest step of the overall process [5–7].

The carbonation of Portland cement (OPC) mortar and concrete is a widely studied and well-understood phenomenon. Carbon dioxide in the atmosphere diffuses inside the material and dissolves in the pore water, forming carbonic acid. Carbonic acid may then attack calcium-containing phases, initially the calcium hydroxide and then calcium silicate hydrates (C–S–H) and calcium aluminate hydrates (C–A–H), to form calcium carbonate. This leads, in the long-term, to a reduction of the alkalinity in the cementitious system, accompanied by reduced mechanical performance and the corrosion of steel reinforcement [1–3,5–7].

Under natural environmental conditions the process of carbonation of cementitious materials is a long-term reaction as consequence of the relatively low CO_2 concentration present in the atmosphere ($\approx$0.038% v/v). Therefore, accelerated carbonation testing is often used in order to induce the carbonation of concretes. Castellote et al. [8], using OPC pastes assessed under accelerated carbonation test conditions, have identified that the reaction products formed at a CO_2 concentration of 3% are comparable with those observed in samples carbonated at natural conditions. This indicates that this degree of acceleration of the carbonation process does not

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introduce new carbonation mechanisms which would not be observed under natural environmental conditions for those materials; the same was not true for CO_2 concentrations of 10% or higher [8].

Several previous studies have examined the carbonation of alkali-activated slag (AAS) and other related alkali-activated binders. Byfors et al. [9] identified that F-concrete (a trade name for a material which used as the binder blast furnace slag activated by a combination of alkali metal compounds) exhibits a higher carbonation rate than Portland cement concrete with the same compressive strength. Bakharev et al. [10] and Puertas et al. [11] also found that alkali silicate- or hydroxide-activated slag mortars and concretes are more rapidly carbonated than comparable OPC mixes, and that this degradation can lead to an important decrease in compressive strength. Those results are coherent with those reported by Palacios et al. [12] and Bernal et al. [13], who suggest that the carbonation mechanism is not the same in Portland and alkali-activated slag cements as consequence of the differences between the reaction products of both systems.

On the other hand, Deja [14] identified a similar carbonation rate in AAS mortars and concretes under service conditions when compared with OPC-based samples. An improvement in the compressive strength with long-term exposure to CO_2 was also reported, and attributed to pore size refinement associated with the deposition of the carbonation reaction products. The previous was more significant in samples activated with $Na_2O \cdot rSiO_2$ in contrast to specimens activated with Na_2CO_3. Xu et al. [15], studying aged concretes (up to 35 years) based on slag activated with carbonates or carbonate/hydroxide blends, observed an acceptable carbonation rate of all samples (0.03–0.5 mm/year), proving the high stability of these AAS binders. These results are contrary to the reports of carbonation problems in AAS mortars and concretes as mentioned above [9–13]. It may also be that there is a distinction to draw here between accelerated and in-service conditions, where the accelerated tests seem to influence alkali-activated materials more severely; this will certainly be an area worthy of further study.

Additionally, it is important to note that there are no previous reports in the literature related to the carbonation mechanism or rate of pastes or mortars based on alkali-activated granulated blast furnace slag/metakaolin (GBFS/MK) blends. Such blends are of interest because the combination of the reaction products obtained after the activation of GBFS/MK (coexisting C–S–H and sodium aluminosilicate hydrate (N–A–S–H) gels) has been recognized as a stable system that could exhibit improved durability when compared to binders prepared from a sole raw material [16–18].

In light of such obvious discrepancies in the previous results regarding the carbonation of AAS binders, and the unknown performance of alkali silicate-activated GBFS/MK blends when exposed to this form of chemical attack, the aim of this work is to study the effect of the activator modulus and the presence of metakaolin on the carbonation of pastes and mortars based on these binders.

2. Experimental program

2.1. Materials

The primary raw material used in this investigation was a Colombian granulated blast furnace slag (GBFS) from the factory *Acerías Paz del Río*. The basicity coefficient ($K_b = CaO + MgO/SiO_2 + Al_2O_3$) and the quality coefficient ($CaO + MgO + Al_2O_3/SiO_2 + TiO_2$) based on the chemical composition (Table 1) were 1.01 and 1.92, respectively. Its specific gravity was 2900 kg/m^3 and Blaine fineness was 399 m^2/kg. The particle size range, determined through laser granulometry, was 0.1–74 μm, with a d_{50} of 5 μm.

The metakaolin used was generated in the laboratory by calcination of a Colombian kaolin containing minor quartz and dickite impurities. Calcination was carried out at 700 °C in an air atmosphere, for 2 h. The particle size range of the MK was 1.8–100 μm, with a d_{50} of 13.2 μm and 10% of particles finer than 4 μm.

Table 1
Composition of the GBFS and MK used, from X-ray fluorescence analysis. LOI is loss on ignition at 1000 °C.

Component (mass % as oxide)	GBFS	MK
SiO_2	32.29	50.72
Al_2O_3	16.25	44.63
CaO	42.45	2.69
Fe_2O_3	2.35	–
MgO	2.87	–
Other	1.88	0.94
LOI	1.91	1.02

Alkaline activating solutions of the desired composition were formulated by blending using a commercial sodium silicate solution with 32.4 wt.% SiO_2, 13.5 wt.% Na_2O and 54.1 wt.% H_2O, and 50 wt.% NaOH solution, to reach the desired modulus (SiO_2/Na_2O molar ratio, denoted Ms) of 1.6, 2.0 or 2.4. A constant activator concentration of 5% Na_2O by mass of GBFS + MK was used.

2.2. Sample synthesis and test procedure

2.2.1. Mortars

Mortars were produced following the standard procedure ASTM C305-06 "*Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency*". River sand with a fineness modulus of 2.75 was used as fine aggregate. All samples were formulated with a constant water/(GBFS + MK + anhydrous activator) ratio of 0.47 and a binder/sand ratio of 1:2.75. While this is quite a high water content for alkali-activated mortars, it was designed to replicate a binder formulation which has been used successfully in the preparation of AAS concretes [18]. The specimens were cast in cubic moulds with dimensions of 50.8 × 50.8 mm, and stored under controlled humidity (relative humidity (RH) ~85%) and ambient temperature (~25 °C) for 24 h. Samples were then demolded and cured under RH of 90% and a temperature of 27 ± 2 °C for 28 days.

2.2.2. Pastes

Pastes with a constant water/(GBFS + MK + anhydrous activator) ratio of 0.23 were produced in accordance with the standard procedure ASTM C305-06. The specimens were cast in a cylindrical mould and stored in hermetic containers with a relative humidity of 90% and a temperature of 27 ± 2 °C for 28 days.

2.3. Carbonation

An accelerated carbonation testing system was used in order to induce the carbonation of concretes. The conditions used were a CO_2 concentration of 3.0 ± 0.2%, a temperature of 20 ± 2 °C, and RH = 65 ± 5%.

In order to perform the carbonation measurements, the specimens were removed from the chamber after 340 or 540 h of exposure. The depth of carbonation was measured by treating the surface of a freshly cleaved specimen with a 1% solution of phenolphthalein in alcohol. In the uncarbonated part of the specimen, where the mortar was still highly alkaline, purple-red coloration was obtained, while no coloration is observed in the carbonated region. Each reported result represents the average depth of the carbonation measured at eight points, using two replicate samples (four points per sample). The properties of uncarbonated samples after 28 days of curing are used as reference values, indicated as zero hours of exposure.

Carbonated and uncarbonated mortars were tested following the standard procedure ASTM C 109/C, *Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (using 2-in. or [50-mm] Cube*