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Effect of the activator dose on the compressive strength and accelerated carbonation resistance of alkali silicate-activated slag/metakaolin blended materials

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Abstract

The effects of activator dose on the properties of alkali-activated slag/metakaolin blends, were studied in fresh and hardened states: heat evolution, strength and accelerated carbonation. High activator concentrations affect the slag dissolution rate, reducing compressive strength when this is the sole precursor. An increased activator concentration favours metakaolin reaction, promoting high strengths and reduced permeability. Metakaolin addition, and increased activator concentrations reduce the susceptibility to carbonation, associated with the refinement of the pore network under extended CO_2 exposure. The effect of adding an aluminosilicate precursor to an alkali-activated slag system is strongly dependent on the activator concentration.

Keywords: Alkali-activated slag, metakaolin, isothermal calorimetry, compressive strength, accelerated carbonation

1. Introduction

Alkali-activation technology is attracting the attention of industry and academy as a suitable alternative for valorisation of large streams of industrial wastes and by-products, for the production of environmentally friendly cementitious materials. Alkali-activated binders can develop advantageous properties for application in the construction sector,

such as high mechanical strength at early times of curing, high resistance to acid attack, and high performance when exposed to elevated temperatures, depending on the nature and dose of the precursor and activator used, and the curing conditions adopted [1-3]. The main raw materials typically used as precursors for alkali-activation are those which are also used as supplementary cementitious materials (SCMs) in Portland cement blends, such as blast furnace slag from the iron making industry, fly ashes from coal combustion, and thermally treated clays such as metakaolin [4, 5]. The nature of these raw materials is highly variable from source to source, and therefore, the production of alkali-activated binders requires higher quality control than conventional Portland cements, in order to develop specific desired properties.

Alkali-activated slag binders can develop high mechanical strengths at early times of curing, with a lower permeability than identified in Portland cements [6]; however, blast furnace slags are already extensively exploited by the construction industry for the production of blended Portland cements. Consequently, in some parts of the world different precursors are needed for the production of alkali-activated binders. As a potential solution, the development of alkali-activated binders using blends of two or more precursors has been carried out over the past decades, including blended systems of fly ash/slag [7-10], fly ash/metakaolin [11] and slag/metakaolin [12-16]. These binders usually present improved properties compared to systems where the aluminosilicate precursors are activated alone, with a microstructure including co-existing Ca-rich and Na-rich reaction products, depending on the fraction of the Ca-rich precursor incorporated in the blend.

There is not yet a standardised methodology for dosing the alkali activator when producing alkali-activated binders. This is a critical factor controlling the properties of these materials, and in the case of blended activated systems it is essential to consider the differences in chemistry of slag and aluminosilicate precursors, and to control the kinetics of dissolution and promote the reaction of each component of the blended activated binder. Typically, when a new precursor or blend is going to be activated, preliminary studies are carried out to identify the amount of activator that allows the production of a workable binder, with moderate initial setting time, that develops compressive strengths within a desirable range, as specified by the needs of the

application of the final product. This means that the activator dose varies from study to study, and therefore there is not a good understanding of the role of the concentration of activation in the microstructural development or durability of alkali-activated materials.

Carbonation of cementitious materials is understood as the chemical reaction taking place between the hydration products composing the binders and the CO_2 from the atmosphere, leading to the formation of carbonates. This has been identified as one of the potential disadvantages of alkali-activated binders, compared with Portland cement, as the earlier studies assessing the susceptibility of degradation of these cements, via acceleration carbonation tests, showed higher potential to develop carbonation problems than conventional Portland cement [17-19]. Recent studies have demonstrated that the mechanism of carbonation in alkali-activated binders is strongly dependent on the type of the precursor used (aluminosilicates or granulated blast furnace slag) [9, 20, 21], the nature of the activator [17] and the accelerated carbonation testing conditions such as relative humidity [22], and CO_2 concentration [23]. Therefore, the general statement that alkali-activated materials will carbonate more than Portland cement is inaccurate, as there are too many variables controlling how and when carbonation of these binders is going to occur, and limited correlation has been identified between natural and accelerated carbonation results for alkali-activated slag materials [23].

In order to gain a better understanding of the effect of the alkali concentration on the fresh paste properties of alkali-activated slag/metakaolin blends, Vicat testing and isothermal calorimetry were carried out in this study. Compressive strength evolution of the pastes was also tested. Mortars were produced with selected paste formulations, and their resistance to accelerated carbonation was evaluated after 28 days of curing.

2. Experimental programme

2.1. Materials

The primary raw material used in this study was a granulated blast furnace slag (GBFS; Table 1) with a basicity coefficient (K_b=CaO+MgO/SiO_2+Al_2O_3) and quality coefficient (CaO+MgO+Al_2O_3/SiO_2+TiO_2) of 1.01 and 1.92, respectively. Its specific gravity was 2900

kg/m^3 and Blaine fineness 399 m^2/kg. The particle size range, determined through laser granulometry, was 0.1 – 74 μm, with a d_{50} of 15 μm.

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

Precursor	*Component (mass % as oxide)*						
	SiO_2	*Al_2O_3*	*CaO*	*Fe_2O_3*	*MgO*	*Other*	*LOI*
GBFS	32.3	16.3	42.5	2.4	2.9	1.7	1.9
MK	50.7	44.6	2.7	-	-	1.0	1.0

The metakaolin (MK) used was generated in the laboratory by calcination of a kaolin containing minor quartz and dickite impurities. Calcination was carried out at 700°C in an air atmosphere, for 2 hours. The particle size range of the metakaolin was 1.8 – 100 μm, with a d_{50} of 13.2 μm and d_{10} of 4 μm, and Blaine fineness 391 m^2/kg. Alkaline activating solutions were formulated by blending a commercial sodium silicate solution with 32.4 wt.% SiO_2, 13.5 wt.% Na_2O and 54.1 wt.% H_2O, together with 50 wt.% NaOH solution, to reach overall desired molar ratios (SiO_2/Al_2O_3 (S/A) and Na_2O/Al_2O_3).

2.2. Sample synthesis and test procedures

2.2.1. Pastes

Pastes formulated with an overall (solid fraction in the activator + solid precursor) SiO_2/Al_2O_3 (S/A) molar ratios of 3.6, 4.0 and 4.4, GBFS/(GBFS+MK) ratios of 0.8 (20 wt.% MK), 0.9 (10 wt.% MK) and 1.0 (0 wt.% MK), with a constant water/(GBFS + MK + solid fraction in the activator) ratio of 0.23, were produced in accordance with the standard procedure ASTM C305-06 [24]. The water/solid ratio of these pastes was determined accordingly to the procedure ASTM C187 [25]. The relationship between the overall oxide ratios and the concentration of the activator (expressed as Na_2O wt.% relative to the amount of precursor to activate), is presented in Table 2. The modulus of solution (Ms = molar ratio SiO_2/Na_2O) of the activators used is between 0.9 – 1.5.

These activation concentrations are considered high for the sole activation of slag, taking into account that the conventional concentrations of activation of slag with sodium

127 silicate solution are usually between 3 – 7% Na_2O [26]; however, production of concretes
128 with these formulations has been achieved [27, 28], which motivates the detailed
129 understanding of the structure developed in these materials.
130
131 In fresh pastes, setting time was determined using the Vicat apparatus by following the
132 standard procedure ASTM C191-08 [29]. The setting process of these mixes was also
133 assessed by isothermal calorimetry (JAF calorimeter) at 25°C, over the first 40 hours of
134 reaction. Fresh paste was mixed externally (~40g of total mix), weighed into polystyrene
135 vessels, and immediately placed in the calorimeter.
136
137 **Table 2.** Equivalence between overall oxide ratios (precursor+activator) and activation
138 concentration (% Na_2O by mass of GBFS + MK) used for the preparation of the pastes
139 assessed

GBFS/ (GBFS+MK)	*Overall SiO_2/Al_2O_3 ratio*	*Activation concentration (wt.%Na_2O)*
1.0	4.4	10.6
	4.0	9.9
	3.6	9.1
0.9	4.4	12.5
	4.0	11.6
	3.6	10.5
0.8	4.4	14.5
	4.0	13.0
	3.6	12.0

140
141 For compressive strength testing, five specimens were cast in a cylindrical mould (40 mm
142 height and 20 mm diameter) and stored in hermetic containers at a relative humidity of
143 90% and a temperature of 27 ± 2 °C for 1, 7, 28, 56 and 180 days.
144
145 **2.2.2. Mortars**
146 Mortars were produced with similar formulations to the pastes (Table 2), following the
147 standard procedure ASTM C305-06 [24]. River sand with a specific gravity, absorption

and fineness modulus of 2450 kg/m3, 3.75% and 2.57 was used as fine aggregate. All samples were formulated with a constant water/(slag + metakaolin + solid fraction in the activator) ratio of 0.47 and a binder/sand ratio of 1:2.75. This water/solids ratio is significantly higher than the used for producing pastes, however, it was selected in order to replicate the content of water used for producing concretes with similar binder formulations [27]. The specimens were cast in cubic moulds with dimensions of 50.8 x 50.8 mm, and stored under controlled humidity (relative humidity (RH) ~85%) and ambient temperature (~25°C) for 24 h. Samples were then demoulded and cured under RH of 90% and a temperature of 27 ± 2 °C for 28 days.

2.3. Accelerated Carbonation

After 28 days of curing the mortar specimens were removed from the humidity chamber, dried at 60°C for 24 h, and then the top ends of the specimens were covered using an acrylic resin (Acronal ®), applying a minimum of 4 layers, to direct the ingress of CO_2 through the selected faces of the cubes during testing. Samples were then transferred to the carbonation chamber for CO_2 exposure, without application of an intermediate drying or conditioning step. This was done to minimise the potential microcracking and differences in sample maturity, which would be observed if they were conditioned for extended periods at the testing relative humidity [22], a step which is specified in many testing protocols. The conditions used were a CO_2 concentration of 1.0 ± 0.2%, a temperature of 20 ± 2ºC, and RH = 65 ± 5 %.

Specimens were removed from the chamber after 340 or 540 h of exposure, and 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 colouration was obtained, while no there was no colour change observed in the carbonated region. Each result is reported as the average depth of carbonation measured at eight points, using two replicate samples (four points per sample; the standard deviation of each carbonation depth measurement is similar to or smaller than the size of the points on the graphs where plotted).

Compressive strength of carbonated and uncarbonated mortars was tested following the standard procedure ASTM C 109. Capillary sorptivity, applying the standard procedure

SIA 162/1 [30], was also determined after the different times of CO_2 exposure (240h and 540h). The properties of uncarbonated samples after 28 days of curing are used as reference values, indicated as zero hours of exposure.

3. Results and discussion

3.1. Characterisation of pastes

3.1.1. Setting time

All the pastes (Table 3) show shorter setting times compared with the expected for conventional Portland cements [31]. Binders solely based on slag (GBFS/(GBFS+MK) = 1.0) formulated with increased S/A ratios (linked to higher concentrations of activation), exhibit substantial increments in the initial setting time (up to 18 min), when compared with pastes formulated with reduced concentrations of activation; however, the total setting time reported for the samples activated with a concentration of activation ~11 wt.% Na_2O (S/A = 4.4) is lower than obtained when activating at reduced concentrations of activator.

This behaviour differs from that which is observed in alkali-activated slag binders activated under conventional activation conditions, where increased concentrations of activators up to 5 wt.%Na_2O promoted reduced initial setting time. This is likely associated with an increased dissolution–precipitation rate of the Ca-rich components of the slag under moderate activation conditions [15, 32-34]. This indicates that the high activator doses used in this study are likely hindering the solubility of Ca from the dissolved slag, as it has been also identified in other studies [35, 36] where the delayed Ca^{2+} precipitating in the system is prone to react with the excessive OH^- in the pore solution forming $Ca(OH)_2$ instead of C-S-H type phases at early stages of reaction.

213 **Table 3.** Setting time of alkali silicate-activated GBFS/MK blends formulated as a
214 function of overall molar ratios

GBFS/(GBFS+MK) ratio	*S/A ratio*	*Initial setting time (min)*	*Final setting time (min)*	*Final - Initial setting time (min)*
1.0	4.4	23	35	11
	4.0	11	30	19
	3.6	5	21	16
0.9	4.4	27	54	27
	4.0	46	70	24
	3.6	17	30	12
0.8	4.4	38	63	25
	4.0	34	66	32
	3.6	14	27	12

215

216 A substantial increment in the difference between initial and final setting times is
217 observed in pastes formulated with a GBFS/(GBFS+MK) ratio of 0.9 (10 wt.% MK) (Table
218 3). Specifically, samples with an S/A ratio of 4.0 (~11 wt.%Na_2O) exhibited an initial
219 setting time twice that of pastes formulated under the same conditions solely based on
220 slag. This high concentration of activation is expected to favour the dissolution of
221 metakaolin over the slag, which extends the setting time of the blended binders. In the
222 activation process of metakaolin it has been identified [37] that an increased alkalinity
223 leads to increased setting times as a consequence of the favoured dissolution of Al and Si
224 species.

225

226 In the blended systems, a higher content of metakaolin leads to longer setting times,
227 which is consistent with delayed dissolution of the Ca species from the slag in the early
228 stages of reaction. The fact that comparable total setting times are identified under the
229 different activation conditions assessed indicate that once the dissolution and
230 polycondensation of the Al and Si species from the metakaolin take place, the Si and Al
231 present in the pore solution shift the speciation equilibrium and drive the dissolution of
232 Ca by complexing with it, forming calcium silicate hydrate type gels and forcing more Ca

to dissolve. A similar effect is identified in pastes with a GBFS/(GBFS+MK) ratio of 0.8 (20 wt.% MK), exhibiting increased setting times when activated at higher concentrations of activation.

3.1.2. Isothermal calorimetry

Alkali activation of slag at highly alkaline concentrations induces changes in the evolution of heat release (Figure 1), compared with the heat release curves reported for comparable binders activated under more moderate alkaline conditions [15], which is associated with modifications in the mechanism of reaction. The heat evolution curves of slag-based pastes activated with an S/A ratio of 3.6 (~9 wt.% Na_2O, Figure 1A) present a sharp and high intensity initial peak at the early stage of reaction, which is assigned to the dissolution of slag particles and simultaneous formation of initially dissolved silicate and aluminate units, as dissolution of calcium species is likely hindered under such alkaline conditions.

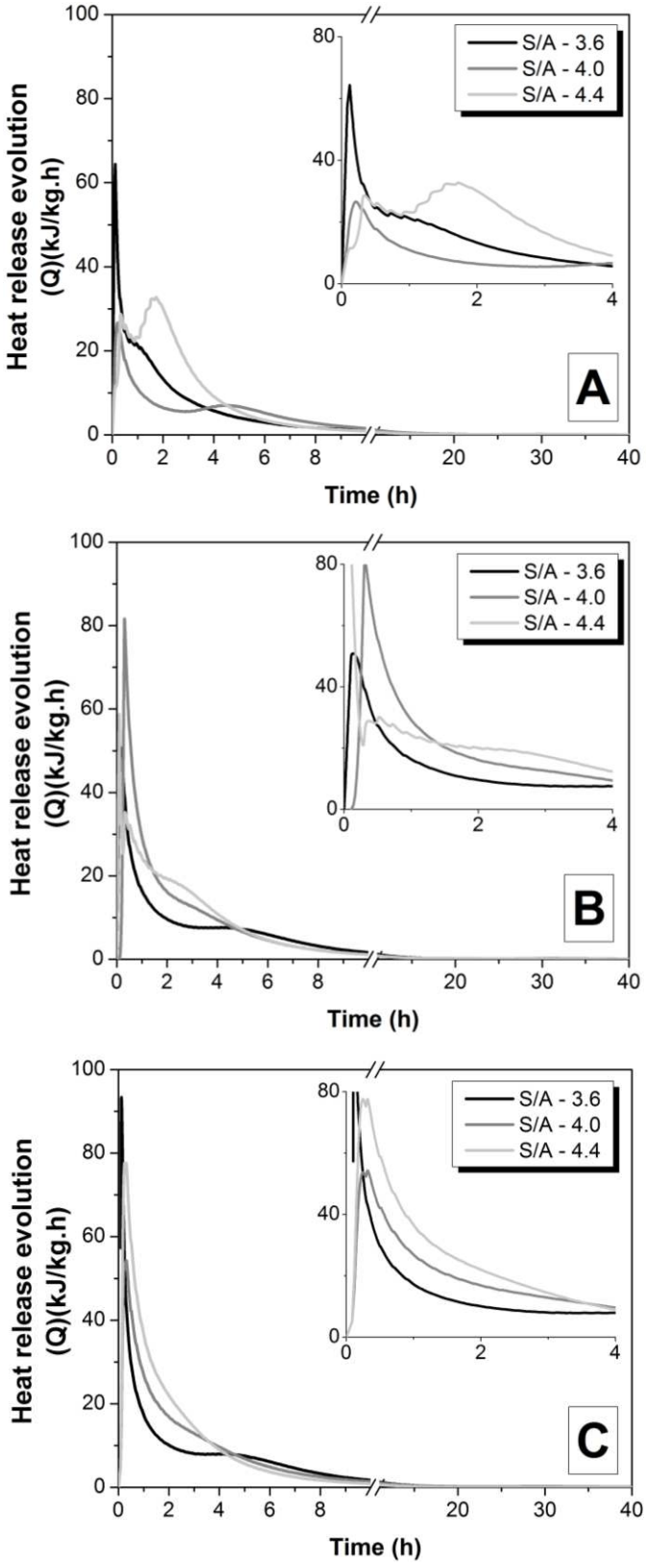


Figure 1. Heat release of alkali-activated GBFS/MK blends with GBFS/(GBFS + MK) ratios of (A) 1.0 (0 wt.%MK), (B) 0.9 (10 wt.% MK) and (C) 0.8 (20 wt.% MK)

After 1 h of reaction, a second peak presenting lower intensity over an extended period of time (~4 h) is observed, and attributed to the formation and subsequent precipitation of the reaction products. This is consistent with the reduced initial setting times identified in the pastes activated under these activation conditions, which suggests that at early stages of the reaction the activation of slag under extremely high alkaline conditions promotes the fast dissolution of Si-rich species, and their condensation over the surface of the partially dissolved slag particles leads to the hardening of the paste. Consequently, it can be suggested that the very short setting times obtained from the Vicat test may correspond to early stiffening and an increased yield stress rather than true setting, and thus cannot be associated with the formation of complex reaction products in the binder, which takes place later in the reaction process.

At the early stage of the reaction, the slag-based paste formulated with increased concentration of activation (9.9 wt.% Na_2O) presents a low intensity initial peak, which is assigned to the pre-induction period of the reaction when the start of dissolution of the slag particles is taking place. With the progress of the reaction, this peak shows a gradual decrease in its intensity until reaching a constant value, consistent with the partial initiation of an induction period. A second peak is observed after four hours of testing, consistent with the acceleration–deceleration period where the precipitation of a large amount of reaction products occurs.

Binders with a GBFS/(GBFS+MK) ratio of 0.9 (Figure 1B) present a single peak of heat release associated with the acceleration period. An increased intensity of this peak is identified at higher concentrations of activation. When samples are activated at ~11 wt.%Na_2O (S/A = 4.0), an increment in the total maximum heat release is identified after 28h of testing compared with mixes activated with lower concentrations of activation, which indicates the delayed precipitation of reaction products at early age. This is associated with the hindrance of the activation reaction by the excessive concentration of alkalis. After the concentration of ionic species in the systems is stabilised, the reaction continues to progress.

An increased concentration of activation associated with an S/A ratio of 4.4 (12.5 wt.% Na_2O) promotes similar behaviour to the binders solely based on slag with S/A = 3.6,

consistent with the precipitation of reaction products during the first minutes of reaction, followed by a sudden reduction of the heat release. For this paste two distinctive peaks are observed, one between 0-1.5 h and the second between 1.5- 6 h, which suggests that the precipitation of different reaction type of products is occurring as the reaction proceed, consistent with the fact that an increased concentration of activation can affect the dissolution of the slag in these blended systems. The greater degree of dissolution of the precursors which is achieved thus enables the progressive precipitation of a higher amount of reaction products than what can be expected in these systems when activated under lower alkaline conditions. Significant differences in the reaction heat are not identified between pastes formulated with S/A 4.0 and S/A 4.4 (Figure 1B), consistent with the fact that both pastes presented similar setting times (Table 3). Those formulation conditions promote the release of higher amounts of heat, when compared with pastes produced at lower concentrations of activation (S/A = 3.6)**,** associated with the formation of an increased amount of reaction products.

The curves of heat release of pastes formulated with increased contents of MK in the binder (20 wt.% MK, Figure 1C) present a sole asymmetric peak, attributed to the acceleration period of the reaction, whose higher intensity is identified in binders formulated with S/A = 3.6. This specific paste exhibit a delayed precipitation of reaction products, which was not identified in binders formulated with higher concentrations of activation.

With increased contents of MK (GBFS/(GBFS+MK) = 0.8), higher reaction heats are released, indicating that increased alkalinity is favouring the enhanced dissolution of MK and the consequent formation of a larger amount of reaction products. This elucidates that although the MK contents in the blended systems assessed are relatively low, the kinetics of reaction are strongly affected by the inclusion of this material, especially at increased concentrations of activation, as consequence of the favoured dissolution and polycondensation of metakaolin under these conditions [38, 39].

3.1.3. Compressive strength development

The compressive strengths of alkali-activated slag/metakaolin pastes cured for 180 days are shown in Figure 2. Pastes based solely on slag (GBFS/(GBFS+MK) = 1.0) show reduced

compressive strength at early times of curing when formulated with an S/A ratio of 3.6; however, after 180 days of curing, similar compressive strengths to those obtained in activated slag pastes formulated with higher S/A are achieved. Higher S/A ratios (4.4) promote the development of higher mechanical strength, especially at longer times of curing. Specimens with a GBFS/(GBFS+MK) ratio of 0.9 (Figure 2) have slightly higher mechanical strength at early times of curing than the slag-only pastes at all of the S/A ratios assessed. This indicates that the metakaolin included in the binder is effectively reacting, as observed in the calorimetry results (Figure 1), and it is contributing to the enhancement of the mechanical strength of the blended binder. The microstructural characterisation of pastes with similar formulations to the used in this study showed [40] that formation of strength giving phases such as C-(N)-A-S-H along with the zeolites gismondine and garronite is taking place in these systems since early times of reaction, despite the high concentration of activation used, and its potential effect in the dissolution of Ca from the slag. These reaction products slightly differ from those typically identified in alkali-activated slag systems produced with lower contents of activator [1], but they are clearly contributing to the strength development of these binders.

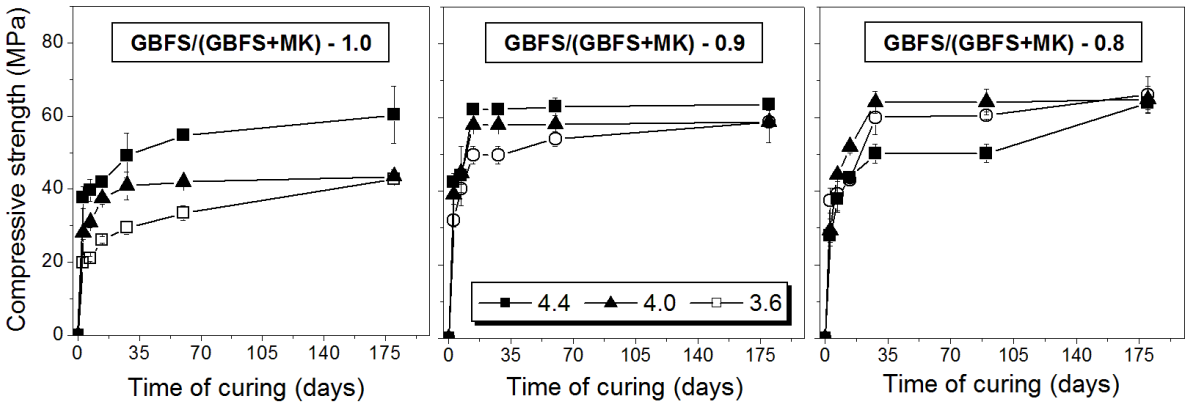


Figure 2. Compressive strength of alkali-activated GBFS/MK blends with GBFS/(GBFS + MK) ratios as shown in each image, as a function of the activation conditions (S/A ratios listed in legend)

For pastes formulated with S/A = 3.6 the mechanical development seems to be slightly delayed compared with the specimens with higher S/A ratios, as the compressive

strength exhibited by these samples is slightly lower until 90 days of curing, and comparable to the other pastes after 180 days of curing when metakaolin is included in the formulations. Under high alkalinity conditions and with metakaolin present, values close to the ultimate strengths are obtained after just 28 days of curing, indicating that these activating conditions accelerate the structural development at early times of curing.

Reduced S/A ratios, associated with increased concentrations of activation, favour the development of higher mechanical strengths in pastes with a GBFS/(GBFS+MK) ratio of 0.8. Those specimens exhibited substantial increments in the mechanical strength during the first days of curing, being higher in the case of pastes activated with S/A ratio of 3.6 and 4.0. The mechanical development seems to be delayed when specimens are produced with increased S/A ratio (4.4); however, comparable compressive strength values are obtained for these mixes at the three activation conditions assessed after 180 days of curing.

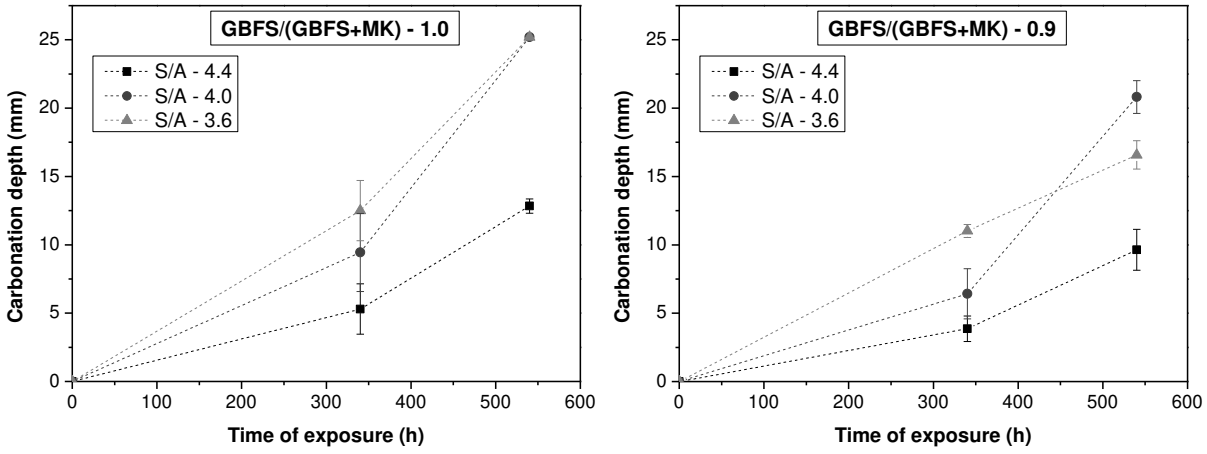
These results are consistent with the kinetics of reaction identified through the calorimetry study (Figure 1), indicating that increased concentrations of activation, associated with higher S/A ratio, favour the dissolution and precipitation of a higher amount of reaction products in specimens including MK as these conditions favour the dissolution and consequent polycondensation of binding gels. The mechanical strengths obtained for pastes solely based on slag are lower than those presented in previous reports assessing the same slag under less-alkaline activation conditions [15]. Those obtained for pastes with GBFS/(GBFS+MK) ratios of 0.9 and 0.8 are somehow consistent with the hindering of the Ca^{2+} dissolution from the slag under the activation conditions used, potentially delaying the formation of binding phases, and consequently promoting reduced mechanical strengths at early times of curing. These results suggest that even though the reaction of the slag is hindered using the activation conditions adopted in study, the effective activation of the metakaolin included is achieved, and the later strengths (70 – 80 MPa) at 180 days of curing are characteristic of high performance materials.

3.2. Accelerated carbonation performance of mortars

3.2.1. Carbonation depth

In Figure 3A it can be seen that there is a reduction in the carbonation depth in mortars of alkali-activated slag, as the concentration of activation increases. Specimens formulated with an S/A ratio of 4.4 exhibited a carbonation depth of 21%, after 340h of exposure to 1% CO_2, while samples formulated with S/A ratios of 4.0 and 3.6 present carbonation depths of 42% and 37% respectively. After 540h of CO_2 exposure, the mortars produced with S/A ratio of 4.4 exhibited a carbonation depth of 51%, conversely the mortars formulated with reduced concentrations of activation, where the 50.8 mm mortar cube samples were fully carbonated after 540h of CO_2 exposure.

In mortars produced with a GBFS/(GBFS+MK) of 0.9 (Figure 3B) a similar trend is identified, so that a higher concentration of activation promotes reduced carbonation depths in the mortars. After 340h of CO_2 exposure the blended slag/metakaolin mortars formulated with S/A = 3.6 exhibited a carbonation depth 8% higher than was observed in activated slag-only mortars produced with a similar concentration of activation (S/A = 4.4). In these blended binders formulated with S/A = 4.4, carbonation depth reductions of up to 65% are identified when compared with the carbonation values identified in samples formulated with lower S/A ratios. After 540h of CO_2 exposure, unlike the slag-only binders, these samples did not reach full carbonation.



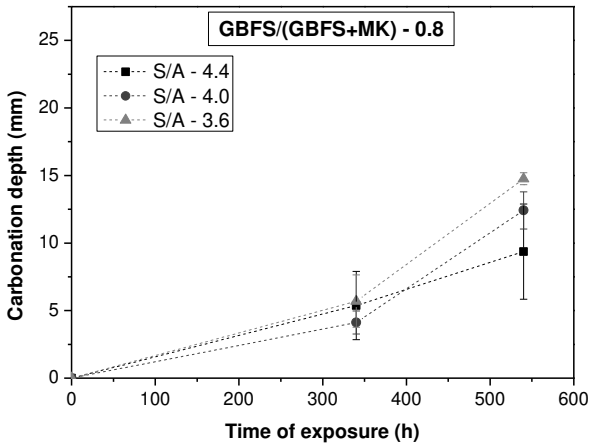


Figure 3. Carbonation depth of mortars based on activated slag/metakaolin blended binders as a function of the GBFS/(GBFS+MK) ratio and activation concentration

In mortars formulated with a GBFS/ (GBFS+MK) ratio of 0.8 no significant differences in the carbonation depth are identified for the different activation conditions adopted in this study, especially after 340h of CO_2 exposure. However, after 540h of CO_2 exposure it is possible to identify (Figure 3C) that higher concentrations of activation (associated with higher S/A ratios) lead to a reduced progress of carbonation. It is worth noting that carbonation depths of these activated blended mortars are significantly lower than those identified in mortars with lower contents of metakaolin, independent of the concentration of activation used.

It is important to note that these results differ from the identified by Burciaga-Diaz et al. [41] who reported that increased concentrations of activation and addition of metakaolin in alkali activated slag binders led to severe carbonation damage of the specimens. In order to elucidate why different results have been identified, it is important to consider the differences in the chemistry of the slag used by Burciaga-Diaz [41] and the slag used in this study (Table 1). The slag used in that study is richer in MgO (8.9 wt%) and has reduced CaO (37.8 wt.%), compared to that used in the present study. The role of the composition of the slag in the determining carbonation resistance of alkali-activated binders has recently been elucidated [21], so that higher contents of MgO in the slag favour the formation of hydrotalcite type reaction products, which can absorb CO_2, enhancing the carbonation resistance of alkali-activated slag binders. Therefore, it might be expected that the binders produced by Burciaga-Diaz et al. [41] will perform better

under accelerated carbonation conditions, than those produced in this study with lower MgO content.

However, the kinetics of reaction of these two slags are completely different. In slags with a higher MgO content than the one used in the present study (2.87 wt.%), such as the slag used by Fernández-Jiménez et al. [42], an increased concentration of activation (>5 wt.% Na_2O) reduces the degree of reaction of the slag. Similar results have been identified by the author (unpublished data) where a threshold value of concentration of activation is typically identified, and increased concentrations of activation reduce the slag reactivity as the MgO content in the slag increases. Conversely, in the low MgO content slag used in this study it has been identified [15] that a higher concentration of alkalis in the system favours a higher degree of reaction of the slag.

Therefore, there is no single factor that can explain the carbonation results identified the activated slag/metakaolin binders assessed in the present study, as there are several important parameters playing a significant role in how carbonation progresses in these systems, including:

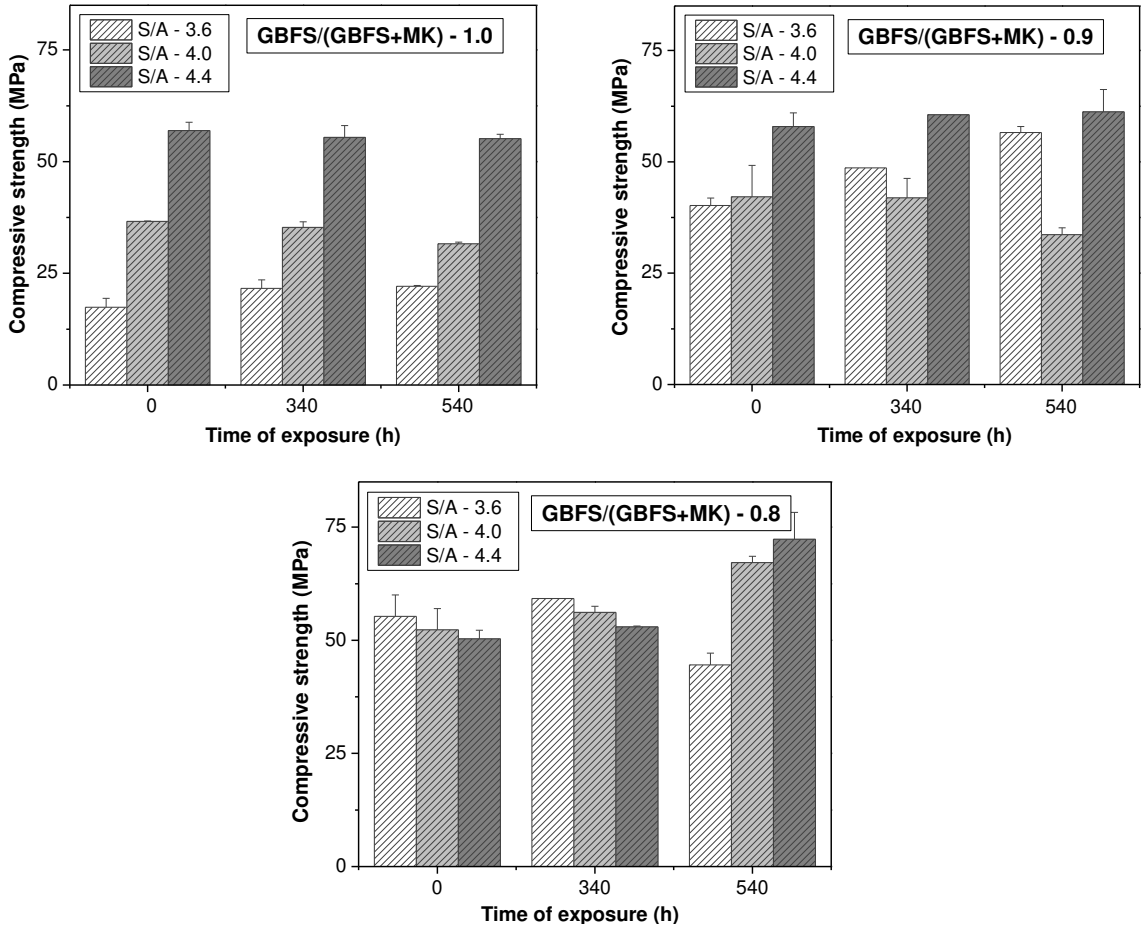
- the evolution of the alkalinity of the pore solution upon carbonation, as the pore water can act as a CO_2 sorbent in presence of high CO_2 concentrations [23],
- the chemistry and microstructure of the reaction products formed, as the nature and Ca/Si ratios of the C-A-S-H forming in these systems will influence the decalcification process taking place in these binders , and
- the changes in permeability of these materials during accelerated carbonation, at the different concentrations of activation and contents of metakaolin added to the system, as this controls the diffusivity of CO_2 within the samples. This will be addressed in detail below, as sorptivity data for the mortars assessed will be reported in Section 3.2.3.

Consequently, detailed microstructural characterisation of these binders after carbonation is required to elucidate the role of the chemistry of the reaction products forming in the carbonation reaction.

3.2.2. Residual compressive strength

Mortars based solely on activated slag (Figure 4A) developed comparable compressive strength than the corresponding paste specimens (Figure 2) at 28 days of curing, with no significant changes when using different concentrations of activation. Upon carbonation for 340 h, the specimens retained their original compressive strength, despite the observation (Figure 3) that significant carbonation is taking place in these specimens. A longer time of CO_2 exposure does not generally seem to impact the compressive strength of the samples, although a slight reduction (14%) is solely observed in the mortar formulated with S/A = 4.0.

In carbonated plain Portland cement systems, increments in the compressive strength with carbonation are typically identified [43, 44], which has been associated with the precipitation of a large amount of calcium carbonate as carbonation products, which provides more contribution to strength than the portlandite it replaces. Conversely, in alkali-activated slag materials, carbonation typically leads to a substantial decrease in the compressive strength [45], associated with the decalcification of the main binding phase, C-A-S-H type gel, along with an increase in permeability. Considering that in alkali-activated slags produced at high [40] and moderate alkalinity [15], formation of comparable reaction products has been identified, it is therefore likely suggest that the hyperalkaline pore solution generated in the binders produced in this study is instead determining the kinetics and impacts of carbonation. In particular, it seems that in this instance carbonation of the pore solution and precipitation of carbonation products contributes to the blockage of the pores, reducing the permeability of the system.



479 **Figure 4.** Residual compressive strength of carbonated mortars based on
480 slag/metakaolin activated blends as function of the time of exposure to 1% CO_2
481

482 Under the activation conditions used here, a significant increase in the compressive
483 strength is identified with the inclusion of higher contents of metakaolin, consistent with
484 a larger extent of reaction of the metakaolin as the concentration of activation increases,
485 as identified by isothermal calorimetry (Figure 1). Mortars formulated with a
486 GBFS/(GBFS+MK) ratio of 0.9 exposed to CO_2 for 340 h exhibited an increase in the
487 compressive strength by up to 35% when the samples were formulated with S/A = 3.6,
488 which is entirely contrary to previous reports [45] of strength losses in alkali-activated
489 binders upon carbonation. No significant differences in strength as a function of
490 carbonation duration were identified in the carbonated specimens formulated with S/A
491 ratios of 4.0 and 4.4. This might be a combined effect of the initial carbonation of the pore
492 solution followed by the gradual progress of carbonation of the reaction products of these
493 samples (less than 10 mm between 340h and 540h of CO_2 exposure), and the progressive
494 activation reaction taking place in the uncarbonated cores of the specimens generating

additional strength. The addition of 20 wt.% MK in these binders does not induce any significant changes in the strength of the mortars upon CO_2 exposure for 340 h. However, after 540 h of CO_2 exposure, the mortars formulated with a S/A ratio of 3.6 exhibited a compressive strength loss of up to 27%. Conversely, in mortars formulated with lower S/A ratios, significant increases in the compressive strength are identified.

There does not seem to be a correlation between the carbonation depth identified for these mortars and the compressive strength determined at the different times of exposure, especially in the case of alkali-activated slag mortars, where the samples were fully carbonated after 540h of CO_2 exposure, but still retained compressive strengths of up to 50 MPa. It has been discussed [45] that the phenolphthalein method is not a reliable test for measuring the carbonation of alkali-activated materials, as this is a measurement of the alkalinity of the system, and it does not give any information regarding any structural changes taking place in these binders upon CO_2 exposure. The reaction products forming in alkali-activated materials are not themselves alkaline, as it is the case of portlandite in hydrated Portland cement, and all of the alkalinity is held in the pore solution. Therefore, the phenolphthalein measurement, reported in this study as carbonation depth, might be solely showing the regions where carbonation of the pore solution has taken place, rather than potential decay of the main binding phases.

3.2.3. Capillary sorptivity

Sorptivity curves of the mortars assessed are shown in Figure 5. In all specimens reduced water absorption is observed in the partially carbonated samples, particularly at extended times of CO_2 exposure. This indicates that the retention of compressive strength of the activated slag/metakaolin mortars can be at least partially explained by refinement of the pore structure, due to precipitation of large amounts of carbonation products. This observation differs from what has been obtained in carbonated specimens with similar contents of metakaolin but activated with reduced activator concentrations [20], in alkali-activated slag specimens [19, 46] and even in concrete specimens with similar binder formulations [22], where accelerated carbonation induced an increase in capillary permeability and water absorption of the material. It is likely that the large fraction of paste in the mortars, compared with the concretes produced with a similar binder

formulation in [22], favours formation of a higher amount of carbonation products, hindering the ingress of CO_2 in the specimens.

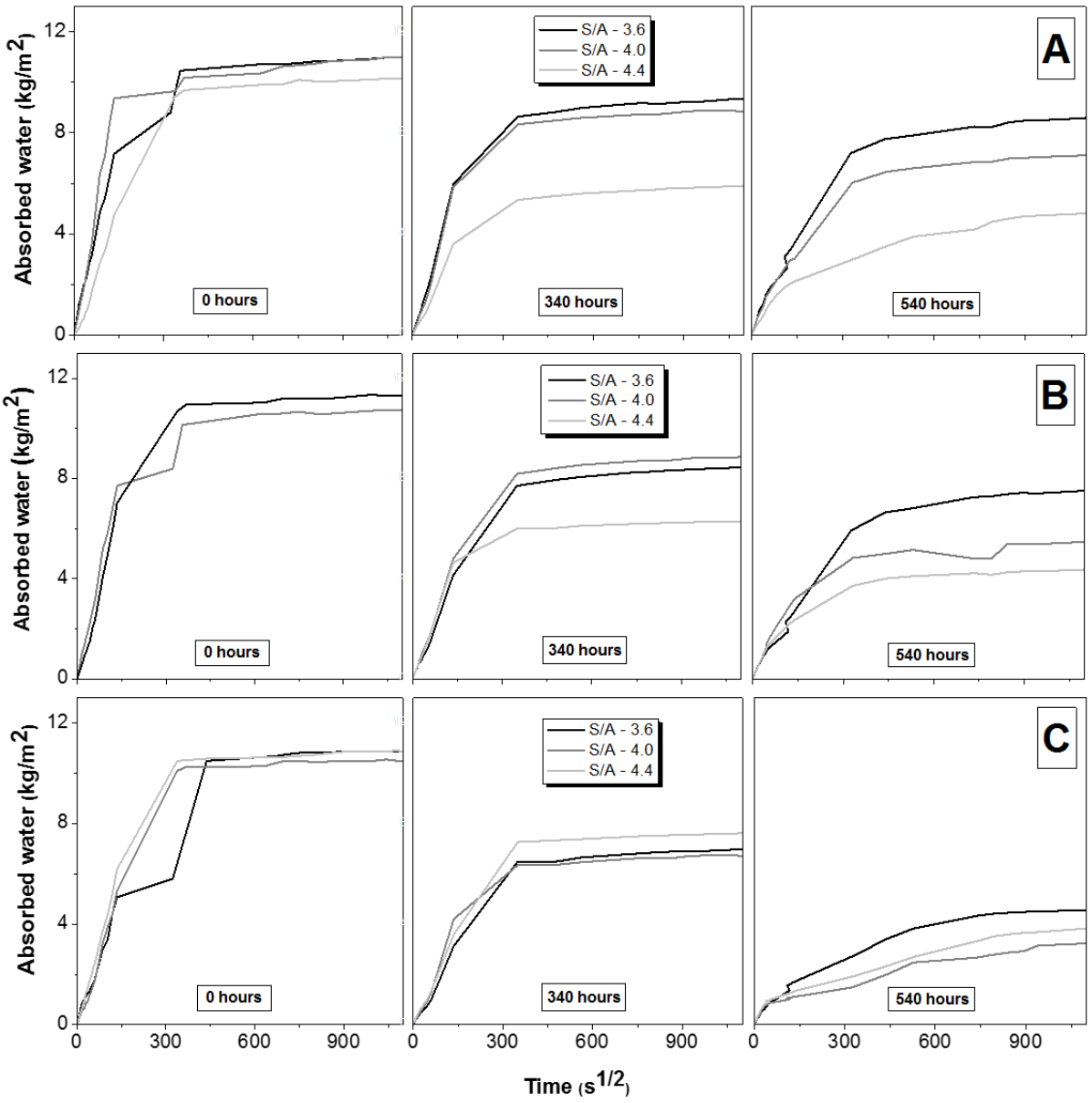


Figure 5. Capillary sorptivity curves of uncarbonated (0 hours) and carbonated (340 and 540 hours) alkali-activated slag/metakaolin mortars, as a function of the MK content: GBFS/(GBFS+MK) = (A) 1.0, (B) 0.9, (C) 0.8

Regardless of the concentration of activation and the content of metakaolin in the binder, after 340h of CO_2 exposure, all the mortars showed (Table 4) a decrease in the capillary coefficient (*k*, the initial slopes of the sorptivity plots in Figure 5) of up to 40%, when compared with non-carbonated samples. Similar results are observed in specimens

539 exposed to CO_2 for 540h. Lower *k* values are associated with a reduced capillary
540 sorptivity, indicating a decrease in the total porosity of the specimens. In all the mortars
541 assessed, the exposure to CO_2 induced an increment in the resistance to water
542 penetration (*m*) (Figure 6), consistent with the reduction in the capillary coefficient (*k*).
543 Carbonated mortars solely based on slag and activated with the lower concentration of
544 activation (S/A – 3.6) report resistance to water penetration values three times higher
545 than observed in non-carbonated reference samples. A similar trend was in observed in
546 mortars including 10 wt% of MK (GBFS/(GBFS+MK) – 0.9) when activated at a similar
547 concentration of activation. In the other specimens, the increments in the resistance of
548 water penetration coefficient were up to 40%.
549
550 **Table 3.** Capillary sorptivity coefficients of alkali-activated slag/metakaolin mortars as
551 function of the time of CO_2 exposure

GBFS/(GBFS+MK) ratio	***SiO_2/Al_2O_3***	***k ($kg/m^2.s^{1/2}$)***		
		0 h	***340 h***	***540 h***
1.0	3.6	0.052	0.038	0.033
	4.0	0.061	0.031	0.026
	4.4	0.039	0.021	0.021
0.9	3.6	0.051	0.024	0.024
	4.0	0.048	0.030	0.027
	4.4	-	0.029	0.027
0.8	3.6	0.029	0.016	0.018
	4.0	0.036	0.020	0.023
	4.4	0.043	0.021	0.025

552

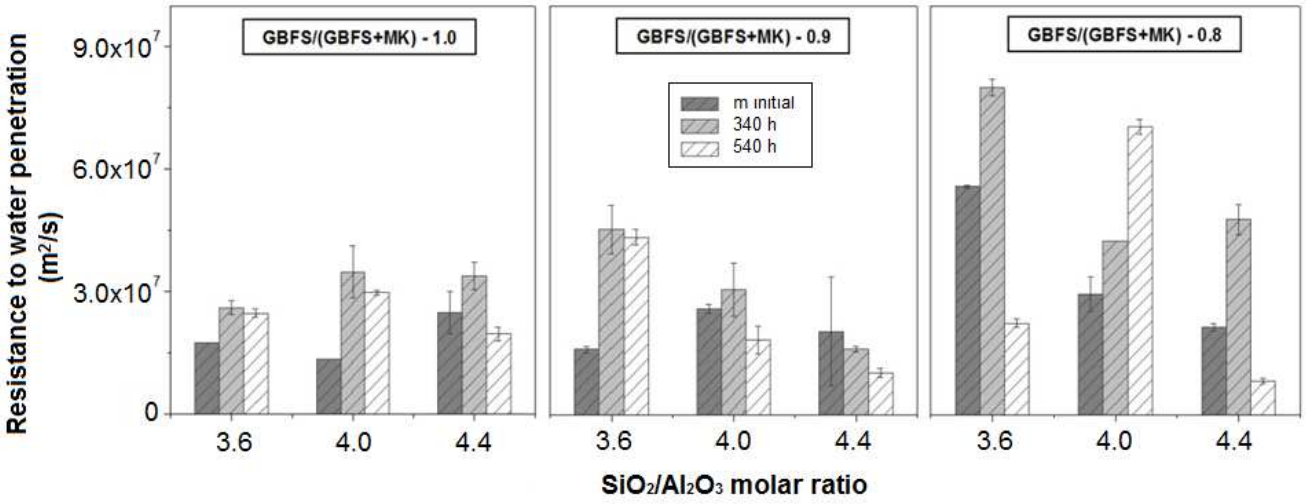


Figure 6. Resistance to water penetration of alkali-activated slag/metakaolin mortars, as function of the activation conditions and time of exposure to CO_2

4. Conclusions

The high alkalinity conditions adopted in this study to produce activated slag/metakaolin blended binders affects the kinetics of reaction of the slag used, so that a higher concentration of activation increased the initial setting times of the pastes, however the time between initial and final setting of the activated slag binders was shortened as the concentration of activation increased. The inclusion of metakaolin increases the total setting time of the pastes produced from this unusually low-MgO slag, independent of the amount incorporated and the concentration of activation used. This might be a consequence of the combined effect of reduced dissolution of Ca from the slag, along with a high dissolution of Al and Si species from metakaolin, which are favoured under the highly alkaline conditions adopted. As the alkalinity in the binders is increased at higher activator concentrations, the reaction of the system is governed by the dissolution and polycondensation of the species from the metakaolin. The alkali-activated slag binders tested here, at high activator concentrations, developed lower compressive strengths than have been achieved when activating this slag under milder concentrations. Under the activation conditions adopted here, the inclusion of metakaolin led to a significant increase in the compressive strength, associated with the simultaneous reaction of slag and metakaolin.

A reduced rate of carbonation was identified in these materials with the addition of metakaolin, and also with increasing the concentration of the activator. Little or no loss of compressive strength, and significant reductions in the water permeability, were observed at longer times of CO_2 exposure. This suggest that under the activation conditions used, precipitation of a large amount of carbonation products might be taking place as a result of interactions between the highly alkaline pore solution and the incoming CO_2, refining the pore network of the mortars. This hindered the ingress of CO_2 within the samples and therefore reduced the carbonation progress. It is important to note that no correlation could be identified between the carbonation front determined using a phenolphthalein indicator, and the compressive strength and water sorption of the test samples. The phenolphthalein indicator is revealing the regions where reductions of the pH are taking place as a consequence of the carbonation of the pore solution, rather than regions where damage to the strength-giving binder products is occurring. Therefore, the methods used for measurement of carbonation depth in alkali-activated materials requires reassessment, as the standard approach using a phenolphthalein indicator may not be providing accurate information.

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