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# Accelerated carbonation testing of alkali-activated slag/metakaolin blended concretes: effect of exposure conditions

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**Abstract**

This paper addresses the effects of relative humidity and $CO_2$ concentration on the rate and effects of accelerated carbonation in alkali-activated slag/metakaolin concretes. Strength and water absorption are used alongside phenolphthalein measurements to monitor carbonation, and the effects of drying at different relative humidities are particularly significant in controlling carbonation rates. Different trends in the carbonation rate as a function of metakaolin content are observed when varying the $CO_2$ concentration, further revealing that the carbonation rates of these materials under accelerated conditions are influenced strongly by the testing protocol. The standard phenolphthalein method for testing carbonation depth appears only to be capturing the change in alkalinity with pore solution carbonation, meaning that it does not correlate well with other performance parameters at high $CO_2$ concentrations.

**Keywords:** alkali-activated cement; concrete; granulated blast-furnace slag; carbonation; durability

## 1. Introduction

Durability of structures and structural concretes, particularly in the presence of aggressive agents, is a topic of fundamental interest and importance in civil infrastructure and construction. Carbon dioxide

($CO_2$) is particularly known to affect the durability of cement-based materials under long-term exposure, through a degradation process referred to as carbonation [1-3]. This phenomenon is controlled by both gas diffusion and chemical reaction mechanisms, and consequently its progress is determined by both the chemistry of the binder and the permeability of the material. The effect of carbonation in concrete structures is a reduction in the alkalinity of the material, leading to an increased susceptibility to corrosion of embedded steel reinforcement, often accompanied by a decrease in mechanical strength [2, 4, 5].

Carbonation of mortars and concretes produced using ordinary Portland cement has been widely studied. In these systems, the $CO_2$ from the atmosphere diffuses through gas-filled pores and dissolves in the pore solution to form aqueous $HCO_3^-$. This uptake of acidic $CO_2$ into the alkaline pore solution reduces the internal pH of the binder, and the dissolved carbonate also reacts with the calcium-rich hydration products present in the matrix, mainly with the portlandite ($Ca(OH)_2$), calcium silicate hydrate (C-S-H) and calcium aluminate hydrate phases, to form solid calcium carbonates [4, 6, 7]. In Portland cement-based systems, it is well known that the progress of carbonation is dependent on the chemical nature of the binder phases with which the $CO_2$ is going to react, as well as the factors determining the diffusion rate of the gaseous $CO_2$, such as the pore network and exposure environment, in particular relative humidity [8-11]. It has been reported [9] that carbonation is more rapid at intermediate relative humidity (50–70%), and this is attributed to interactions between drying and carbonation processes [12], as the presence of a very high fraction of pores filled with water hinders the diffusion of $CO_2$, while sufficient water is required to promote the solvation and hydration of the carbon dioxide. Under intermediate moisture conditions both reaction kinetics and diffusion of $CO_2$ are favoured, which leads to acceleration of the carbonation process [4].

In the case of concretes based on alkali-activated binders, there is limited existing knowledge about the long-term in-service stability of these materials, although the studies that have been published show generally moderate to low carbonation rates (<0.5 mm/yr), similar to the carbonation rate of Portland cement concretes, under service conditions in continental climates [13-15]. Shi, Krivenko and Roy report the natural carbonation rates of concrete structures with ages between 12 and 40 years, located in Russia, Ukraine and Poland [14]. The concretes were produced from alkali-activated slag, using alkaline activator solutions of sodium metasilicate, sodium carbonate and potassium carbonate, and had 28-day compressive strengths between 35 - 82 MPa. The in-service carbonation rates, measured using the phenolphthalein method, did not exceed 1 mm/year in any of the cases described. Similar results were identified in 7-year-old silicate-activated slag concretes [16], where the carbonated depths identified were much lower than would be predicted through calculations based on

accelerated carbonation testing, demonstrating that the exposure conditions used in accelerated testing do not replicate the phenomena that take place under natural service conditions.

On the other hand, laboratory studies of pastes and mortars of alkali-activated slag, and slag/metakaolin blends [15, 17-21], have indicated high susceptibility to carbonation in these materials under accelerated conditions, compared with conventional cements. It is proposed that this is due particularly to effects related to pore solution alkalinity [22] and binder chemistry, especially the absence of portlandite as a reaction product in these binders. More recently it has been identified [23] that drying of alkali-activated materials induces changes in their microstructure. This causes severe microcracking, which is deleterious when pre-conditioning specimens prior to analysis of water absorption properties and accelerated carbonation testing. Considering these observations, it is evident that there is the need to develop a better understanding of the real meaning of the results obtained in alkali-activated materials, and how accelerated carbonation tests should be conducted, as the divergences between accelerated and natural carbonation rates of alkali-activated concretes are remarkable [16].

The carbonation of concrete under ambient conditions is generally relatively slow, as a consequence of the relatively low concentration of $CO_2$ in the atmosphere (0.03 – 0.04%). This has led to the development of experimental methods based on accelerated carbonation under controlled conditions, through exposure to high $CO_2$ concentrations for shorter periods of time. It has been noted [24] that a short period of accelerated carbonation in Portland cement-based materials is not necessarily directly analogous to long term exposure to natural atmosphere, which involves differences in moisture distribution under different drying periods, and gradual changes in the micropore structure due to ageing and carbonation. A proposed European standard method [25] for testing the susceptibility of Portland cement-based materials to carbonation has been discussed in detail by Harrison et al. [26], and adopted recently by some nations, but not in general across the EU [26]. Some limitations of common accelerated test methods, such as repeatability and reproducibility, have also been identified, even in application to Portland cement-based systems [27, 28].

For the specific case of alkali-activated binders, recent results [22] reveal that the mechanism of carbonation in alkali activated slag which is induced using accelerated test methods is strongly affected by the $CO_2$ concentration, leading to differences in the chemistry of the alkali carbonate phases formed as a result of carbonation, and also the pH and carbonate/bicarbonate ratio of the remaining pore solution. This will therefore change both the $CO_2$ uptake rate and the influence of the carbonated pore solution on steel corrosion chemistry, meaning that the test results must be carefully interpreted in order to give an accurate prediction of either the rate or the effects of carbonation in these materials under natural conditions. In particular, it appears from thermodynamic calculations

related to pore solution chemistry [22] that accelerated testing will overestimate both the rate and degradation effects of carbonation in alkali-activated binders. From these results, it seems likely that if an alkali-activated concrete and a Portland cement concrete show the same carbonation depth in an accelerated test, the alkali-activated material will suffer less carbonation under natural conditions, and thus the service life would be much higher. However, further detailed experimental work related to understanding the effects induced by different accelerated testing conditions is undoubtedly required before such statements can be fully validated.

This indicates that the exposure conditions which are used to induce accelerated carbonation of alkali-activated materials need to be studied, in order to provide recommendations for appropriate testing protocols, and also to aid in interpretation of the results obtained. The aim of this study is therefore to assess the effects of relative humidity and $CO_2$ concentration on the carbonation rate of alkali-activated concretes during accelerated testing. The concretes tested have a binder based on a combination of granulated blast furnace slag (GBFS) and metakaolin (MK), activated by sodium silicate solutions, where the addition of the metakaolin serves to regulate the setting of these materials which are based on an otherwise very rapidly-reacting slag, and also enhances strength when the activator dose is sufficient [29, 30]. In addition to carbonation depth measurements, variations in mechanical strength and pore network properties, investigated in an indirect way via water absorption tests, are monitored during $CO_2$ exposure, to obtain a deeper understanding of the microstructural changes in the concretes which are induced under different exposure conditions.

## 2. Materials and methods

### 2.1. Materials

The primary raw material used in this study was a Colombian granulated blast furnace slag (GBFS) from the factory Acerías Paz del Río. 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 15 μm. The metakaolin (MK) used was generated in the laboratory by calcination of a kaolin containing minor quartz and dickite impurities [29]. 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.

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

| Raw material | Component (mass % as oxide) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | CaO | $Fe_2O_3$ | MgO | $TiO_2$ | Others | LOI |
| GBFS | 32.29 | 16.25 | 42.45 | 2.35 | 2.87 | 0.50 | 0.57 | 2.72 |
| MK | 50.72 | 44.63 | 2.69 | - | - | - | 0.94 | 1.02 |

Alkaline activating solutions were formulated by blending a commercial sodium silicate solution (32.4 wt.% $SiO_2$, 13.5 wt.% $Na_2O$ and 54.1 wt.% $H_2O$), and 50 wt.% NaOH solution, with the slag and metakaolin, to reach the desired overall molar ratios (specified as $SiO_2/Al_2O_3$ (S/A)), and corresponding to a concentration of activation of 11-12% $Na_2O$ relative to the amount of binder (i.e., 11-12 g $Na_2O$ per 100 g GBFS+MK).

Crushed gravel and river sand were used as coarse and fine aggregates. The coarse aggregate was of 19 mm maximum size, with a specific gravity of 2790 kg/m$^3$ and absorption of 1.23%. The specific gravity, absorption, and fineness modulus of the sand were 2450 kg/m$^3$, 3.75% and 2.57, respectively.

### 2.2. Concrete mixes

The concretes were produced with total binder (GBFS+MK) contents of 400 kg/m$^3$ and a total water/(GBFS+MK+anhydrous activator) ratio of 0.47. Fresh concrete was mixed, poured into cylindrical steel moulds ($\phi$ = 76.2 mm, h = 152.4 mm), tamped and levelled. The concrete specimens were then cured in a humidity-controlled chamber at 25±5°C and 90% relative humidity (RH), for 28 days, with the moulds removed after 24 hours. The mix designs are given in Table 2. Detailed analysis of the evolution of engineering (compressive and flexural strength) and durability properties (water absorption properties, chloride permeability and carbonation) of the concrete mixes assessed in this study as a function of the time of curing is reported in [30].

**Table 2.** Mix designs of the concretes. All quantities are in kg/m$^3$ of fresh concrete

| **Component** | **GBFS/(GBFS+MK)** | | |
|---|---|---|---|
| | **1.0** | **0.9** | **0.8** |
| GBFS | 400 | 360 | 320 |
| MK | - | 40 | 80 |
| Sodium silicate solution | 120 | 136 | 132 |
| NaOH (50 wt.% solution) | 68 | 72 | 78 |
| Coarse aggregate | 832 | 816 | 808 |
| Sand | 832 | 816 | 808 |
| Free water | 132 | 124 | 124 |
| Overall $SiO_2/Al_2O_3$ molar ratio | 4.4 | 4.0 | 3.6 |
| Activator concentration | 10.6 | 11.6 | 12.0 |

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| | |
|---|---|
| | (% $Na_2O$ by mass of GBFS + MK) |

### 2.3. Accelerated carbonation testing

After 28 days of curing the specimens were removed from the humidity chamber, 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 curved face of the cylinders 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 any potential microcracking or differences in sample maturity which would be observed if they were conditioned for extended periods at the testing relative humidity, a step which is specified in many testing protocols for Portland cement systems.

#### 2.3.1. Variation of relative humidity

An accelerated carbonation testing system with automated control of temperature, humidity and $CO_2$ concentration was used to induce the carbonation of concrete specimens. A $CO_2$ concentration of 1.0 ± 0.2%, was used, at a temperature of 25 ± 2 °C, and RH values of 50 ± 5%, 65 ± 5%, and 80 ± 5%, where the uncertainties quoted here are the maximum allowable deviations from setpoints as specified by the supplier of the chamber control systems. Specimens were removed from the chamber after 250 or 500 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 concrete was still highly alkaline, purple-red colouration was obtained, while 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 as plotted). The properties of uncarbonated samples after 28 days of curing are used as reference values, indicated as zero hours of exposure.

#### 2.3.2. Variation of $CO_2$ exposure concentration

Specimens were exposed to $CO_2$ concentrations of 1 ± 0.2% and 3.0 ± 0.2%, at a relative humidity of 65 ± 5%. After 250, 500, 750 and 1000 h of exposure, carbonation depths were determined as described above.

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### 2.4. Testing protocols

Carbonated and uncarbonated concretes were tested for compressive strength following the standard procedure ASTM C39/C39M-09a (Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens). Total porosity and absorption were determined before and after carbonation according to the standard procedure ASTM C642-06 (Standard Test Method for Density, Absorption, and Voids in Hardened Concrete), where the samples are dried and then boiled in water to determine the total volume of permeable voids. Capillary sorptivity was assessed by applying the standard procedure EMPA–SIA 162/1 [31], in which water is allowed to pass from a damp sponge into a dried cylindrical sample through a process of capillary suction, and the mass of the sample is monitored as a function of time.

## 3. Results and discussion

### 3.1. Effect of relative humidity on the accelerated carbonation of alkali-activated GBFS/MK blends

#### 3.1.1. Carbonation rate

Figure 1 shows the carbonation depth as a function of time and relative humidity for the samples containing different percentages of metakaolin. There are two clearly distinct types of behaviour shown by the samples when considering carbonation as a function of time:

- All of the GBFS-only samples, and the sample with GBFS/(GBFS+MK) = 0.9 exposed at 80% RH, show relatively slow initial carbonation, but then the ingress of the carbonation front accelerates, and the increment in carbonation depth from 250-500 h is more than the carbonation observed in the first 250 h
- All of the samples with GBFS/(GBFS+MK) = 0.8, and the samples with GBFS/(GBFS+MK) = 0.9 exposed at 50 and 65% RH, show a deceleration in carbonation with time, with more carbonation in the first 250 h than in the subsequent 250 h.

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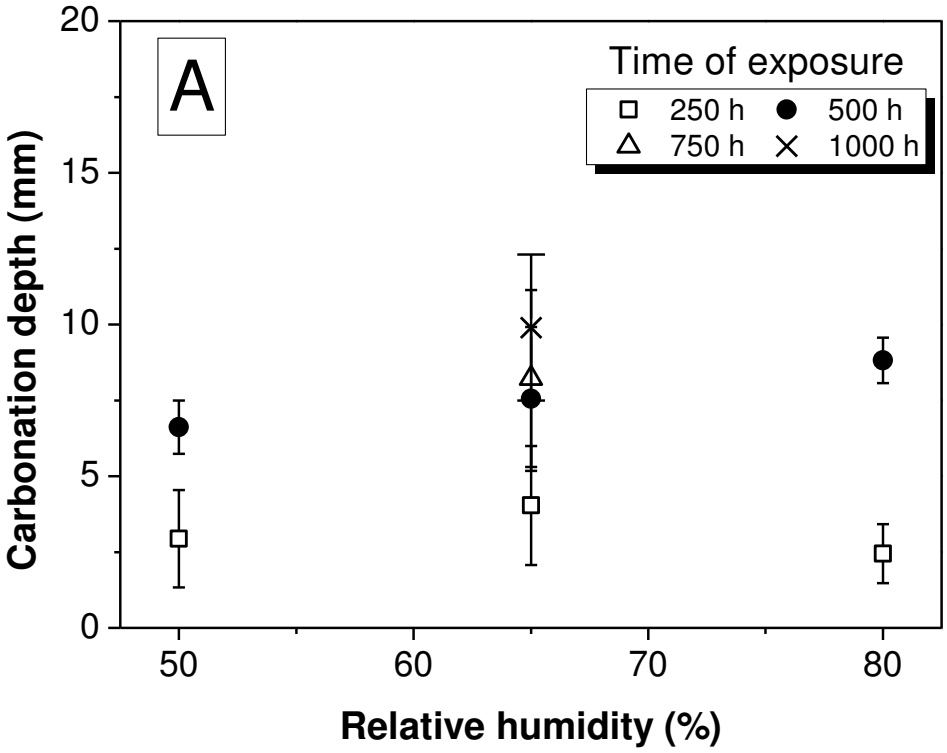


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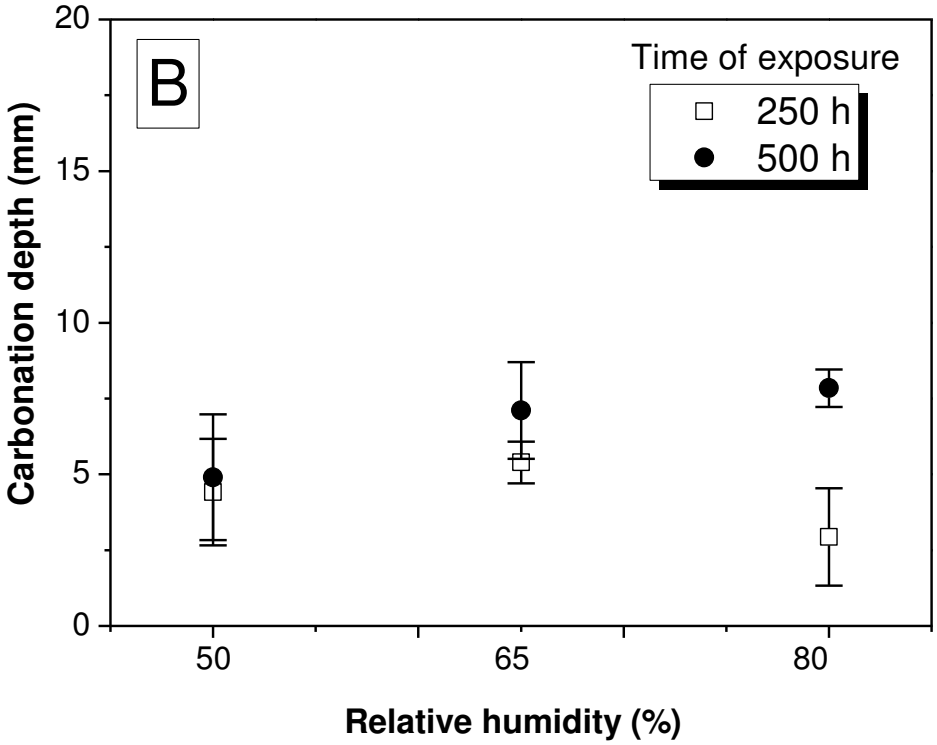


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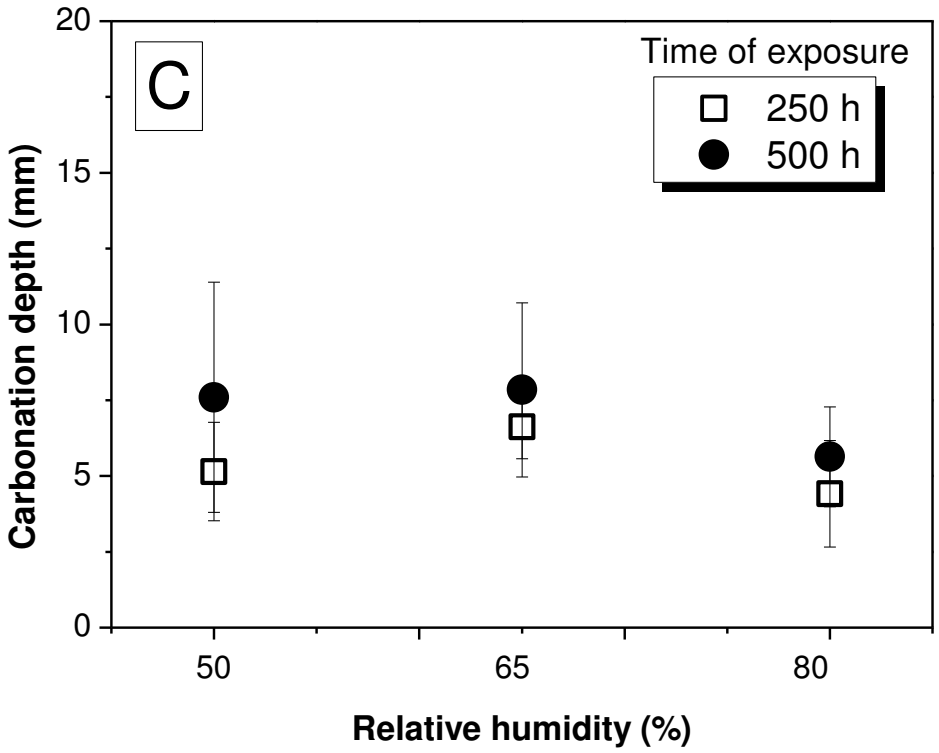


**Figure 1.** Carbonation depth as a function of the relative humidity and time of exposure in alkali-activated GBFS/MK concretes, formulated with GBFS/(GBFS+MK) ratios of (A) 1.0, (B) 0.9 and (C) 0.8, at 1% $CO_2$. Error bars show ± 1 standard deviation among 5 measurements per sample.

Figure 1 also shows differences in the trend in carbonation depth as a function of relative humidity, depending on the binder composition and the exposure time. In specimens solely based on GBFS (Figure 1A) similar carbonation depths are identified at each different RH during the first 250 h of exposure, and the carbonation depth increases with RH after 500 h of $CO_2$ exposure. A similar trend is observed in specimens with GBFS/(GBFS+MK) = 0.9, although the carbonation rate within the first 250 h at 80% RH is notably lower than at the other relative humidities studied. Similar results are observed at higher content of MK in the binder (GBFS/(GBFS+MK) = 0.8, Figure 1C) with the most rapid carbonation observed at intermediate humidity.

The acceleration in carbonation of some of the concretes (Figure 1A,B) between the first 250 h and the subsequent 250 h of curing is to some extent counterintuitive; such a change in kinetics would not be expected if the process were simply controlled by either diffusion or chemical reaction mechanisms [32, 33]. Even if the microstructural damage associated with the carbonation-induced decalcification of the C-A-S-H gel to form calcium carbonate products [17] was so severe that the damaged material did not provide any barrier to $CO_2$ diffusion, this would result in a linear rate of

carbonation, but could not explain an acceleration in rate. There must therefore be a combination of drying and carbonation effects which leads to this apparent acceleration during this timeframe. There is only one dataset available (Figure 1A) which contains data at 750 and 1000 h for a sample which showed an acceleration effect; these data show that the carbonation decelerated again after 500 h, which is consistent with the development of some extent of diffusional resistance to mass transport in the later stages of carbonation, as would be expected from the thickness of the carbonated layers on the samples.

The higher final extent of carbonation at higher relative humidities is consistent with the trends reported for Portland cement concretes containing supplementary cementitious materials [34, 35], where it is expected that the presence of water-saturated pores will hinder the diffusion of $CO_2$ through the material. Partially water-filled pores are known to accelerate carbonation through convective mass transport, and also by providing high interfacial areas for transfer of $CO_2$ from gas to liquid (and thus subsequently to solid) phases [9, 11]. For the GBFS-only samples, which have the lowest water absorption in the uncarbonated state [30], and for the GBFS/(GBFS+MK) = 0.9 sample at high (80%) relative humidity, it is likely that the pores are more extensively filled with water, so the start of carbonation is slowed after the drying front has begun to enter the sample. The higher water absorption measured for the uncarbonated GBFS/(GBFS+MK) = 0.8 samples [30] indicates that there are already unsaturated pores within the concrete prior to the start of the carbonation tests for these concretes, and the observed carbonation behaviour does not show an acceleration event.

Comparing the samples with different MK contents, it appears that when concretes are exposed under comparable relative humidity conditions for 500 h, increased metakaolin content will usually give a lower extent of carbonation. The only exception to this trend in Figure 1 is the sample with GBFS/(GBFS+MK) = 0.8 at 50% RH, which is more rapidly carbonated than the sample with GBFS/(GBFS+MK) = 0.9 under the same conditions. It is likely that this is related to the higher porosity of the concretes with GBFS/(GBFS+MK) = 0.8 [30], as will be discussed in detail below.

#### 3.1.2. Residual compressive strength

The residual compressive strength (Figure 2) represents the ratio of the strengths of the concretes before and after exposure to $CO_2$, providing a direct means of comparison of the samples which had different strengths before carbonation (GBFS/(GBFS+MK) = 1.0: 63 MPa; GBFS/(GBFS+MK) = 0.9: 73 MPa; and GBFS/(GBFS+MK) = 0.8: 53 MPa). Concretes based solely on GBFS (Figure 2A) and with GBFS/(GBFS+MK) = 0.9 (Figure 2B) show, over the first 250 h of exposure, only slight reductions in the compressive strength relative to the uncarbonated concretes at relative humidities of

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65% and 80%, while specimens exposed at an RH of 50% exhibit a reduction in the compressive strength of around 15%. Similar trends are visible for specimens exposed for longer periods of time (500 h), although the extent of strength loss increases notably with time. The effect of RH on the carbonation progress of the concretes assessed seems to be more significant with the inclusion of MK in the binder.

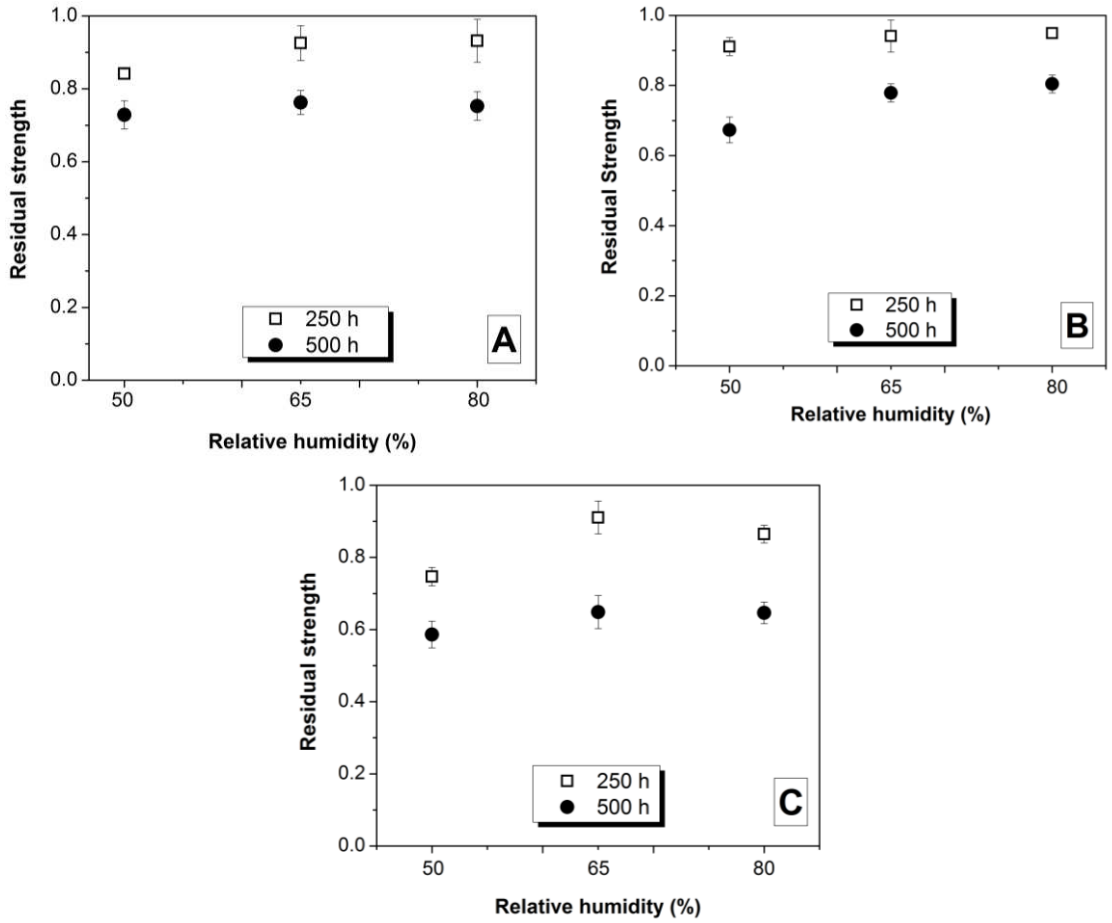


**Figure 2**. Residual compressive strengths of partially accelerated-carbonated concretes based on alkali-activated slag/metakaolin blends formulated with GBFS/(GBFS+MK) ratios of (A) 1.0, (B) 0.9 and (C) 0.8, as a function of the relative humidity, at 1% $CO_2$. Error bars correspond to one standard deviation of three measurements.

In a previous study where carbonation of some of these mix designs was studied at a single RH (65%) for up to 1000 h [30], the correlation between carbonation depth and residual strength was observed to be approximately linear for the concretes containing no more than 10% MK (GBFS/(GBFS+MK) ≥ 0.9). However, such a relationship is not evident across the different RH values when comparing Figures 1 and 2, particularly for the samples containing MK. The samples with GBFS/(GBFS+MK) = 0.9 exposed at 50% RH showed almost no additional carbonation depth (Figure 1B), but a marked loss of strength (Figure 2B), between 250-500 h of exposure. The same mix exposed at 80% RH

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showed a relatively rapid progression of the carbonation front, but almost no change in compressive strength, between 250-500 h. However, the main disagreement between the carbonation depth and carbonation rate data is visible when comparing the influence of RH on these two parameters: in each case, 65% RH leads to the highest carbonation depth after 250 h of exposure, but the highest residual strength after the same exposure time. The samples with GBFS/(GBFS+MK) = 0.8 are most deeply carbonated, and lose the most strength, after 500h at 50% RH, but agreement between the conditions which cause the greatest extent of damage as determined by these two different measures is not observed for the concretes with GBFS/(GBFS+MK) = 0.9 or 1.0.

### 3.1.3. Total porosity and absorption

The carbonation of alkali-activated concretes leads to an increase in the volume of permeable pores (Figure 3) so that the volume of permeable voids of carbonated specimens is twice the porosity of uncarbonated samples, when the porosity of the sample as a whole is measured; considering the fact that there is an undamaged core in most of the cylinders tested, this change may even be more notable if solely the carbonated part of the sample were to be considered. This increase in porosity is in general slightly greater when carbonation is carried out at increased relative humidities, but the differences between different RH values are not highly significant.

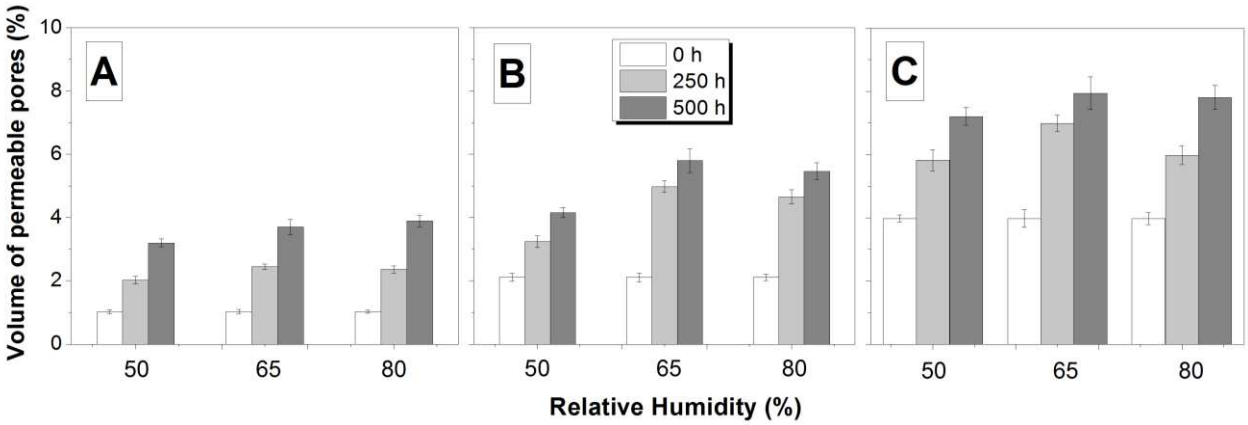


**Figure 3**. Porosity of partially carbonated concretes based on alkali-activated slag/metakaolin blends formulated with GBFS/(GBFS+MK) ratios of (A) 1.0, (B) 0.9 and (C) 0.8, as a function of the relative humidity, at 1% $CO_2$. Error bars correspond to one standard deviation of four measurements

Increased porosity is exhibited by concretes exposed to $CO_2$ over longer times, as expected with reference to the progress of the carbonation reaction in the material. Mixes with GBFS/(GBFS+MK) = 0.8 show the highest total porosity of the specimens studied, which might contribute to the higher carbonation rate identified in these concretes after 250 h of exposure compared with the systems

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including lower contents of MK. In this case, the samples exposed at 65% RH show the largest increment in total porosity after 250 h of exposure; however, comparable porosities can be observed after 500 h when the exposure to $CO_2$ is conducted at 65% or 80% RH.

These results agree reasonably well with the trends in carbonation depth as a function of relative humidity (Figure 1C), but disagree with the residual compressive strength data obtained for these specimens, where the lowest residual strengths were reported when the exposure was conducted at 50% RH (Figure 2C). It is thus suggested that the different protocols for assessing the progress and influence of carbonation on an alkali-activated concrete are influenced in different ways by the relative humidity conditions under which the test is conducted, and this is likely to be very important when comparing data across different investigations, where various parameters are assessed under different conditions. This means that different trends will be obtained, depending on which performance parameters are selected for analysis.

Total water absorption values for the concretes assessed are shown in Table 2, and it can be seen that although the influence of exposure RH on water absorption (as measured by the ASTM C642 test) is relatively minor, higher absorptions are generally observed in concretes with MK in the binder when exposed to carbonation at 65% RH, especially at longer times of exposure. It has been reported that, for conventional Portland cement-based concretes [36], absorption values of 3% and total porosity values of 10% are able to be related to concretes with good durability. Based on this, it is possible to suggest that all the concretes assessed here, both before and after $CO_2$ exposure, have the potential to be highly durable.

**Table 2.** Water absorption (wt.%) of concretes based on alkali-activated GBFS/MK blends exposed to $CO_2$ under different relative humidities

| GBFS/(GBFS+MK) | Relative humidity (%) | Time of exposure to $CO_2$ (hours) | | |
|---|---|---|---|---|
| | | 0 | 250 | 500 |
| 1.0 | 50 | 0.28 | 1.27 | 1.53 |
| | 65 | | 0.99 | 1.27 |
| | 80 | | 1.20 | 1.32 |
| 0.9 | 50 | 0.58 | 2.09 | 2.15 |
| | 65 | | 2.16 | 2.29 |
| | 80 | | 2.10 | 2.30 |
| 0.8 | 50 | 1.38 | 2.68 | 2.98 |
| | 65 | | 2.95 | 3.11 |
| | 80 | | 2.73 | 2.99 |

As $CO_2$ can diffuse through both large and capillary pores, the total porosity is not the only factor that can determine the progress of carbonation in alkali-activated concretes. For the mixes assessed here, it has been observed when applying the standard procedure EMPA – SIA 162/1 [31] to study the capillary uptake of water into a dried sample, that before carbonation the concretes present similar resistance to water penetration (~$1\times10^7$ s/m$^2$) [30]. This parameter is one of the main coefficients describing the capillary sorptivity of these materials, and provides information regarding the geometry of the pore network of the assessed samples, where a higher resistance to water penetration indicates a more tortuous pore structure hindering mass transport through the material. The fact that similar values of resistance to water penetration are obtained across the concrete mixes studied indicates that these materials present approximately comparable pore structures. Consequently, the differences in the rates of carbonation at early stages of reaction of the mixes assessed are more likely to be associated with the carbonation starting in the capillary pores, increasing the pore size (as previously identified in alkali-activated mortars [9-10]), and thus diminishing the effect of the different quantities of water present at different RH values.

### 3.2. Effect of the $CO_2$ concentration on the carbonation of concretes based on activated GBFS/MK blends

Results reported in a previous study [22] show that accelerated carbonation induced in the pore solutions of alkali-activated binders under different $CO_2$ concentrations promotes the formation of different carbonation products, depending on both the $CO_2$ concentration and the temperature of the test. This indicates that increased partial pressures of $CO_2$ shift the reaction equilibrium expected under natural carbonation conditions, and therefore promote mechanisms which may lead to disproportionately faster degradation of the material compared to what is likely to occur in actual service. Thus, conflicting results could be obtained if the carbonation progress in alkali-activated concretes is tested under different $CO_2$ exposure conditions, and this issue is examined in detail in the following section. All the tests described in this section are conducted at 65% RH.

#### 3.2.1. Carbonation rate

As discussed in detail in section 3.1 above, concretes exposed to 1% $CO_2$ (Figure 4A) show a higher carbonation extent at increased contents of MK in the binder; however, the difference between GBFS/(GBFS+MK) ratios of 0.8 and 0.9 is in general minor, while there is a notable difference between the concretes with and without MK. Increasing the $CO_2$ concentration to 3% (Figure 4B) promotes much faster carbonation of the specimens, as expected. However, its effect is more detrimental in the concretes with GBFS/(GBFS+MK) = 0.8 than with GBFS/(GBFS+MK) = 0.9 or

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1.0. This indicates that 3% $CO_2$ is too high a concentration of $CO_2$ to enable reliable prediction of the in-service carbonation performance of alkali-activated concretes with different binder mix designs, as it may not be possible to distinguish which differences are due to actual better or worse carbonation resistance of the samples, and which are due to differences in the aggressiveness of the test towards different binder chemistries. This is an important point, and further discussion is required to determine the reasons for this behaviour.

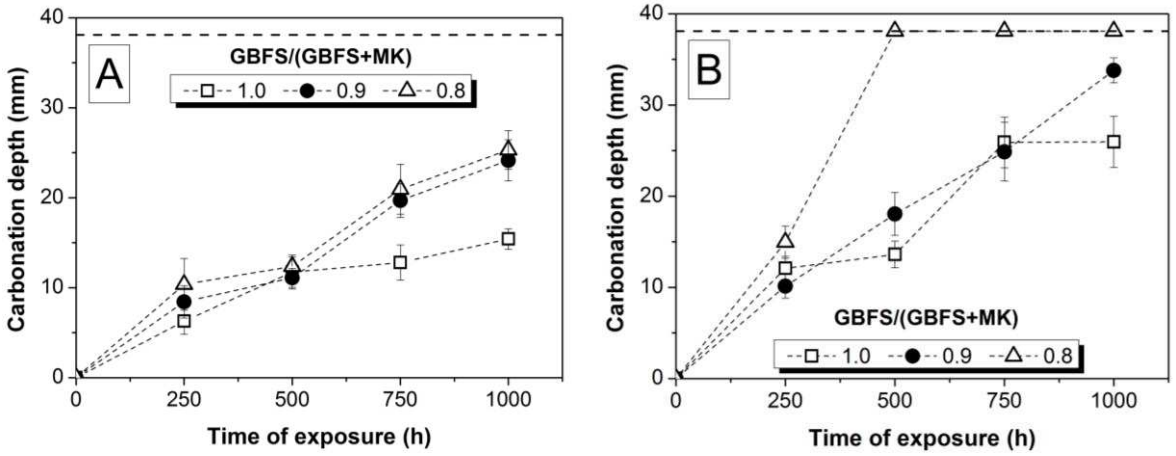


**Figure 4.** Accelerated carbonation progress of alkali-activated slag/metakaolin blended concretes induced at (A) 1% $CO_2$ and (B) 3% $CO_2$, and 65% RH. The horizontal dashed line in each plot represents full carbonation of the cylindrical specimens used in the tests. Each value is the average of 20 measurements taken from two specimens. Error bars correspond to one standard deviation.

After 250 h of exposure, the concretes with GBFS/(GBFS+MK) = 0.8 show the highest carbonation depths, consistent with the greater volume of permeable pores determined in these specimens before testing, when compared with the concretes with GBFS/(GBFS+MK) = 0.9 or 1.0. At longer times of exposure, the carbonation rates of concretes with GBFS/(GBFS+MK) = 0.9 or 1.0 remain comparable when exposed to 3% $CO_2$ (Figure 4B), although there was a notable difference between these specimens at 1% $CO_2$ (Figure 4A). When including 20% MK in the binder (GBFS/(GBFS+MK) = 0.8) and exposing the material to 3% $CO_2$, the carbonation progresses so rapidly that the concrete specimens tested here (38.1 mm radius cylinders) are completely carbonated after only 500 h of exposure.

This, combined with the porosity data in Figure 3 and in reference [30], indicates that concretes presenting a higher volume of permeable pores before testing will be more aggressively subject to carbonation penetration at higher $CO_2$ concentrations than would be expected when the material is exposed to more moderate $CO_2$ concentrations. It is noted that 3% $CO_2$ is actually not a particularly

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high concentration for use in an accelerated carbonation test for Portland cement systems. Concentrations far exceeding this value (and even up to 100%) are widely used in international testing programs for Portland cement concretes [28], although there has been limited systematic study of the influence of these parameters on the chemistry of non-traditional cements and concretes [37]. This strong dependence on $CO_2$ concentration when comparing binder types may also provide misleading conclusions about the 'real' quality of the material in service, considering that alkali-activated concretes often exhibit a substantial reduction in permeability at advanced ages of curing, and therefore will behave differently if they are assessed at more mature ages [30].

### 3.2.2. Residual mechanical strength

Residual mechanical strengths of specimens carbonated under 1% and 3% $CO_2$ environments are shown in Figure 5. These results show that decreases in the compressive strength are induced as consequence of the carbonation of the specimens, and that this is not strongly dependent on the concentration of $CO_2$ exposure. The concretes including MK as a secondary binder component show very little effect of $CO_2$ concentration on residual strength, while the slag-only binders show slightly more loss of strength at 3% $CO_2$ than at 1%. However, although some samples revealed complete carbonation when determined using the phenolphthalein indicator (Figure 4B; samples with GBFS/(GBFS+MK) = 0.8 at 3% $CO_2$), the remnant compressive strength of those concretes (Figure 5B) is comparable with what is obtained in specimens of the same mix design carbonated at 1% $CO_2$ (Figure 5A), where these specimens showed only partial carbonation when carbonation depth was determined using the same methodology.

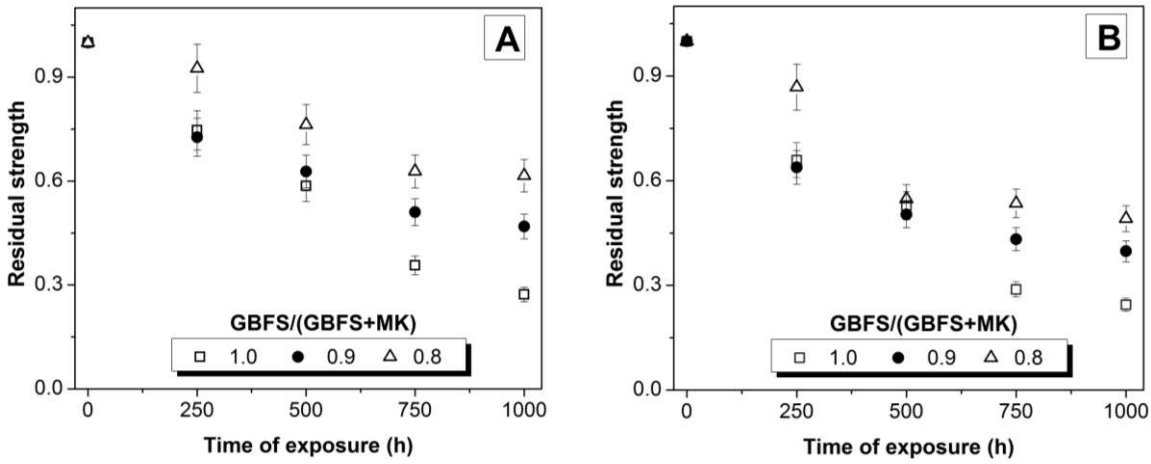


**Figure 5.** Effect of the $CO_2$ concentration of exposure on the residual compressive strength of partially carbonated concretes based on alkali-activated slag/metakaolin blends, exposed to

carbonation at (A) 1% or (B) 3% $CO_2$, and 65% RH. Error bars correspond to one standard deviation of three measurements.

It therefore becomes evident that there is not a direct correlation between the degree of ingress of the carbonation front, as identified using the phenolphthalein indicator, and the degree of degradation of the material as measured by residual mechanical strength. If complete carbonation of the matrix was taking place in these systems, the loss of loading capacity should be approximately proportional to the loss of undamaged cross-section area, considering that carbonation is usually assumed to be associated with the decalcification of the C-A-S-H gel formed during the activation of the slag [20]. However, ongoing reduction in the compressive strength with $CO_2$ exposure is identified in the specimens with GBFS/(GBFS+MK) = 0.8, which were apparently completely carbonated (according to the phenolphthalein test) within the first 250 h of exposure. This highlights the fact that carbonation in alkali-activated binders cannot be understood solely as taking place via either pore solution effects, or by the decalcification of the solid binder phases, but rather that both stages of the interaction between $CO_2$ and the binder components (liquid and solid) must be considered.

The chemical reactions controlling the extent of carbonation in alkali-activated materials involve the carbonation of the highly alkaline pore solution, and subsequently carbonation of secondary products such as layered double hydroxides (i.e. hydrotalcite) and decalcification of C-A-S-H type products [22]. Recent work [22] has shown that under accelerated carbonation conditions, the pore solution pH in alkali activated binders is highly dependent on the partial pressure of $CO_2$, so that a decrease in the pH to values below 10 could only be expected at $CO_2$ partial pressures higher than ambient, as the pore solution chemistry changes from carbonate-dominated to bicarbonate-dominated. Considering that the phenolphthalein indicator used here shows a colour change at pH values between 8.2 and 10 [38], it is likely that the colourless area observed in the carbonation testing is more likely to represent the carbonation of the pore solution, rather than rather than the potential extent of degradation of the C-A-S-H type phases in the binder matrix.

This is consistent with the fact that the concretes exposed to different $CO_2$ concentrations present comparable compressive strengths, and that those showing complete carbonation within the first 250 h of exposure report ongoing changes in residual strength after longer times of exposure to $CO_2$. These later changes in compressive strength are associated with ongoing decalcification processes in the binder, which take place after the local pH has decreased sufficiently to cause phenolphthalein to remain colourless when sprayed onto the samples. It is entirely possible that there is also some decalcification taking place simultaneously at the reaction front where the pH is decreasing, and this will cause the start of the strength loss, but this is seen to continue long after the ‘carbonation front’

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has passed, showing that the traditional conceptual model of this process taking place at a sharp reaction front in Portland cement systems [39] is not appropriate for the systems studied here. It is noted that some authors have also observed a multi-stage process in Portland cement carbonation, e.g. [40], but the details of the mechanisms are likely to be very different in these specimens which do not contain portlandite.

### 3.2.3. Water absorption properties

Given this apparent disconnect between measured carbonation depths and gel decalcification during accelerated carbonation testing of alkali-activated binders, it thus appears valuable to analyse alternative methods by which the progress and effects of the actual decalcification process can be easily determined in an engineering sense, and it is likely that changes in the gel microstructure and pore structure will provide useful information in this regard. Water absorption is a relatively straightforward, although in many cases very sensitive and subtle, means of examining changes in pore network structure. In this section, the effects of inducing carbonation at different $CO_2$ partial pressures on the water absorption parameters of alkali-activated concretes are assessed.

- Volume of permeable pores (ASTM C 642)

Concretes based solely on GBFS present the lowest volume of permeable pores among the concretes studied prior to carbonation (Figure 6), and an increased volume of pores is identified with the inclusion of higher contents of MK in the binder. This might be an intrinsic property of the more MK-rich binders, but may also be related to the reduced workability identified in these concretes, which makes moulding and compaction of the specimens more difficult. Exposure to 1% $CO_2$ (Figure 6A) induces a gradual increment in the volume of permeable pores of the specimens throughout the time of exposure, and a very consistent trend in this parameter is observed across the different binder formulations. These results and trends differ from what is usually identified in Portland cement-based materials, where the porosity is generally reduced by carbonation, along with a decrease in the content of small radius pores due to pore blocking by carbonate reaction products [10].

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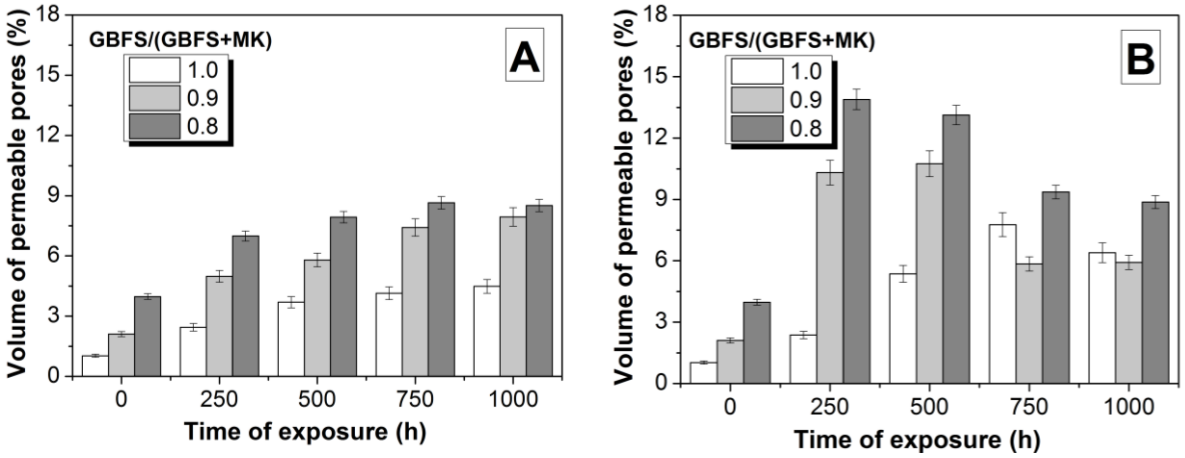


**Figure 6.** Volume of permeable pores of accelerated carbonated concretes based on alkali-activated slag/metakaolin blends exposed to (A) 1% and (B) 3% $CO_2$, at 65% RH. Each value is the average of four measurements. Error bars correspond to one standard deviation.

However, an entirely different trend in the variations of the volume of permeable pores is identified in alkali-activated concretes subjected to accelerated carbonation at 3% $CO_2$ (Figure 6B). Concretes based solely on GBFS show a gradual increase in porosity during the first 750 h of exposure under these conditions, consistent with the trend identified in these specimens at 1% $CO_2$ (Figure 6A), but then a decrease in porosity after this time. The concretes with MK in the binder start from a slightly higher porosity, but with exposure to 3% $CO_2$ show a very substantial increment in their porosity up to 250 h (with GBFS/(GBFS+MK) = 0.8) or 500 h (with GBFS/(GBFS+MK) = 0.9), followed by a significant reduction in porosity up to 1000 h of exposure. These results do not correlate well with the observations related to carbonation front progress or residual compressive strength, where samples with GBFS/(GBFS+MK) = 0.8 were apparently fully carbonated after 250 h of exposure to the same $CO_2$ concentration, and the variations in strength (Figure 5B) were all monotonic rather than showing any inflection points. It is currently unclear why the samples show a maximum in pore volume after an intermediate duration of carbonation, as this would not logically be expected based on the current understanding of the carbonation mechanisms in these systems, and this issue is identified as being worthy of further analysis as a key part of the future development of reliable carbonation testing protocols for alkali-activated concretes.

This behaviour provides further evidence that the use of increased concentrations of $CO_2$ to induce carbonation of alkali-activated concretes leads to unrepresentative, and thus undesirable, changes in the structure and chemistry of alkali-activated binders at early times of $CO_2$ exposure. This leads to a faster reduction of the pH in the pore solution of the sample, decreasing into the phenolphthalein colour change range, than what would be expected under natural carbonation conditions, and therefore

549 the identification of a 'false' carbonation. Consistent with this is the fact that there are ongoing
550 changes in the strength and permeability of 'completely' carbonated specimens, as a consequence of
551 reactions that continue taking place over time. This also agrees with the observation that reductions in
552 the volume of permeable pores are observed here as a consequence of the deposition of solid
553 carbonation products, which appear to contribute to the plugging of some of the additional pores
554 formed during carbonation.
555
556 • Capillary soptivity
557
558 The degradation of reinforced concrete under $CO_2$ exposure involves both the carbonation of the
559 matrix, leading to a reduction of the alkalinity of the system, and the consequent depassivation of the
560 steel rebars, which makes them susceptible to a series of corrosive attacks such as pitting, which is
561 accelerated by the presence of chloride and is extremely harmful for the integrity of the concrete
562 structure as a whole. It has been reported [41] that similar to the situation for Portland cement based
563 materials, the ingress of chlorine anions into alkali-activated concretes takes place through the
564 capillary pores. Several studies agree [30, 33, 42, 43] that uncarbonated alkali-activated mortars and
565 concretes present low capillary sorptivity, and consequently a high resistance to chloride penetration,
566 when compared with conventional Portland cement concretes; however, the changes in the capillary
567 sorptivity of these concretes induced by carbonation have not previously been studied in detail.
568
569 The exposure to 1% $CO_2$ of concretes based solely on GBFS (Figure 7A) for 250 h leads to a
570 substantial increment in the total capillary water uptake of the material, which is higher by as much as
571 a factor of 3 than in uncarbonated specimens. However, this dramatic increase is only temporary, and
572 the exposure of these samples to 1% $CO_2$ for longer periods of times then brings the amount of
573 absorbed water down to be similar to the unexposed material after 750 h of exposure to 1% $CO_2$. The
574 same is true for the samples with GBFS/(GBFS+MK) = 0.9 (Figure 7B). This indicates that partial
575 carbonation of the specimens may inhibit the ingress of aggressive agents such as chlorides into the
576 concrete, but that the complete carbonation of alkali-activated concretes after this time leads to
577 reductions in the capillarity as a consequence of the precipitation of carbonation products. This time-
578 dependent behaviour was not observed in any other material parameters analysed during exposure to
579 1% $CO_2$, but shows some subtle effects in changes in pore size distribution which were not observed
580 in the overall porosity data.
581

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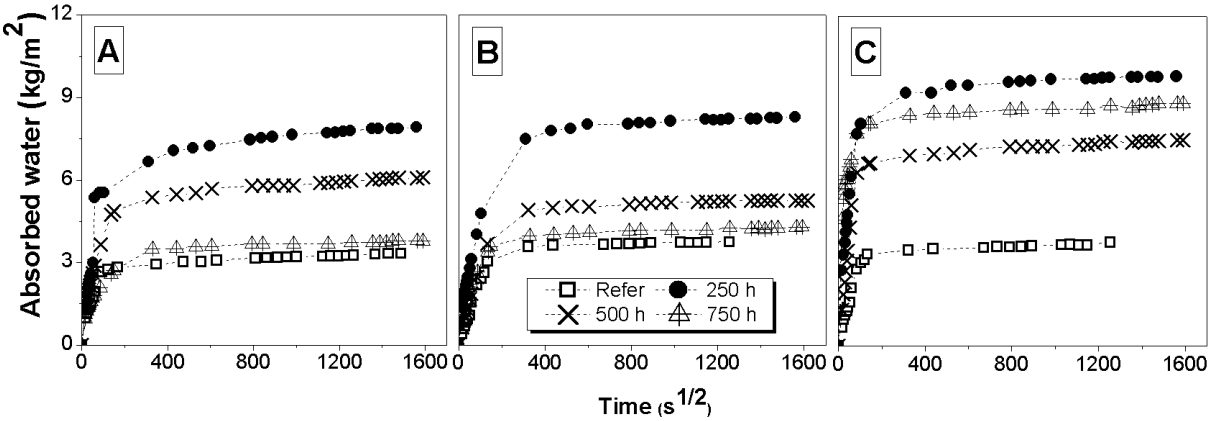


**Figure 7.** Capillary sorptivity curves of accelerated carbonated concretes based on alkali-activated slag/metakaolin blends formulated with GBFS/(GBFS+MK) ratios of (A) 1.0, (B) 0.9 and (C) 0.8, exposed to 1% $CO_2$ at 65% RH.

However, concretes formulated with GBFS/(GBFS+MK) = 0.8 (Figure 7C) do not display such a notable reduction in the capillary suction with the progress of carbonation in the specimens. The total water absorbed by the samples exposed to 1% $CO_2$ for 750 h is almost as high as after 250 h of exposure, and almost three times as high as the water uptake of the unexposed material. This may be associated with the lower Ca content of the gel in this mix, leading to the formation of less solid carbonation products to plug the pores in the material, or may be attributed to factors related to shrinkage and/or microcracking in the gel, which is also likely to be changed by the differences in Ca and Al content as a function of MK addition [29, 30].

Concretes carbonated at a $CO_2$ concentration of 3% (Figure 8) display water saturation after a shorter period of time than similar concretes carbonated at 1% $CO_2$ (Figure 7). Concretes exposed to 3% $CO_2$ for 250 h again show a marked increase in capillary water uptake compared with uncarbonated specimens. After 500 h of exposure (Figure 8A), a substantial reduction in water uptake is identified in specimens based solely on GBFS; however, exposure to this $CO_2$ concentration for longer periods of time leads again to increments in the amount of absorbed water compared with those identified after 250 h, and the water uptake after 1000 h of carbonation is approximately double the uptake of the unexposed concretes.

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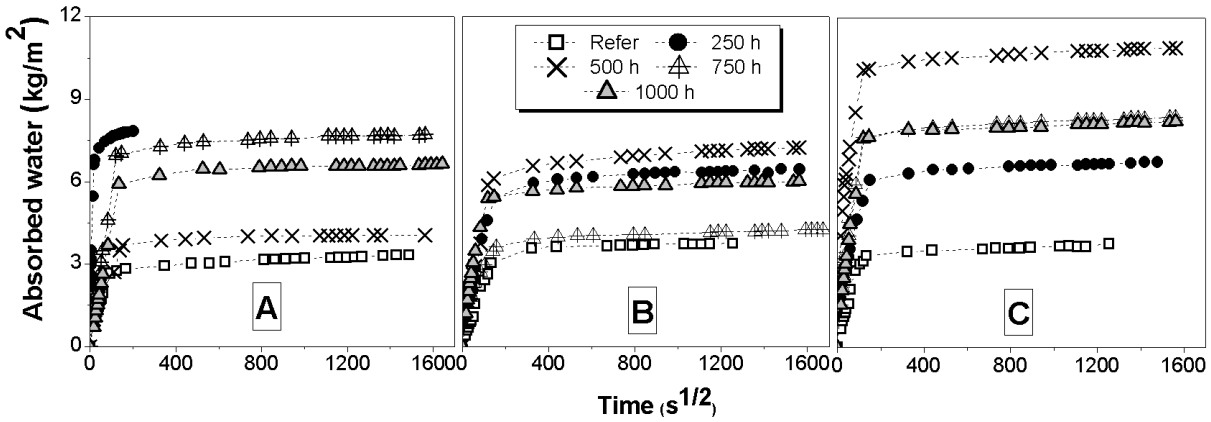


**Figure 8.** Capillary sorptivity curves of accelerated carbonated concretes based on activated slag/metakaolin blends formulated with GBFS/(GBFS+MK) ratios of (A) 1.0, (B) 0.9 and (C) 0.8, exposed to 3% $CO_2$ at 65% RH.

In concretes formulated with GBFS/(GBFS+MK) = 0.9 (Figure 8B), a similar trend is observed, with a reduction in absorbed water after 750 h of exposure but an increased permeability observed at the other times of exposure. This differs from the observations for these concretes when exposed to 1% $CO_2$, where reductions in the capillary permeability at extended periods of exposure were observed (Figure 7B). This again demonstrates that exposure of alkali-activated concretes to different $CO_2$ concentrations promotes the development of different pore structures, and therefore variations in the transport of $CO_2$ inside the material, which can give potentially misleading indications regarding the carbonation performance which would be identified in service in these concretes.

Increasing the MK content of the binder to 20% (GBFS/(GBFS+MK) = 0.8) again leads to increased water absorption at extended times of $CO_2$ exposure (Figure 8C). This is consistent with the high total porosity observed in these specimens when compared with concretes with lower contents of MK. In this case, similar behaviour is observed at 1% and 3% $CO_2$ – which may mean either that both of these testing conditions are appropriate for the analysis of these concretes, or that even 1% $CO_2$ is too high a concentration to provide a good representation of the performance of the concretes in service. At this point it is not possible to say which of these possibilities is more likely, but the effect of elevated $CO_2$ concentrations on pore solution chemistry [22] indicates that the concentrations are probably too high to fully accurately represent the in-service carbonation of alkali-activated concretes, even at these levels which are quite moderate by the standards of most carbonation tests [28].

The kinetics of the capillary sorption of water into concrete can be described by the resistance to water penetration ($m = \frac{\text{saturation time}}{(\text{penetration depth})^2}$). The values of this parameter, as determined from

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capillary sorption curves of concretes exposed to 1% $CO_2$ (Figure 7) and 3% $CO_2$ (Figure 8), are shown in Figure 9. Concretes exposed to 1% $CO_2$ display lower resistance to water penetration at extended periods of exposure, which is consistent with the increased volume of permeable pores observed in those concretes (Figure 6). On the other hand, for concretes exposed to 3% $CO_2$, the fluctuations in the m values are approximately consistent with the total porosity of these concretes, indicating the high variability of capillary pore structure induced during carbonation at such a high $CO_2$ concentration.

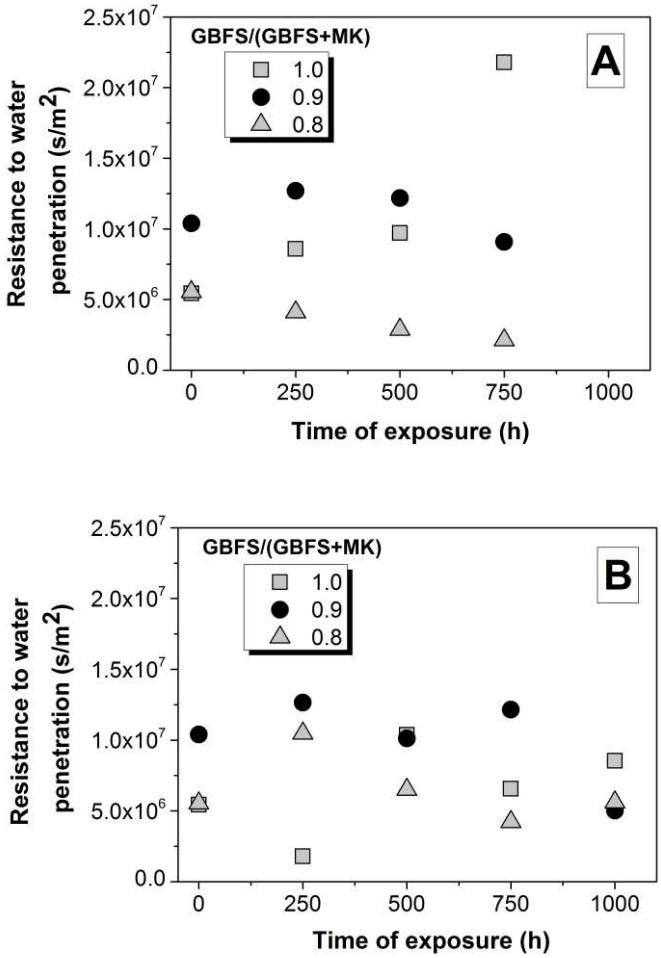


**Figure 9.** Resistance to water penetration (m) of carbonated alkali-activated concretes exposed at 65% RH, and (A) 1% $CO_2$ or (B) 3% $CO_2$, for durations as marked.

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## 4. Conclusions

The key outcome of this study is the observation that accelerated carbonation testing of alkali-activated concretes depends strongly on both the testing conditions and the chemistry of the binder. The inclusion of more than 10% MK (GBFS/(GBFS+MK) < 0.9) in activated-slag binders leads to notably increased carbonation rate and extent, as these specimens develop increased permeability. The performance of samples with GBFS/(GBFS+MK) = 0.9 or 1.0 is sometimes similar, or sometimes the samples with GBFS/(GBFS+MK) = 0.9 carbonate more rapidly, depending on the test conditions. In the relative humidity range tested (50-80%), the highest carbonation rates are generally observed in specimens exposed at a relative humidity of 65±5%, indicating that a partially saturated moisture condition accelerates the carbonation reaction process. For carbonation tests where the specimens were not dried prior to testing, the water absorption of the uncarbonated samples provides a good indication of whether drying effects during the test duration will retard the initial stages of carbonation. Testing samples with low water absorption (i.e. initially highly saturated and refined pore networks) at high relative humidity gives a very low carbonation rate in the early stages of the test, as the carbonation of the saturated binder is slow, followed by an acceleration of the carbonation process as the drying front begins to enter the sample to a more significant extent.

The progress of carbonation in alkali-activated concretes is also very strongly dependent on the $CO_2$ concentration used during the accelerated testing, as differences in the total porosity and mainly in the capillary pore structure are induced at higher $CO_2$ concentrations. At relatively low $CO_2$ concentration (1%), a monotonic increase in porosity, along with an eventual reduction in capillarity, can be identified in the concretes assessed, indicating that the formation of carbonation products in these systems is contributing to changes in the pore network structure during the test. On the other hand, carbonation induced at higher $CO_2$ concentrations (3%) shows less clarity in the relationships between measured carbonation depth, residual strength and porosity.

Concretes which appear fully carbonated after only 250 h of testing when the pH is revealed by a phenolphthalein indicator continue to show structural changes over 1000 h, showing that there are likely to be multiple steps in the carbonation process (most probably carbonation of the alkali-rich pore solution in the first instance, followed by later decalcification of the gel), and that the phenolphthalein method shows only the progress of the first of these processes. The rates of pore solution carbonation and gel carbonation seem to be particularly distinct from each other at higher $CO_2$ concentration, meaning that such test conditions lead to the prediction of poor performance in alkali-activated concretes, which may not accurately represent the behaviour of the materials under exposure to natural carbonation. It is therefore not recommended to carry out accelerated carbonation

testing of alkali-activated binders at $CO_2$ concentrations higher than 1% $CO_2$. The results obtained from these experiments are more an indication of the loss of alkalinity in these materials due to pore solution chemistry (which is highly subject to differences in $CO_2$ partial pressure), rather than the degradation due to decalcification of the binding gel, and it cannot be considered as a sole predictor of their durability.

Finally, it is noted that the interaction between carbonation and drying in alkali-activated concretes certainly requires further investigation – there is a coupling effect whereby drying influences carbonation, and carbonation influences drying, and the study of these effects in parallel in a laboratory (or field) setting has not yet been fully developed. This is an area requiring further research, as highlighted by the fact that this paper has opened almost as many questions as it has answered in this area.

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