CARBONATION OF A LOW CALCIUM FLY ASH GEOPOLYMER CONCRETE

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ABSTRACT: This paper investigates the carbonation resistance of a blended slag and low calcium fly ash (FA) geopolymer concrete. The geopolymer binder is composed of 90% low calcium FA and only 10% ground granulated blast furnace slag (GGBFS). The alkalinity of the pore solution plays a pivotal role in carbonation progression and subsequent corrosion initiation. pH profiles were measured to assess the pore solution alkalinity. Phenolphthalein indicator was used to measure the carbonation depth. X-ray diffraction (XRD) and quantification were carried out to identify and quantify the carbonation products. The obtained pH profiles illustrated a wider semi-carbonation zone in the geopolymer specimens although pH drop was insignificant in most cases. XRD revealed that nahcolite mainly formed at 3% CO₂ concentration and led to a significant drop in pH values. The results further demonstrated that 1% accelerated carbonation well replicated the natural carbonation process where only natron was identified as a carbonation product. This work contributes to the assessment of the risk of carbonation-induced reinforcement corrosion in low calcium FA geopolymer concrete.

Keywords: Geopolymer concrete; carbonation; pH profile; XRD; class F fly ash.

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INTRODUCTION

The increasing potential threats to environment imposed by CO₂ and the growing demand for concretes have promoted the development of inorganic polymer binder called ‘geopolymer’ which involves the reaction between solid aluminosilicate materials with alkaline solutions [1-3]. With the introduction of geopolymer concrete (GPC), the industrial by-products such FA and GGBFS, have been proposed and researched as aluminosilicate source materials due to their low cost and widespread availability.

GPC has the potential to be a suitable alternative to Ordinary Portland Cement (OPC) concrete; however, its long term durability is yet to be established [4]. Carbonation process plays a detrimental role to concrete as CO₂ diffuses through pore structure and reduces the alkalinity of the pore solution [5]. This may lead to the depassivation of reinforcing steel leaving them prone to corrosion. To date, there is relatively little existing knowledge on carbonation process in low calcium FA geopolymer concrete. Bernal et al. [6] carried out a detailed microstructural analysis to investigate the effects of accelerated carbonation on alkali activated FA and slag. It is important to mention that their study only focussed on powder samples allowing understanding some important and fundamental aspects of carbonation chemistry but the results were unlikely to represent the performance of concrete under natural exposure condition. Law et al. [4] measured the pH of the extracted pore water in geopolymer mortar specimens exposed to 5% accelerated carbonation and recommended a pH value of 11 to protect the reinforcing steel following carbonation. However, the pore solution extraction method is unlikely to provide the pore solution composition at the vicinity of the steel to assess the degree of depassivation. This necessitates an accurate measurement of pH profile along the depth of geopolymer concrete cover under natural and accelerated carbonation conditions.

This paper presents a wide range of pH profiles of low calcium FA geopolymer concrete exposed to natural and accelerated carbonation. XRD was carried out to identify and quantify the carbonation products. A correlation was established between natural and accelerated carbonation. The pH profile along with the identification and quantification of the carbonation products provide a precise evaluation of the degree of carbonation of low calcium FA geopolymer concrete.

EXPERIMENTAL PROGRAM

Materials

Low calcium FA (class F), ultra-fine FA also known as Kaolite high performance ash (HPA) and GGBFS were used in this study as aluminosilicate sources. Low calcium FA and Kaolite HPA were obtained from Eraring Power Station in New South Wales, Australia and Callide Power Station in Queensland, Australia respectively while GGBFS was obtained from Blue Circle Southern Cement Australia. The chemical compositions of these supplementary cementitious materials are available in Noushini et al [7]. A mixture of sodium hydroxide (NaOH) solution and sodium silicate (Na₂SiO₃) solution were used with the ratio of 1:2.5 (by mass) according to Hardjito and Rangan [8]. The technical grade NaOH pellets obtained from Ajax Finechem were used to prepare NaOH solution and 361 g of NaOH pellets were dissolved into 639 g of Sydney tap water in order to obtain 12M NaOH solution. The Na₂SiO₃ solution was obtained from PQ Australia and has a chemical composition of Na₂O = 14.7%, SiO₂ = 29.4% and H₂O = 55.9% (by mass) with a modulus ratio (Ms) of 2 (Ms = SiO₂/ Na₂O = 2). It is to be noted that the activator solutions were mixed together 24 hours prior to usage.
Sydney sand with specific gravity of 2.65 and water absorption of 3.5% was used as fine aggregate. The coarse aggregate was 10 mm nominal size crushed basalt with specific gravity of 2.8 and water absorption of 1.6%. To accurately adjust the mix water, all aggregates were oven dried to drive away the moisture content.

Geopolymer concrete mix design and batching procedure

The geopolymer concrete mix detail is presented in Table 2. The solid contents except GGBFS were mixed dry for 5 minutes which followed further 15 minutes mix while gradually adding the alkaline solution and then the free water. To avoid rapid setting, GGBFS was added at the end and the mixing was continued for another 5 minutes. The moulds were filled in three layers and compacted using a vibrating table. The obtained slump and air content of the freshly mixed concrete were 120 mm and 3.5% respectively.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Proportion, kg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse aggregate</td>
<td>1221.2</td>
</tr>
<tr>
<td>Fine aggregate</td>
<td>620.8</td>
</tr>
<tr>
<td>Fly ash</td>
<td>271.6</td>
</tr>
<tr>
<td>Kaolite HPA</td>
<td>77.6</td>
</tr>
<tr>
<td>GGBFS</td>
<td>38.8</td>
</tr>
<tr>
<td>NaOH solution</td>
<td>55.3</td>
</tr>
<tr>
<td>Na₂SiO₃ solution</td>
<td>138.7</td>
</tr>
<tr>
<td>Free water</td>
<td>13.3</td>
</tr>
<tr>
<td>Na₂SiO₃ / NaOH</td>
<td>2.5</td>
</tr>
<tr>
<td>Molarity of NaOH solution</td>
<td>12 M</td>
</tr>
</tbody>
</table>

Curing and CO₂ exposure conditions

In a previous study by Noushini et al. [7], the influence of 12 different heat-curing regimes on mechanical properties of a FA GPC was investigated. The curing regimes included three temperatures of 60, 75 and 90°C, and four curing durations of 8, 12, 18 and 24 h. The optimum heat-curing regime for GPC, combining best performance and energy efficiency, was found to be 75°C for 18 h. Therefore, in this study, the sealed samples were placed in an oven at 75°C for 18 hours for heat curing and the samples were then demoulded. To achieve a uniform moisture redistribution, the samples were kept in an environmental chamber for two weeks at a constant temperature of 23 ± 2°C and 55% relative humidity. After the dry conditioning, 25 mm section was removed from top and bottom of each cylinder and remaining segment was cut into 50 mm sections for subsequent carbonation testing. 50 mm discs were sealed using aluminium tapes along the perimeter leaving top and bottom sides exposed for CO₂ diffusion. For natural carbonation, the specimens were kept in a controlled environmental room. For accelerated carbonation, the specimens were placed in a carbonation chamber with a CO₂ concentration of 1% and 3%. It is to be noted that the exposure temperature and relative humidity, in all cases, were 23°C and 55% respectively. The carbonation depth, pH profiles and the microstructure analysis were performed after 2, 4 and 6 weeks of exposure. Some of the specimens exposed to the natural carbonation were analysed after 6 and 18 months to establish a correlation between natural and accelerated carbonation.
pH profile and carbonation depth

pH profiles were obtained by combining water extraction method [9] and pore solution extraction method [10]. For water extraction method, concrete powder was sampled every 1mm over 25mm depth of the GPC specimen by using a Profile Grinder PF-1100 purchased from Germann Instruments. The powder was then mixed with de-ionised water with a solid to liquid ratio of 1:1 and the pH of the solution was measured using a pH probe. Water extraction method always overestimates the pH value [9]. As a result, the trend provided by the pH profile is accurate but not the pH values. To overcome this effect, pore solution was extracted from uncarbonated paste samples (having the same mix design and curing condition as the GPC) [10]. The pH of the extracted pore solution was directly measured by using a calibrated pH probe and then compared to the one obtained by using water extraction method for uncarbonated specimen. The difference between these two pH values were then deducted from all water extracted pH values in order to obtain the calibrated pH profile.

Identification and quantification of the carbonation products in geopolymer concrete

X-ray diffraction (XRD) was carried out in this study to identify and quantify the carbonation products in the geopolymer specimens. 50 mm cube specimens were cast with geopolymer paste having the same mix design and curing conditions as the GPC. Samples were collected from the surface of the cube for the XRD analysis. The paste samples were ground to powder and the powder were analysed using X-ray diffractometer Phillips X’Pert Pro Multi-purpose (MPD) system housed at the Mark Wainwright Analytical Centre at the University of New South Wales, Australia. This used Cu-Kα radiation with wavelength of 0.15418 nm and operated at 45 kV and 40 mA, scan range 5-65° and 0.026° 2θ step size. The scan results were interpreted using the software package HighScore Plus for phase identification. The crystalline phases were also quantified by using the software package HighScore Plus that is based on Rietveld method [11].

RESULTS AND DISCUSSIONS

The average compressive strength and the elastic modulus of the GPC samples at 28 days were 55.7 MPa and 23.8 GPa respectively.

Identification and quantification of carbonation products by using XRD

XRD patterns of geopolymer pastes exposed to natural, 1% accelerated carbonation (AC) and 3% AC are shown in Figures 1, 2 and 3 respectively. Figure 1 shows that natron (Na2CO3.10H2O) was identified after 6 weeks of natural carbonation and this was the only carbonation products under natural conditions. It is interesting to note that the same carbonation product was observed for 1% AC. Figure 3 reveals that the elevated CO2 concentration led to the formation of nahcolite (NaHCO3) even after 2 weeks of exposure. It is important to mention that Bernal et al. [6] observed nahcolite in the powder sample even at 1% AC after 1 week of exposure. This indicates that GPC powders exposed to accelerated carbonation are likely to suffer a higher extent of carbonation reaction compared to GPC specimens.

Table 3 shows the quantification of the crystalline phases formed in the geopolymer pastes exposed to carbonation. Table 3 reveals that natron comprised almost one-fourth of the
crystalline phases in the specimens after 6 weeks natural carbonation and 2 weeks 1% AC respectively. Its proportion increased to 29.4 wt.% after 6 weeks 1% AC. However, it can be seen that the proportion of nahcolite was 17.4 wt.% while the proportion of natron decreased to 6.3 wt.% after 2 weeks of 3% AC. This shows that high CO$_2$ concentration (>1%) can lead to the transformation of natron to nahcolite.

Figure 1  XRD traces of geopolymer pastes exposed to natural carbonation for 6 weeks

Figure 2  XRD traces of geopolymer pastes exposed to 1% AC for 2 & 6 weeks

Figure 3  XRD traces of geopolymer paste exposed to 3% AC for 2 weeks
Table 3  Quantification of the crystalline phases formed in pastes exposed to CO$_2$

<table>
<thead>
<tr>
<th>Exposure condition</th>
<th>Mullite (wt.%)</th>
<th>Quartz (wt.%)</th>
<th>Natron (wt.%)</th>
<th>Nahcolite (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural carbonation – 6 weeks</td>
<td>42.2</td>
<td>33.8</td>
<td>24.0</td>
<td>-</td>
</tr>
<tr>
<td>1% AC – 2 weeks</td>
<td>42.6</td>
<td>33.0</td>
<td>24.3</td>
<td>-</td>
</tr>
<tr>
<td>1% AC – 6 weeks</td>
<td>38.5</td>
<td>32.2</td>
<td>29.4</td>
<td>-</td>
</tr>
<tr>
<td>3% AC - 2 weeks</td>
<td>41.4</td>
<td>34.9</td>
<td>6.3</td>
<td>17.4</td>
</tr>
</tbody>
</table>

**pH profile and carbonation depth in GPC**

The pH values obtained from pore extraction and water extraction method for an uncarbonated specimen were 11.46 and 12.13 respectively. This difference of 0.67 was deducted from each water extracted value to obtain the calibrated pH profiles. The split uncarbonated GPC specimen sprayed with phenolphthalein indicator and the pH profile are shown in Figure 4. As expected, the dark pink colour throughout the fractured surface of the specimen indicates no carbonation. Figure 4 also shows that the pH values of uncarbonated GPC is close to 11.5 which has also been previously reported by other researchers, showing that pH value can range from 11.5 to 12.5 in GPC [12]. In the case of OPC concrete, the pH value is greater than 12.5 in the uncarbonated zone and around 8.5 in the fully carbonated zone. The pH value of 8.5 in carbonated OPC concrete is due to the formation of calcium carbonate [12-14]. These two values were considered in this study to compare to the alkalinity of GPC exposed to carbonation.

Figure 5 illustrates the pH profiles of GPC exposed to natural carbonation. Up to 6 weeks exposure, the maximum drop in pH value was about 0.46 and all the profiles converged to uncarbonated profile at about 6 mm depth. The pH profiles suggest that for natural carbonation, 6 weeks exposure may not be sufficient to assess the durability and therefore GPC specimens were exposed for extended period to evaluate their resistance against natural carbonation. It can be seen that the minimum pH value was 10.76 after 6 months exposure. The minimum pH values were 10.2 and 9.8 for specimen 1 and 2 respectively after 18 months exposure although the pH values reached above 10.5 beyond 3mm depth.

Figure 6 shows the pH profiles for GPC exposed to 1% AC. It can be seen that the profiles were very similar after 2 and 4 weeks exposure while the profile after 6 weeks exposure experienced a higher drop in pH. In all cases, the pH value dropped below 10 at 1mm depth and then gradually converged to uncarbonated zone. Pore blockage plays a vital role in controlling the diffusion of CO$_2$ through concrete. Natron has a very large molar volume (196.56 cm$^3$/mol) compared to nahcolite (38.66 cm$^3$/mol) and calcite (36.93 cm$^3$/mol) (www-mincryst - IEM Databases). Therefore, natron fills a large pore space, and thus provides a significant degree of pore blockage in carbonated low calcium FA GPC [15]. The significant amount of natron formed in 1% AC specimens might have slowed down CO$_2$ diffusion by enhancing the degree of pore blockage, and thus the pH profiles did not experience a significant drop compared to the pH profiles obtained with 3% AC (Figure 7).
Figure 4  pH profile of uncarbonated GPC

Figure 5  pH profiles of GPC exposed to natural carbonation
Figure 7 shows the pH profiles of GPC specimens exposed to 3% AC. Each of the profiles experienced a significant drop in pH and attained a fully carbonation stage with pH values ranging between 9.25 to 9.45. After 2 weeks exposure, the fully carbonated depth was 8mm and beyond that point, the pH values gradually increased and converged to uncarbonated profile at around 25mm depth. After 4 and 6 weeks of exposure, the fully carbonation depth extended further and none of them could reach uncarbonated pH at 25 mm depth. The quantification revealed that a significant amount of nahcolite formed even after 2 weeks of exposure. The molar volume of nahcolite is five times smaller than that of natron. This fills less space and thus provides lower degree of pore blockage which might have inspired CO$_2$ diffusion to a greater extent. Furthermore, the alkalinity of nahcolite is much lower than that of natron (http://www.engineeringtoolbox.com/). Therefore, nahcolite formation is the most possible reason for the significant lower pH values measured in the specimens exposed to 3% AC compared to natural and 1% AC conditions.
Carbonation depth of GPC

Figures 8 and 9 show the pH profile and the split specimen sprayed with phenolphthalein indicator after 18 months natural carbonation and 6 weeks 1% AC respectively. It is to be noted that the specimen exposed to 18 months natural carbonation was sealed in bottom side only.

Three stages were observed in all specimens: carbonated (colourless), partially carbonated (faded colour) and uncarbonated (coloured). Figure 8 reveals that after 18 months natural carbonation, the fully carbonated depth was only 3mm. The faded colour zone was about 30mm and beyond 33mm depth, the concrete was uncarbonated. After 6 weeks 1% AC, the colourless depth was only 2 mm and the faded colour zone was 21mm. OPC concrete usually displays a clear border between the coloured and colourless zone when sprayed with phenolphthalein indicator [5] and the pH profile shows a narrow partially carbonated zone [13]. However, this was not the case of GPC in this study where faded colour was scattered throughout an elongated depth. The pH profiles suggest that the pH value did not drop below 10.5 in the partially carbonated zone after 18 months natural carbonation. Furthermore, the minimum pH value was 10.42 after 6 weeks 1% AC in the faded region (Figure 9). These results indicate that this partially carbonated zone may still provide chemical protection against corrosion. Therefore, it may not be appropriate to consider the faded colour region or the partially carbonated zone as an integral part of the carbonation depth in GPC. Instead, the colourless depth offered a range of pH values that, in some case, may be inadequate to sustain the passivity of steel bar and it would be more appropriate to consider this colourless depth as carbonation depth in low calcium FA GPC. To provide a more precise and conclusive result
in this matter, experiments are in progress to measure the corrosion current of steel bar embedded in similar concrete.

![Figure 9 pH profile and carbonation depth of GPC exposed to 1% AC for 6 weeks](image)

**Correlation between natural and accelerated carbonation**

The natural carbonation process may last more than tens of decades. To assess the long term performance of concrete structures, it is desirable to accelerate the carbonation process to curtail the duration. If an accelerated carbonation test would accurately replicate the natural carbonation conditions, a correlation between natural and accelerated carbonation could be established [15]. However, the CO$_2$ concentration used during the accelerated testing strongly affects the pore structure and the composition of pore solution in alkali activated concrete. It is therefore not recommended to carry out accelerated carbonation testing of alkali activated binders at CO$_2$ concentration exceeding 1% [16]. It can be seen from Figure 10 that both pH profiles of 18 months natural carbonation reasonably converged to the pH profile of 6 weeks 1% AC. This indicates that the carbonation products so as the pore solution composition might have been similar in both cases. It is therefore reasonable to conclude that 6 weeks 1% AC is likely to replicate what is happening after 18 months natural carbonation of low calcium FA GPC. Thus 1% AC test is likely to provide an accurate service life prediction of low calcium FA GPC.
CONCLUSION

XRD results revealed that natron was the only carbonation product in the specimen exposed to natural and 1% AC for 6 weeks. Quantification showed that natron is about one-fourth of the crystalline phases in both exposure conditions. On the other hand, nahcolite started to form just after 2 weeks of 3% AC and its crystalline proportion was 17 % (wt.) while the proportion of natron was only 6.3 % (wt.).

Under natural and 1% accelerated carbonation exposure, the pH values did not experience a significant drop and none of the pH profiles showed a clear indication of a fully carbonation zone due to the formation of natron only. On the other hand, the specimens exposed to 3% AC experienced significant drop in pH values and the pH profiles offered an extended fully carbonated zone.

The phenolphthalein indicator test showed faded colour throughout an elongated depth although the pH values did not drop significantly. Therefore, this faded colour region may not be an integral part of the carbonation depth in low calcium fly ash geopolymer concrete. Instead, colourless depth would be more appropriate to consider as carbonation depth in geopolymer concrete.

The results demonstrated that 1% AC for 6 weeks replicated 18 months natural carbonation and thus 1% AC is likely to provide an accurate natural carbonation prediction of geopolymer concrete.

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REFERENCES


