Mechanical properties, durability characteristics and shrinkage of plain cement and fly ash concretes subjected to accelerated carbonation curing

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The paper presents an experimental study on assessment of the effect of accelerated carbonation curing (ACC) on the performance of two concrete mixtures having the same mixture proportions but different cementitious materials (plain-cement and fly-ash-blended-cement). Different sets of specimens were cast utilising both concrete mixtures and were then subjected to ACC for ten hours at a constant pressure of 414 kPa (60 psi). After exposing the specimens to ACC, they were tested for weight gain, carbonation depth, compressive and tensile strengths, modulus of elasticity, water penetration depth, rapid chloride permeability, shrinkage, SEM and XRD. ACC of the concrete specimens for ten hours resulted in a significant weight gain with less than 2 mm of carbonation depth. Both mixtures gained compressive strength above 20 MPa after ten hours of ACC. The strength increased further when ACC-treated specimens were exposed to air, with a significant increase up to seven days for plain-cement concrete and up to 28 days for fly-ash-blended-cement concrete. Compared to reference moist-cured concretes, the ACC-treated concretes were found to exhibit a slightly lower long-term strength (15% for plain-cement and 5% for fly-ash-concrete). However, the overall performance of the ACC-treated concrete mixtures was comparable with the respective moist-cured concrete mixes.

INTRODUCTION

Carbonation is a process in which the CO₂ present in the atmosphere penetrates concrete and reacts with calcium hydroxide Ca(OH)₂ to form calcium carbonates CaCO₃ (Rostami et al. 2012). This chemical reaction is considered harmful to concrete durability characteristics if it is allowed to occur for a long period, since it is associated with a significant decrease in the pH of concrete, which in turn leads to the initiation of corrosion of steel bars embedded in the concrete when the concrete pH falls below a threshold value of about 10. However, accelerated carbonation curing (ACC), which involves exposing
Concrete to CO₂ under pressure for a short duration of time at an early age (after a few hours of casting), has been reported to improve the mechanical and durability properties of hardened concrete (Rostami et al. 2012). The CO₂ sequestered into young concrete reacts with Ca(OH)₂ and C-S-H generated by the cement hydration process, leading to the formation of geologically stable calcium carbonates (Rostami et al. 2012; Fernández Bertos et al. 2004; Mo & Panesar 2013; Shao et al. 2014). Unlike the long-term natural carbonation process of hardened concrete, which has been the focus of several research studies on concrete durability, ACC eliminates the loss-of-alkalinity problem, since the accompanying reduction in pH occurs to a negligible depth below the concrete surface, rather than in the concrete core. Therefore, reinforcing steel bars are safe from de-alkalisation-induced reinforcement corrosion (Rostami et al. 2012; Shao et al. 2014; Monokman & Shao 2010).

ACC changes the mineralogy, morphology and microstructure of concrete, leading to an increase in the density of concrete, which implies higher strength and durability, compared to that offered by the microstructure of concrete developed by conventional curing (Rostami et al. 2012; Mo & Panesar 2013; Pizzol et al. 2014). In addition, ACC involving sequestration of CO₂ in concrete helps in reducing the carbon footprint, mitigating the environmental problems associated with cement and concrete production.

Many factors affect the effectiveness of ACC, such as the concentration of CO₂, temperature, relative humidity, pressure in the carbonation chamber, exposure duration to CO₂, the age of concrete when exposed to CO₂, type and amount of binders, and water/cement ratio (Fernández Bertos et al. 2004; Chen et al. 2011; El-hassan et al. 2013; Mohammed et al. 2014; Shao & Monkmann 2006; Zhan et al. 2013a; Zhan et al. 2013b). Kashef-Haghighi and Ghoshal (2013) found that CO₂ uptake could be increased significantly through the use of cements having higher amounts of reactive minerals and more fineness, which would provide a higher reactive surface area. Carbonation shrinkage resulting from ACC can be reduced by incorporating mineral admixtures such as slag (Monkmann & Shao 2010). Rostami et al. (2012) reported that keeping specimens in the air for some time before exposure to CO₂ is very important to allow better diffusion of CO₂ into concrete.

The consumption of CO₂, captured from the manmade stationary sources of CO₂ emissions and stored for usage (carbon capture), in ACC of concrete would significantly help in reducing the global greenhouse gas emission and, therefore, the problems around global warming, which are of great environmental concern. About 1.5 million tons of CO₂ can be sequestered in concrete products made with 16.4 million tons of cement in the USA, based on about 9% of CO₂ by mass of cement (Kashef-Haghighi & Ghoshal 2013).

The present study was conducted to investigate the mechanical properties, durability characteristics, shrinkage and microstructure of plain-cement and flyash-blended-concrete mixtures cured using accelerated carbonation. The main objective of the present work was to explore the possibility of using ACC as an alternative curing method that can be adopted by precast concrete industries.

**EXPERIMENTAL PROGRAMME**

**Materials**

ASTM C 150 Type I Portland cement with a specific gravity of 3.15 was used in this study to prepare the concrete specimens. A class F fly ash was used to prepare the concrete mixture, consisting of a blend of Portland cement and fly ash. Table 1 shows the chemical compositions of Portland cement and fly ash used in this work.

Coarse aggregate with a maximum size of 12 mm, specific gravity of 2.60 and water absorption of 1.4% was used. Dune sand with a specific gravity of 2.56 and water absorption of 0.4% was used as fine aggregate. Figure 1 shows the grading curves of coarse and fine aggregates. CO₂ gas with 99.9% purity was used for carrying out ACC of the concrete specimens.

**Concrete mixtures**

Two concrete mixtures having the same mixture proportions, but with different cementitious materials, were considered in this study. The first mixture was prepared with a plain Portland cement as a cementitious material, and this concrete mixture was abbreviated as plain-cement concrete (PCC). In the second mixture, a blend of 20% fly ash and 80% Portland cement was used as cementitious material and this concrete mixture was abbreviated as flyash-blended-cement-concrete (FA-BCC). Table 2 shows the weights of the constituent materials for preparing one cubic metre
moist-curing was carried out by sandwich-preliminary study (Ahmad et al. 2017). The crete mixture was determined by crushing initially for a period of seven days. The curing chamber, which was kept continuously moist for a period of seven days. The CO2 exposure duration, as reported in a with the optimum levels of pressure and pressure of 414 kPa (60 psi) was maintained in the ACC chamber where a constant CO2 in the ACC chamber was kept at 414 kPa. The specimens were weighed before and after ACC to determine the average CO2 uptake of each mixture, expressed as percentage weight gain by mass of cement. Figure 2 shows the weight gain for the two concrete mixtures considered in this study. It can be seen from Figure 2 that FA-BCC had a 13% lower weight gain, compared to PCC. This can be attributed to the availability of a lower amount of hydration-generated Ca(OH)2 for CO2 uptake in FA-BCC, where 20% of Portland cement was replaced by fly ash.

### Preparation and curing of concrete specimens

The specimens made of both concrete mixtures were demolded after 18 hours of casting, and the specimens of each of the two concrete mixtures were divided into two sets. One set of specimens was cured by ACC for ten hours, while the other set was moist-cured for seven days. ACC was carried out by exposing the specimens to CO2 in the ACC chamber where a constant pressure of 414 kPa (60 psi) was maintained for a period of ten hours, in accordance with the optimum levels of pressure and CO2 exposure duration, as reported in a preliminary study (Ahmad et al. 2017). The moist-curing was carried out by sandwiching the specimens in layers of burlap in a curing chamber, which was kept continuously moist for a period of seven days. The initial compressive strength of each concrete mixture was determined by crushing four cubes of 50 mm size immediately after demolding.

Prior to applying ACC, all specimens were weighed using a precision electronic balance with a resolution of 0.01 g. Thereafter, the specimens were arranged inside the ACC chamber on a perforated platform. The flow control valve of the CO2 gas cylinder was then released while the chamber outlet was still open. This setup was continued for one minute to clean the chamber before ACC commenced. Subsequently, the outlet was closed, and the pressure regulator was adjusted to maintain a constant ACC pressure of 414 kPa (60 psi). The ACC process continued for ten hours before the cured specimens were taken out of the chamber. The post-ACC weight gain was recorded.

After the curing process for both ACC and moist-curing regimes, the specimens were tested to assess their mechanical properties, durability characteristics, shrinkage behaviour and microstructure.

### Microstructure and identification of carbonation products

The morphology of the carbonated hydration products was studied by examining the secondary electron image (SEI) of near-surface zones of fractured concrete samples under a JEOL (JSM-6610LV model) scanning electron microscope (SEM), which was equipped with an energy dispersive spectroscopy (EDS) detector. Additionally, crystalline phases present in the ACC-cured specimens were analysed by X-ray diffraction (XRD), using a Rigaku (Ultima IV model) X-ray diffractometer with Cu-Kα radiation (λ = 1.5418 Å), over a 2θ range of 10 to 70° in steps of 0.02° 2θ.

### RESULTS AND DISCUSSION

#### Weight gain observations

For each of the two concrete mixtures, the weight gain was calculated after exposure of 20 cube specimens to ACC for ten hours at 414 kPa. The specimens were weighed before and after ACC to determine the average CO2 uptake of each mixture, expressed as percentage weight gain by mass of cement. Figure 2 shows the weight gain for the two concrete mixtures considered in this study. It can be seen from Figure 2 that FA-BCC had a 13% lower weight gain, compared to PCC. This can be attributed to the availability of a lower amount of hydration-generated Ca(OH)2 for CO2 uptake in FA-BCC, where 20% of Portland cement was replaced by fly ash.

#### Carbonation depth

After exposure to ACC, the carbonation depths were measured by splitting the specimens into two and then spraying phenolphthalein solution on the split surfaces of concrete. The carbonation depth was indicated by the thin outer layer of the discoloured portion of the concrete surface. Figure 3 schematically shows the carbonation profile, indicated by the portion with phenolphthalein staining (represented by the black colouring) and the colourless portion (represented by white colouring) on the fractured surface of a concrete.
specimen after exposed to ACC. For each sample, the carbonation depth was taken as the average value of the largest CO₂ penetration depth measured on all sides of the specimen, as indicated in Figure 3.

Table 3 presents the average carbonation depths in mm for the two concrete mixtures considered in this study. It can be observed from Table 3 that the carbonation depth was around 2 mm for both concrete mixtures studied. However, FA-BCC experienced a slightly (11%) higher carbonation depth than PCC. A reverse of this observation might be expected, because a higher CO₂ uptake was recorded for the plain cement mixture. However, it is known that the pozzolanic action of fly ash is a slow process. Therefore, after 18 hours of casting when ACC commenced, the lower cement content in the FA-BCC would result in higher gas porosity because of the lower density of the primary C-S-H gel in the mixture. In addition, for the same reason (lower cement content), the lower amount of Ca(OH)₂ available for CO₂ uptake also poses less hindrance to further penetration at later stages of carbonation. Hence, the higher penetration depth in the fly ash mixture, despite its lower CO₂ uptake, can be justified. Subsequently, the lower reduction of CO₂ uptake of the fly ash mixture (13%), compared to the 20% reduction of cement content, can be explained by the deeper reach of the CO₂ front.

It is worth noting that the carbonation depth obtained using the method described earlier is an underestimate of the true depth of the carbonation front. Phenolphthalein indication only highlights the region with pH lower than 10. This implies that the measured average depth does not include the carbonated regions that are deeper than the phenolphthalein-highlighted zone of which the pH levels are higher than the sensitive range of phenolphthalein indicator. Nevertheless, the actual depth of carbonation is not expected to exceed two to three times that obtained through phenolphthalein indication measurements, which does not constitute a threat of corrosion to a steel bar embedded in a reinforced concrete element made with these mixtures, since the usual minimum cover to rebars is 20 mm. In addition, ACC of concrete elements results in densification of the thin carbonated surface layer (or skincrete). The densification of skincrete is expected to slow down the diffusion rate of CO₂ into concrete through the skincrete, leading to higher resistance to natural carbonation during the service life of the concrete element. Further, subsequent hydration of CO₂-cured concrete (upon contact with water) re-alkanises the concrete to pH in excess of 12.0 (Zhang & Shao 2016), offering additional protection of CO₂-cured concrete from natural carbonation during the service life.

**Evolution of compressive strength**

For concrete specimens subjected to ACC regime, the first test was conducted directly after ten hours of ACC, while the first test on specimens exposed to moist-curing regime was carried out after seven days of moist-curing. Subsequently, concrete specimens from both curing regimes were subjected to air-curing under laboratory conditions and were tested after 7, 14, 28 and 90 days of additional air-curing. The compressive strength development of PCC and fly ash FA-BCC for both ACC and moist-curing are shown in Figures 4 and 5. It can be observed from Figures 4 and 5 that both PCC and FA-BCC gained a compressive strength of more than 20 MPa only after subjecting them to ten hours of the ACC.

As can be seen from Figure 4, the ACC specimens achieved a higher compressive strength during the first seven days of air exposure. About 63% increase in the compressive strength due to the air-curing for the first seven days after ACC was recorded. However, very little benefit of post-ACC air-curing was observed after the first seven days of air exposure, as is evident from the nearly flat portion of strength evolution curve shown in Figure 4. A similar trend of strength evolution was observed for moist-cured specimens. An increase of about 30% in compressive strength was noted when moist-cured specimens were exposed to air for the first seven days. As in the case of ACC, the benefit of air exposure after moist-curing was found to be insignificant beyond seven days of air exposure.

It is important to note from Figure 4 that the strength of ACC specimens after seven days in the air was found to be about 14% higher than the strength of seven days moist-cured specimens. However, the strength of moist-cured specimens kept in the air for seven days was found to be around 10% higher than the strength of ACC specimens kept in the air for 14 days. This can be explained by the fact that the carbonation process is of exothermic nature. The heat generated from the process tends to increase the cement hydration rate as ACC progresses. Additionally, during the post-ACC air exposure, the carbonated layer around the surface of the ACC specimen significantly reduced the evaporation of moisture from the core of the specimens, which resulted in continuation of the hydration process until most of the free concrete water had been consumed, resulting in a lower rate of strength gain. On the contrary, in the specimens subjected to seven days moist-curing, the rate of strength gain during the moist-curing period was slower.

**Table 3 The depth of carbonation for ACC specimens**

<table>
<thead>
<tr>
<th>Mixture ID</th>
<th>Average depth of carbonation (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCC</td>
<td>1.8</td>
</tr>
<tr>
<td>FA-BCC</td>
<td>2.0</td>
</tr>
</tbody>
</table>
than that of ACC specimens exposed to the air for seven days, due to the absence of carbonation-induced heating. Due to the slow rate of hydration, the amount of residual moisture available in the pores of moist-cured specimens would be more than that of ACC specimens (because ACC specimens consumed almost entire pore water for further hydration during the first seven days of air exposure). This therefore explains the observed higher strength gain during air exposure of moist-cured specimens compared to ACC specimens.

It can further be seen that the difference in the strength of ACC and moist-cured specimens is almost constant (about 15%) during the long-term air exposure. Therefore, it may be concluded that the difference in the strength of ACC and moist-cured specimens can be taken as 15% during the service life of the concrete. It is worth mentioning that the ACC concrete achieved a strength of 27 MPa only after ten hours of accelerated carbonation, making it possible to handle the carbonation-cured concrete only after ten hours of curing.

However, unlike the PCC made with only cement as binder, the strength of ACC specimens made of FA-BCC after exposure to air for seven days is almost similar to that of the seven days moist-cured specimens of FA-BCC. This observation may be explained by the relatively lower degree of carbonation achieved for FA-BCC due to the availability of a lower amount of Ca(OH)\(_2\), as a result of its lower cement content. This relatively lower amount of Ca(OH)\(_2\) was further reduced in secondary hydration with silica from the admixed fly ash. Due to the lower degree of carbonation, the enhancement of strength owing to the increased surface hardness was relatively lower, leading to the development of lower strength.

Unlike the case of PCC, where the rate of strength gain became almost negligible after seven days of air exposure of both ACC as well as moist-cured specimens, the rate of strength gain for both curing regimes in the case of FA-BCC was considerable up to 28 days of air exposure, as can be seen from Figure 5. This can be attributed to the slow rate of hydration due to the addition of fly ash to FA-BCC, which involved secondary hydration.

Furthermore, it can be seen from Figure 5 that the difference in the strength of ACC and moist-cured specimens is almost constant (by around 5%) during the long-term air exposure. Therefore, it may be concluded that the difference in the strength of ACC and moist-cured specimens of FA-BCC will be taken as only 5% during the service life of concrete. Again, it must be noted that the FA-BCC subjected to ACC achieved a strength of 24 MPa only after ten hours of carbonation.

**Splitting tensile strength**

Figure 6 shows the values of splitting tensile strength of both concrete mixtures at an age of 14 days for both ACC and moist-curing regimes. As can be seen from Figure 6, ACC appears to improve the tensile strength for PCC by 21% in comparison with the moist-curing regime, while a reversed situation is noted in the case of FA-BCC. However, even in the case of FA-BCC, the ACC regime maintained a tensile strength falling within the range recommended for a structural concrete mixture.

**Elastic modulus**

Figure 7 illustrates the 14-day chord modulus values for the two concrete mixtures subjected to ACC and moist-curing. Specimens subjected to ACC exhibited
a slightly lower stiffness than that of the moist-cured specimens for both mixtures. However, for both mixtures, the reduction was less than 10% with respect to moist-cured specimens. This slight stiffness reduction is still in line with the little reduction in strength of ACC specimens at 14 days, in relation to moist-cured specimens. Therefore, it can be concluded that the elastic modulus of ACC specimens is comparable to that of the moist-cured specimens.

**Water and chloride permeability**

Figure 8 presents the water penetration depths, performed according to the DIN 1048 standard (DIN 2004), for the two concrete mixtures, PCC and FA-BCC. In each mixture, the test was conducted for both ACC and moist-cured specimens at 14 days, in relation to moist-cured specimens. Therefore, it can be concluded that the elastic modulus of ACC specimens is comparable to that of the moist-cured specimens.

The specimens made of PCC and subjected to ACC had a slightly lower water penetration depth than that of the moist-cured specimens. By making a connection to the higher CO$_2$ uptake in PCC and lower CO$_2$ penetration depth (as discussed earlier), ACC specimens are expected to exhibit higher surface layer density. This is in agreement with the claim that the carbonation of concrete makes the microstructure of concrete surface denser, thereby decreasing the porosity of the surface layer of concrete that resists fluid penetration (Ahmad et al 2017). Although the improvement of the surface density is not significant, as indicated by water penetration depth, it can be inferred that ACC does not have negative effects on the properties of PCC.

On the other hand, a higher water penetration depth was noted in specimens made of FA-BCC and subjected to ACC compared to moist-cured specimens. A converse of the case for PCC may be used to explain this observation. FA-BCC exhibited lower CO$_2$ uptake than PCC, as a result of a lower amount of Ca(OH)$_2$ at the time of ACC, and for the same reason it also exhibited a higher CO$_2$ penetration depth. The combined effects of these two factors tend to reduce the surface layer density of FA-BCC ACC specimens, hence the recorded larger water penetration depth.

Figure 9 presents the results of the rapid chloride permeability test, performed according to the ASTM C1202 standard (ASTM 2012), for the two concrete mixtures. Even though the results are in the same range of ‘moderate permeability’ according to the referenced standard’s classification, the behaviour pattern recorded here is similar to that of the water permeability test.
Drying shrinkage

Figures 10 and 11 show the variations of drying shrinkage strain with time for ACC and moist-cured specimens belonging to PCC and FA-BCC mixtures, respectively. For the two concrete mixtures, the recorded drying shrinkage in ACC specimens was higher than that in moist-cured specimens, as is evident from Figures 10 and 11. Higher shrinkage in ACC specimens may be attributed to the shrinkage action associated with the chemical reactions involved in carbonation of the surface concrete, as well as the accompanying moisture loss to the exothermic process. It should be stated that the ACC-induced shrinkage can be controlled by spraying water on carbonated concrete immediately after ACC to compensate for the water loss during the ACC process which may significantly reduce the shrinkage.

Concrete microstructure characterisation

Figure 12 shows a micrograph of a fractured specimen exposed to ACC. The lower edge of the image is the edge of the concrete sample exposed to ACC. The red line indicates the actual profile of the carbonated area penetrated by CO₂. The dense structure of hydrates shown in Figure 12 is attributed to the formation of CaCO₃ which was caused by the accelerated carbonation of Ca(OH)₂ (portlandite) and conventional calcium silicate hydrate (C-S-H). The intermixing between CaCO₃ and C-S-H may be explained by the fact that the primary C-S-H was highly porous after about 18 hours of casting when the ACC was commenced. Therefore, the pores were available for diffusion of CO₂ and its associated reaction with the portlandite formed during the primary hydration process, resulting in the formation of CaCO₃. Based on the scale of the SEM image, the carbonation depth was estimated as 80 µm at the section imaged. Obviously, ACC reduced the permeability significantly by filling the pores and minor cracks with CaCO₃. Furthermore, this layer may reduce the evaporation of the internal water in the long term, imparting a self-curing ability to the concrete. All these explain the improved properties of the concrete cured with the ACC method.

In addition to the SEM imaging, the chemistry of selected areas of carbonated regions of near-surface concrete samples was also examined through quantitative EDS analysis (QEDS). Figure 13(a) shows the EDS profile of the area marked ‘spectrum 8’ in Figure 12 for a PCC sample exposed to ACC.
The EDS shown in Figure 13(a) indicates a high carbon content of 18.9% and a low amount of silica at 3.1%. Since the mortar phase sample examined was free of limestone aggregates (as seen in Figure 12), the high carbon content captured by the QEDS implies that the examined region of the carbonated specimen contained a significant amount of carbonation products. Figure 14(a) depicts the mineralogical composition of concrete specimens cured with the ACC method. The presence of calcite of about 25% by mass of the tested sample was noted. This observation implies that most of the high amount of carbon indicated by QEDS was from calcite that resulted from the reaction of CO₂ with portlandite, as well as carbonated C-S-H gels.

A micrograph of a fractured sample of FA-BCC concrete specimen exposed to ACC is shown in Figure 15. Some carbonation products can be recognised, but the amount of CaCO₃ produced was less than that of products can be recognised, but the amount is shown in Figure 15. Some carbonation FA-BCC concrete specimen exposed to ACC portlandite, as well as carbonated C-S-H gels. Carbonation and deeper penetration of CO₂, combined results of a lower degree of carbonation as chloride permeability) of the FA-BCC, as a durability indices (water permeability and chemical analyses.

**CONCLUSIONS**

From the results presented and the explanations offered for the reported observations, the following conclusions can be drawn:

- The carbonation depth was in the order of a few mm for both concrete mixtures, which may be considered a safe depth for a reinforced concrete element against reinforcement corrosion.
- Carbonation depth and weight gain analyses have established that the higher strength gain in plain-cement mixture can be attributed to a higher degree of carbonation coupled with lower depth of CO₂ penetration.
- An increase in the compressive strength by around 60% was recorded in both mixtures when they were exposed to air-curing for seven days after ten hours of ACC.
- ACC specimens exhibited 5 to 15% lower long-term strength compared to moist-cured specimens, indicating that the ultimate strength of concrete exposed to ACC is not much different from that of the concrete exposed to seven days of moist-curing.
- Although the shrinkage of ACC-treated specimens was generally higher than that of moist-cured specimens for the two concrete mixtures studied, post-ACC water spraying was required to compensate for the water loss during the ACC process.
- The tensile strength and modulus of elasticity of the ACC specimens were found to be comparable to those of moist-cured specimens. However, the measured durability indices indicated some negative effect of ACC on the durability characteristics of fly-ash-concrete, while the plain-cement-concrete exhibited improved durability characteristics.
- The negative effect of ACC on the measured durability indices of the fly-ash-concrete was well captured by morphological and chemical analyses, through SEM and XRD.

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