An Experimental Study On Carbonation Of Plain And Blended Cement Concrete

Yunusa Alhassan, Yunus Ballim

Abstract: This paper presents a laboratory investigation on the early age properties and carbonation of concrete containing Ground Granulated Blast Furnace (GGBS) in an inland environment. Properties of concrete made with GGBS blended cement was characterized in terms of physical and chemical composition at early-age. In addition, the effects of inland exposure condition on the durability performance of companion concrete were also investigated in the medium term. Concrete cubes were made using various concrete mixtures of water-binder ratios (w/b) = 0.40, 0.50, 0.60, 0.75 and binder contents = 300, 350, 400, 450 kg/m³. Concrete cube of 100 mm size were cast and cured in water for 3, 7, or 28 days, then characterized at early-ages in terms of its physical and chemical properties. Companion concrete samples were exposed indoor or outdoors to undergo carbonation under natural environment. At the end of the varying exposure period (6, 12, 18 and 24 months), the concrete cube samples were characterized in terms of carbonation depths. The results of the concrete early-age properties and medium-term durability characterisation were analyzed. The results show that, increased knowledge of concrete materials, concrete early-age properties and its exposure conditions are vital in durability considerations for RC structures.

Keywords: Concrete durability, Ground granulated blast furnace slag, Reinforced concrete, Pore structure, Pozzolans.

1 INTRODUCTION

The ability of concrete carbonization resistance is a very important index of durability. The durability of reinforced concrete structures is mainly embodied in concrete cover to reinforcement. Carbonization of concrete cover leads to reinforcement corrosion and serious compromise on reinforced concrete durability performance. Thus, carbonation of concrete must be considered at the design stage of a proposed reinforced concrete structure as well as during the service life of an existing reinforced concrete structure. The rate of carbonation in concrete depends on the permeability of the concrete and the quantity of the hydroxides, which are, in turn, controlled by the characteristics of the concrete making material and its processing, for example curing and compaction. In addition, carbonation rates also depend on the concrete exposure condition environments [1], [2], [3], [4]. While the permeability of concrete depends on many factors among which are the water/binder ratio and processing of the concrete which influences its hydration, the amount of hydroxides (CH) available in the concrete depends on the type and content of the binder used. Since the 1970s, the use of by-products like fly ash, ground granulated blast-furnace slag, silica fume, rice husk ash, and metakaolin in cement and concrete has gained rapid development. The incorporation of mineral admixtures has been of great interest and gradually been applied to practical projects, because it could not only reduce concrete production cost, conserve energy and resources, reduce environmental pollution impact [5], but also improve resistance to the deterioration of aggressive chemicals and permeations [6], [7], [8].

To ensure the required service life and durability performance of concrete structures in inland environment, designers and property owners are expected to have a reliable estimate of the carbonation rate for different binder types used in concrete and for the different inland environmental exposure conditions. This allows the specification of mixture proportions and cover depths for specific binder types and exposure condition for the attainment of the desired service life. Similarly, it is necessary for effective scheduling of maintenance and repair plans for the extension of the residual service life of existing concrete structures. The authors investigated GGBS blended cement concrete at early-age in terms of its pore structure and chemical composition via the durability index tests and the thermogravimetric analysis test respectively. Additionally, the influence of exposure conditions and the concrete early age properties on the rate of carbonation of these blended cement concretes were also investigated. Based on the investigation, mix proportioning for GGBS blended cement concrete and cover depths for the varying exposure conditions in an inland environment can be established.

1.1 Research Significance

Even though the partial replacement of Portland cement (PC) with GGBS result in significant benefits in terms of dense pore structure for the concrete, the reduction in portlandite contents due to dilution and pozzolanic reaction affect the ingress of CO₂ into such blended cement concrete. Hence, an understanding of the effects of GGBS blended cement on the physical characteristics and chemical composition of the concrete thus, the durability performance is important, and can help in the development of more durable concretes. In addition, exposure condition of the concrete influence the efficacy of such blended cement concrete in terms of its durability performance. Micro-climatic condition of the exposure plays a major role in the durability performance of concrete. It is important that concrete durability performance is investigated for the different exposure sites so that the extent of the carbonation is known for blended cement concretes. This is particularly important for mix proportioning and cover depth determination. This study is specifically important in the South African context.

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2 MATERIALS AND METHODS

2.1 Materials
A single source of PC complying with SANS was used throughout this study and its chemical and Bogue compositions are given in Table 1. The GGBS used was selected to provide ash with a range of 45 µm sieve retention value. The physical and chemical properties of the ash can be found in Table 1. Granite crusher sand and 19 mm granite coarse aggregate were the fine and coarse aggregate used in the concrete [10], [11]. A commercially available plasticizer, was used in some of the mixes.

Table 1 Oxide analysis of binders (%) used

<table>
<thead>
<tr>
<th>Oxides</th>
<th>CEM I</th>
<th>GGBS</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOI</td>
<td>3.04</td>
<td>None</td>
</tr>
<tr>
<td>SiO₂</td>
<td>21.85</td>
<td>36.59</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.10</td>
<td>13.35</td>
</tr>
<tr>
<td>CaO</td>
<td>62.84</td>
<td>36.33</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.41</td>
<td>0.78</td>
</tr>
<tr>
<td>MgO</td>
<td>2.28</td>
<td>7.35</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.43</td>
<td>0.65</td>
</tr>
<tr>
<td>MnO₂</td>
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<tr>
<td>Na₂O</td>
<td>0.07</td>
<td>0.24</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.32</td>
<td>1.11</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.09</td>
<td>0.02</td>
</tr>
</tbody>
</table>

2.2 Concrete Mixes
The concrete were made from two binders, 100% CEM I and 50/50 CEM I/GGBS blend, reflecting the standard blend ratio in South Africa. The concrete mixtures consisted of w/b = 0.40, 0.50, 0.60, 0.75 and binder contents = 300, 350, 400, 450 kg/m³. Slumps in the range of 25 to 140 mm were achieved. Table 2 gives the concrete mixes proportion and their respective slumps.

2.3 Mixing and Casting
Concrete was produced in 50 litres batch mixes using a horizontal forced action pan mixer of 0.05 m³ capacity. The mixer was charged with coarse aggregate, fine aggregate and binder respectively and the constituents dry mixed for approximately 30 s. Water mixed with plasticiser was slowly added for some mix until the mixture was visually consistent. Plasticiser was added in concrete mixes of 0.40 and 0.50 w/b, achieving slumps of 30 and 60 mm for CEM I and 25 and 40 mm for CEM I/GGBS respectively. The dosage of the admixture as shown in Table 2 is given as a percentage of total binder content by mass. The total mixing time was about 3 min. After testing for slump, 100 mm cube moulds were filled, compacted on a vibrating table, and covered with polythene sheets for 24 hours at room temperature before demoulding.

2.4 Curing and Subsequent Storage
The concrete cubes were thereafter placed in a water bath maintained at 23 ± 2 °C for continuous water curing until their respective test ages of 3, 7 or 28 days. For each mixture, 54 concrete cubes were cast, with a set of three cubes, each set having been cured for 3, 7 or 28 days were tested for compressive strength, two concrete cubes, each set having been cured for 3, 7 or 28 days were tested between 28 and 32 days after casting for permeability via the oxygen permeability and water sorptivity tests. One cube, each having been cured for 3, 7 or 28 days were tested for chemical composition of the concrete mixtures in terms of Ca(OH)₂ content. Additionally, for durability characterisation of the concrete mixture in terms of carbonation, a set of four concrete cubes, each set having been cured for 3, 7, or 28 days and exposed to the natural environment. Prior to exposure of samples to designated sites, all four sides running from the finishing surface through to its opposite end surface, were coated with two layers of epoxy coating, leaving the two adjacent opposite sides uncoated. After sufficient drying of surface coatings over a 24 hour period, samples were taken to their respective exposure sites and placed at a spacing of at least 50 mm from each other such that the two non-coated surfaces were exposed to air. The natural exposure conditions were chosen based on the EN Classification XC3 and XC4 [12] as indoor, outdoor sheltered, outdoor exposed. These exposure conditions are the highest aggressiveness classification for carbonation-induced corrosion of reinforced concrete in the inland environment. In order to replicate these conditions, concrete cube samples were stored in a basement parking garage (indoor exposure), under a bridge alongside a busy highway (outdoor sheltered) and on the roof top of a building in an urban setting (outdoor exposed).

2.5 Testing Concrete
At the end of the various curing periods and air storage, the concrete cubes were characterized as follows:

2.5.1 Strength
To characterise the concrete mixtures in compressive strength terms, 100 mm concrete cube samples were tested at 3, 7 and 28 days after casting under standard moist curing conditions. The compressive strength test were carried out in accordance with the SANS 5863 [13] method using an Amsler compression testing machine with a capacity of 2000 kN. All samples were weighed in a saturated, surface dry condition to an accuracy of 5 g before being tested;
2.5.2 Pore structure
The durability index test for micro structure characterisation of the concrete mixtures were carried out on specimen obtained from concrete cube samples at between 28 and 32 days after casting under saturated moist curing conditions. This is in accordance with the durability index tests method. The oxygen permeability and water sorptivity were performed in a temperature and humidity controlled room following the procedures outlined in the SANS test specification of 2010 [14], it is a revised version of the Durability Index Testing Manual originally developed by Ballim [15]. At the appropriate time after moist curing concrete cube samples were removed from the laboratory for the coring operation. The discs (70±2 mm Ø and 30±2 mm thick) were then transferred to a 50±2 °C ventilated oven to be dried for a minimum of 7 days ± 4 hours before being tested for oxygen permeability and water sorptivity. The discs permeability and water sorptivity measurement were carried out using the falling head permeameter and water sorptivity tests respectively.

2.5.3 Portlandite contents
The portlandite content of the concrete mixtures was determined from specimen obtained from concrete cube samples after 3, 7 and 28 days of standard moist curing periods after casting. Thermogravimetric analysis (TGA) was performed on powdered specimens. The powdered specimens are obtained following the procedure described in Alhassan [16]. The procedure involve drilling to a depth of 20±5 mm with a 7 mm diameter drill bit on the interior surface of a cube after it has been oven dried. The samples obtained is then sieved through a 63 µm sieve size and preserved under vacuum in airtight bottles until tested. The chemical composition of the specimens were determined in terms of the Ca(OH)₂ content using the TGA test. The thermal decomposition behaviour of the powder specimens were studied by tracing mass and heat changes using a Perkin Elmer TG400 thermogravimetric analyser coupled to a Setaram differential analyser. The thermal analyser used in this study, enables the thermogravimetric (TG) curve and the derivative thermogravimetric (DTG) curve to be obtained simultaneously on the specimen. A plot of temperature against mass loss (TG curve) and derivative mass loss (DTG curve) is obtained automatically. The weight loss obtained from the TG and the DTG curves were used to estimate the amounts of calcium hydroxide (Ca(OH)₂) and calcium carbonate (CaCO₃) present in the specimen;

2.5.4 Durability characterisation
For the durability performance of the concrete mixture, the set of four cubes, exposed to each of the three natural sites after 14 days of preconditioning were taken to the laboratory after varying ages for carbonation testing. Carbonation measurements were done at ages of 6, 12, 18, and 24 months after exposure. A solution of 1 % phenolphthalein in ethanol was sprayed onto the freshly broken surface of the concrete, and average of six measurement of the depth of the colourless section was taken as the carbonation depth.

2.5.5 Exposure condition measurement
The microclimatic conditions of the exposure sites were monitored using a 24-hour, automated data logger set up on each of the site to record the micro-climate conditions. The CO₂ concentration, relative humidity (RH) and temperature were monitored throughout the period of exposure. Data was recorded every one minute and downloaded monthly into a computer hard-drive. These micro-climate data were analysed for each exposure sites in terms of the mean value of CO₂ concentration, RH and temperature.

3 RESULTS AND DISCUSSION
Results of tests and discussion on early-age characterisation of the concrete are given in Figures 1-4 for the compressive strength, permeability, sorptivity and chemical composition respectively. From the presented results, it is evident that these characteristics are influenced by w/b, extent of initial moist curing and the binder type and content. Results for the micro-climatic variations for the exposure sites concrete samples were kept in terms of CO₂, RH and temperature as well as the results of the carbonation depth for the concrete cubes are presented in Figure 5 - 9. The results on carbonation depth presented are discussed in terms of the concrete physical and chemical properties while the influence of the exposure condition on the depth of carbonation was also examined and discussed.

3.1 Compressive strength
The development in strength for the different mixtures as influenced by w/b, and curing time is presented in Figure 1. As expected, compressive strengths increase steadily with decrease in w/b for any given mixture. Similarly, strengths increase progressively with age, as is typical of concrete mixtures under moist curing. Note that as the moist curing age of the concrete increases, hence the hydration of its binder components, the gain in compressive strength with GGBS blended concretes becomes more apparent especially at low w/b.

![Fig. 1 Compressive strength results for the concrete mixtures](image)

It may be recalled that while 28-day strength is a standard value, it is the 3 or 7 day strengths that are realistically representative of site curing practice. Analyzing the ratios of the 28 days and 7 days compressive strengths for all the concrete mixtures tested, the GGBS concretes presented higher values compared to the CEM I concretes. Increased compressive strength gain at later ages for this SCM can be attributed to its slower hydration rate and chemical pozzolanic effect, as well as to the physical effect of the generally tiny SCM particles. Detwiler and Meht [17] and Goldman and Bentur [18] suggested in their work that the improvement in compressive strength in blended cement concrete is primarily dependent on the micro filler effect of the SCMs.
3.2 Oxygen Permeability
The permeability results for the concrete mixtures are presented in Figure 2. This result shows that, increasing w/b and decrease extent of initial moist curing of concrete resulted in decreased oxygen permeability index (OPI) values with the GGBS blended concretes presenting lower OPI values. Although the influence of moist curing on the permeation properties of the concrete can be seen clearly in some of the mixtures, it is clustered for the others. However, there are distinct trends of improvement in concrete permeation as the w/b decreases.

![Oxygen permeability results for the concrete mixtures](image)

This is due to the increasing volume and degree of interconnection of capillary pores within the cement paste. In addition, as w/b decreases or as curing time increases (therefore the degree of hydration increases), the reduction of concrete paste porosity is mainly due to the reduction in pores of larger dimensions that have been filled or are connected by C-S-H gel pores. Graf and Grube [17] state that as hydration proceeds, the initially water filled and fully interconnected pores within the cement paste are filled with hydration products and become discontinuous. The increased gain in impermeability at later ages for the GGBS blended concretes can be attributed to a combination of the pozzolanic and micro filler effects of GGBS. The GGBS blended concretes however performed better than the CEM I concretes at all w/b under continuous initial moist curing.

3.3 Water Sorptivity
Figure 3 present the sorptivity results for the concrete mixture. From the sorptivity plot presented, it can be seen that the sorptivity values decrease as the w/b reduces and the extent of initial moist curing period increases for all the concrete mixtures investigated. However, the decrease in sorptivity values as a result of the decrease in w/b are more marked than the increase in the extent of initial moist curing. Similar lower sensitivity of the concretes to the extent of extended initial moist curing was noted with the permeability results. The improved sorptivity for all the concretes at low w/b and prolonged duration of initial moist curing are attributed to the reduction in the volume and size of the pores within the concrete microstructures as well as the interconnections. The beneficial effect of SCMs in improving concrete pore structure can be seen for the GGBS blended concretes in comparison to the CEM I concretes at 28 days. GGBS blended concretes presented better sorptivity values at lower w/b and extended initial moist curing periods. Improvement in sorptivity for these blended concretes can be attributed to the pozzolanic effect of the SCMs at later ages and also to their pore filling effect.

![Sorptivity results for the concrete mixtures](image)

3.4 Portlandite Content
The portlandite contents for the concrete mixtures are given in Figure 4. The use of different binder type and content influenced the Ca(OH)₂ content of the concretes, with increasing w/b and decreasing binder contents resulting in decreased Ca(OH)₂ content for all the concrete mixtures investigated. From the Ca(OH)₂ results plot presented, it can be noted that the Ca(OH)₂ content increases as the concrete moist curing ages increases for the plain concretes while a decrease in Ca(OH)₂ content were noted for the GGBS blended concretes. The reason for the increase in portlandite for the plain concretes is that, CEM I concrete produces Ca(OH)₂ during hydration and its content increases with hydration time. While, the decrease in Ca(OH)₂ content for the blended cement concrete can be attributed to both the high dilution effect related to the fact that Ca(OH)₂ results from cement hydration which in turn is directly related to the cement proportion in the mixture, as well as the pozzolanic reaction between Ca(OH)₂ and GGBS which consumes some Ca(OH)₂, and may extend over a long time period [19]. It can also be noted from the figure that the Ca(OH)₂ content for both the blended and unblended concretes are not significantly different at 3 and 7 days.

![Ca(OH)₂ content results for the concrete mixtures](image)
3.5 Micro Climate Results

The micro climate results for the exposure sites in terms of CO\(_2\) concentration, relative humidity and temperature are presented in Figures 5 to 7, while Figure 8 shows the annual precipitation results for the town as obtained from the literature.

**Fig. 5** Variation in atmospheric CO\(_2\) content at the different exposure sites [16]

**Fig. 6** Variation in relative humidity at the different exposure sites [16]

**Fig. 7** Variation in atmospheric temperature at the different exposure sites [16]

**Fig. 8** Annual average precipitations in Johannesburg [20]

From the RH result presented, concrete cube samples exposed outdoor but sheltered from rain and sun will have the highest carbonation rates because the RH profile mostly lies in the zone (50 – 70%) for maximum carbonation rate. The RH of the exposure sites is influenced by precipitation and the influence is higher for samples outdoor and unsheltered. The influence of temperature variations is not very significant for concrete carbonation as noted from this investigation, and from the literature [21]. However, results of the temperature variation shows that carbonation rates should be lower for concrete cube samples exposed indoors, while it may be similar for the other two exposure sites since their temperature profiles are similar.

3.6 Carbonation Depth

From the carbonation coefficients results for the different concrete types, it is evident that the carbonation rate of the concretes followed similar pattern for the different w/b investigated. Hence, it is only the 0.5 w/b concretes carbonation rates results that is presented for the different exposure sites. Generally, the trends observed were distinctly influenced by the concrete physical and chemical characteristics as well as the micro climate condition of the exposure sites. Thus, variations of the carbonation rates for the concretes will be explained in relation to each of these influencing factors. In earlier discussion of compressive strength results, it was shown that GGBS, and CEM I
concretes gave different strength results. It can now be seen that even the carbonation behaviours of these particular concrete types are not similar, especially under unsheltered exposure. Accordingly, correlations or similarities exist between strength and carbonation behaviors of mixtures containing known SCMs [16]. The general carbonation behaviors of the mixes under indoor, sheltered and unsheltered exposure conditions are compared in Figure 9. Clearly, the concretes stored under indoor and sheltered exposure give higher carbonation rates than those kept under the unsheltered exposure condition. The differences in behavior are related to effect of rain for the exposed samples, which tends to temporarily block the pores at surface concrete, thereby inhibiting CO₂ ingress during periods of precipitation. The wetting and drying period experienced by samples on the exposed site is probably the reason for the reduced carbonation rate, since both the outdoor sheltered and unsheltered exposure conditions have similar micro-climates in terms of CO₂ content, RH and temperature and concrete cube samples exposed outdoor to rain and sun have higher internal humidity during the summer months from precipitation effects, thus reducing CO₂ ingress during this period. Furthermore, these concretes had improved pore structures from rapid hydration effects as a result of its high internal moisture content during the summer months.

The influence of GGBS is clearly evident in the concrete, generally showing increase in carbonation regardless of the exposure site’s microclimate. Under sheltered exposure, GGBS behaved similarly as CEM 1, with both mixtures giving relatively high carbonation progressions. However, the same GGBS mixtures behaved differently under unsheltered exposure conditions, exhibiting lower carbonation. The different behavior of GGBS mixes in relation to the CEM I mixes under unsheltered exposure may be related to availability of precipitation which in turn promotes pozzolanic activity in a manner not attainable under the partial saturation conditions of sheltered exposures. From Figure 9, It can be seen that GGBS addition led to a greater carbonation rate, which is consistent with the trend observed by Osborne, [22], and Papadaki, [23]. The changes in pore structure were not adequate in GGBS concrete to counteract the reduction in CH content, and hence the carbonation rate increased. The reason for this is that GGBS had a low free lime content and the greater amount of hydrated products formed after the pozzolanic reaction were noncrystalline low alkaline C-S-H with a large specific surface area hence, these samples were easily carbonated [24]. In addition, in the presence of GGBS, the amount of CH available to react with CO₂ is lower, for two reasons; first, less CaO is added to the concrete. Second, some of the CH reacts with the added GGBS. However, if the concrete pore structure modification does not govern over the reduction in CH, the carbonation may proceed faster due to the fewer amounts of carbonatable materials available per unit area of CO₂ to react with. This explains why carbonation tends to proceed faster in concrete containing mineral admixture. Additionally, due to the slower pozzolanic reaction in blended concrete, porosity can be expected to be higher during the initial stage, thus allowing more rapid diffusion of CO₂.

Generally, carbonation rate increases with increase in w/b irrespective of the concretes’ initial moist curing periods. This is attributed to increased pore connectivity of the concrete since w/b primarily determines the gel/space, the capillary porosity and thus the permeability of the concrete. Concretes of lower w/b ratio had better resistance against the diffusion of CO₂, possibly due to the denser pore structure and higher Ca(OH)₂ content (see Figure 4). Similar findings in relation to the effect of low w/b on carbonation have also been reported in the literature [25], [26], [27]. The decrease in the carbonation rates of the concretes at lower w/b can be attributed to the fact that the cumulative pore volume and the amount of pores are lower compared to a higher w/b concrete. This fact was also evident from the permeation test results of the concretes (see Figures 2 and 3). Hence, the lower w/b concretes, showed superior resistance against carbonation. It can be noted from the figure that a longer initial moist curing duration generally resulted in a lower carbonation rate. This is attributed to the fact that as curing increases hydration in concrete, and the pore spaces in concrete reduces, particularly in the near surface zone. Additionally, curing influences the chemical properties of the concrete, for instance in plain concrete it increase the Ca(OH)₂ content of the concrete thereby improving its buffering effect against CO₂. Curing, however reduces the Ca(OH)₂ content in blended concretes but improves the concrete microstructure. In the case of concrete containing GGBS, the carbonation rate continued to decrease even after 7 days of curing again pointing to the later hydration effect of these SCMs.

4. EXPERIMENTAL CONCLUSIONS

From this investigation, the effect of concrete material, processing and exposure on the rate of carbonation of reinforced concrete thus its durability performance and service life were examined. Based on the mixture proportion, cementitious materials, and test conditions adopted in this study, the following conclusion can be drawn:

1. A lower w/b and prolonged moist curing age of concrete generally led to a slower rate of carbonation, mainly due to pore structure densification, as indicated by a decrease in cumulative and differential pore volume;

2. Structural elements exposed outdoor but sheltered will present the highest carbonation rate. Thus, sheltered elements should be more carefully designed and constructed if its design service life in terms of the initiation limit state is to be achieved;

3. It is evident that concrete elements exposed outdoor to
The pore size modification due to pozzolanic reaction of GGBS had better pore volume and hence the densest pore structure. Although the pore structure of GGBS concrete was denser than that of OPC concrete, the carbonation coefficients of these GGBS mixtures were higher than that of the plain concrete. This suggests that pore structure is not the only parameter that controls the rate of carbonation, the amount of CH present within the hydrated cement is important.

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