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Accelerated carbonation testing of alkali-activated binders significantly underestimates service life: The role of pore solution chemistry

Susan A. Bernal [a], John L. Provis [a,*], David G. Brice [b], Adam Kilcullen [a,b], Peter Duxson [b], Jannie S.J. van Deventer [b]

[a] Department of Chemical and Biomolecular Engineering, The University of Melbourne, Victoria 3010, Australia
[b] Zeobond Pty Ltd., P.O. Box 210, Somerton, Victoria 3062, Australia

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ABSTRACT

The carbonation resistance of alkali-activated binders is often tested via accelerated test protocols designed for Portland cements, without questioning whether the tests replicate the mechanisms observed in service. Thus, validation of accelerated methods is required to enable realistic prediction of material performance. Changes in pore solution equilibria cause the formation of sodium bicarbonates during accelerated carbonation, compared with hydrous sodium carbonates in natural carbonation. This shifts the carbonation mechanism to favour more rapid reaction progress, to give a higher apparent degree of acceleration (compared to natural conditions) than in Portland cements. The pore solution pH under accelerated carbonation is significantly lower than at natural CO_2 concentrations, leading to a falsely short predicted service life (time to expected corrosion of embedded steel), as natural CO_2 concentrations appear not to reduce the pH below 10. Thus, accelerated carbonation testing is unduly aggressive towards alkali-activated binders, and test results must be cautiously interpreted.

1. Introduction

Carbonation of cement and concrete materials in service has been identified as a critical problem in many parts of the world, particularly where the environment is warm and relatively humid. In order to predict, in a short period of time, how a material will perform in service when subjected to CO_2 exposure, accelerated carbonation testing of binders, mortars and concretes is widely applied to the study of materials based on both Portland cement [1–5] and alkali-activated [6–12] binders. Carbonation of alkali-activated binders has been identified from accelerated testing to be a potentially significant problem in some important applications, with laboratory tests often showing relatively high carbonation rates [6–11]. However, alkali-activated concretes removed from service after extended periods have not in general shown problems related to carbonation [8,13,14]. This indicates that the outcome of the accelerated test is not as accurate a predictor of in-service performance of alkali-activated materials as it is for Portland cement-based systems. Establishing and validating durability testing methods for alkali-activated concretes remains the major obstacle to their commercial adoption in demanding structural applications, and ultimately their acceptance in national and international regulatory standards for structural concrete [15,16]. Therefore, the availability of a reliable method for predicting the service life of alkali-activated concrete under carbonating conditions is an important issue which needs to be addressed.

In all widely applied tests, acceleration of carbonation is achieved by increasing the concentration of CO_2 in the atmosphere surrounding the specimens under a controlled relative humidity (RH). However, the testing methodologies have mostly not been validated in detail by comparison to natural carbonation of comparable samples, and there is still ongoing discussion regarding the most applicable testing methodologies and conditions [4], with no testing methodology or conditions being universally preferred. The work of Ho and Lewis [2] provided a detailed study of Portland cement carbonation in service, as well as direct comparisons with the results of accelerated testing, which has given some validation for the accelerated carbonation testing conditions used in that study (4% CO_2, 50% RH, 23 °C) as applied to the particular materials investigated. However, there are three key areas in which information is lacking with regard to the understanding of the carbonation of alkali-activated binders under service conditions:

- CO_2 concentrations ranging from 1% to 100% CO_2, relative humidities from 50% to 90% and temperatures from 5 to 37 °C have been reported as test conditions for accelerated carbonation of Portland cement concrete [4]; it remains to be determined in which environments alkali-activated materials show carbonation mechanisms which accurately replicate natural carbonation mechanisms. Castellote et al. [17]

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* Corresponding author. Tel.: +61 3 8344 8755; fax: +61 3 8344 4153.
E-mail address: jprovis@unimelb.edu.au (J.L. Provis).

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showed that CO_2 concentrations exceeding 3% lead to changes in the mechanism of Portland cement carbonation when compared to natural carbonation, but no similar studies have been published for alkali-activated binders.

- The relationship between accelerated carbonation rates and in-service carbonation rates in alkali-activated concretes, which is essential in using the results of accelerated carbonation testing to calculate cover depths required for a given service life, is unknown. Ho and Lewis [2] showed that, for a range of Portland cement concrete mixes, 1 week at 4% CO_2, 50% RH and 23 °C gave a carbonation depth equivalent to 1 year indoors in ambient air in a laboratory environment, but also noted that exposure outdoors under uncontrolled conditions gave as much as a factor of 3 difference (reduction) in natural carbonation rate. Carbonation rates are well known to be sensitive to wet/dry cycling, humidity, temperature and other exposure parameters [4,5,18], which means that a detailed mechanistic understanding of the carbonation phenomenon itself is necessary for such predictions to be made with any confidence.
- During natural carbonation the binder structure is evolving over the extended time periods (years) in contrast with accelerated tests which are generally conducted on relatively young concretes for short time periods (weeks). There is thus a need to incorporate an understanding of the influence of gel ageing into the analysis of natural carbonation, but the structural changes taking place during long-term ageing of alkali-activated binders remain incompletely understood on a mechanistic level.

The carbonation of Portland cement concrete proceeds predominantly by the reaction of atmospheric CO_2 (via its dissolution in the water present in the pores) with the calcium in $Ca(OH)_2$ and/or Ca-rich C—S—H phases in the binder, to form calcium carbonate, mainly as the calcite polymorph [17]. Alkali-activated binders are synthesised with lower calcium content (including systems with no calcium), and thus show a binder structure based on gels which are enriched in alkalis and aluminium and lower in Ca/Si ratio than those which are observed in hydrated Portland cements [15,19,20]. This is expected to lead to differences in the carbonation mechanisms depending on the chemistry of the binder source materials, which will influence both the rate of natural carbonation and the degree of acceleration of carbonation induced by a given CO_2 concentration.

The fact that the pore solution chemistry in alkali-activated binders is dominated by alkali hydroxides [20–23] will lead to differences in the CO_2 uptake rates, as these solutions are well known to absorb CO_2 from gas streams or the air [24], to form alkali carbonates and/or bicarbonates. The low to zero Ca content and high degree of crosslinking of the binder gel in alkali-activated binders is also likely to be relevant, as the degradation of gels by decalcification will be influenced by these parameters. The maturity of the alkali activated concrete is anticipated to play a significant role in determining the accelerated carbonation rates, considering the modification of both gel densification and the structure of the pore network. These issues will be addressed in detail in future studies, while the focus of this paper is specifically on the role of the pore solution chemistry in alkali-activated slags, containing significant levels of Ca, but much lower than in Portland cement, in determining accelerated carbonation rates and mechanisms. As the carbonation of Portland cement is to a large extent controlled by chemical reactions involving the solid hydration products, the influence of the pore solution on the carbonation rate has rarely been analysed. Most studies have taken the reverse approach, and instead focused on the influence of carbonation on pore solution chemistry [18,25]. In this paper, we address the differences in carbonation rates induced by accelerated carbonation of alkali-activated binders when compared with Portland cement binders, and show that this is related to differences in alkali carbonate phase chemistry. The thermodynamic basis for these differences is discussed, and comments are provided regarding the validity of accelerated carbonation testing procedures in analysing the durability of alkali-activated materials.

2. Experimental program

2.1. Concrete samples

A Colombian granulated blast furnace slag (GBFS 1) from the factory Acerías Paz del Río was used as the primary raw material for the production of concrete specimens. The basicity coefficient ($K_b = CaO + MgO/SiO_2 + Al_2O_3$) and the quality coefficient ($K_q = CaO + MgO + Al_2O_3/SiO_2 + TiO_2$) based on the chemical composition (Table 1) were 1.01 and 1.92, respectively. 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 alkaline activating solution was formulated by blending a commercial sodium silicate solution with 31.7 wt.% SiO_2, 12.32 wt.% Na_2O and 56.9 wt.% H_2O, and 50 wt.% NaOH solution, to reach a silicate modulus ($M_s = SiO_2/Na_2O$) of 1.3, and a concentration of activation of 4 wt.% Na_2O with respect to the mass of slag.

The concretes were formulated with slag contents of 340 kg/m^3, 412 kg/m^3 and 512 kg/m^3 and a water/(slag + anhydrous activator) ratio of 0.48. Crushed gravel and river sand were used as coarse and fine aggregates in the manufacture of the concretes. 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 fine aggregate were 2450 kg/m^3, 3.75% and 2.57, respectively. Cylindrical specimens were produced, 76.2 mm in diameter and 152 mm in length, and the ends covered with an acrylic resin to give solely radial penetration of CO_2. Samples were cured for 28 days at 25 °C and RH >90% prior to the start of testing. Accelerated carbonation exposure was carried out in a controlled environmental chamber at 25 °C, with 7% CO_2 and 65% RH. Natural carbonation exposure was carried out in a laboratory in Cali, Colombia, with average daily conditions approximately 25 ± 5 °C and 75% RH.

As a reference material, Portland cement concretes were also produced, using a commercial Colombian Portland cement type I, which includes 25% limestone. Detailed information regarding the mix designs, along with analysis of the engineering and durability properties of the concrete mixes assessed in this study, is reported elsewhere [26].

2.2. Paste samples

To enable detailed analysis of binder mineralogy, paste samples were synthesised from a different supply of granulated blast furnace slag (GBFS 2), whose basicity coefficient K_b and quality coefficient K_q based on the chemical composition (Table 1) were 1.00 and 1.79 respectively. Its specific gravity was 2800 kg/m^3 and Blaine fineness 450 m^2/kg. In order to regulate strength development, ordinary Portland cement (OPC) type GP was incorporated in the binders as a minor admixture (4% of total binder). All raw materials were supplied by Zeobond Pty Ltd., Australia.

Table 1
Compositions of the GBFS supplies used, from X-ray fluorescence analysis. L.O.I. is loss on ignition at 1000 °C.

Component (mass % as oxide)	GBFS 1	GBFS 2
SiO_2	31.08	33.80
Al_2O_3	13.98	13.68
Fe_2O_3	3.09	0.40
CaO	43.92	42.56
MgO	1.79	5.34
SO_3	0.66	0.83
Others	3.49	1.45
L.O.I.	2.08	1.81