

Impact of Water Content on the Performance of Alkali-Activated Slag Concretes

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ABSTRACT

In this study, we report the effect of varying the water/binder (w/b) ratio on the performance of sodium silicate activated concretes. Compressive strength development and water transport properties of these concretes were assessed, along with their resistance to carbonation. The results demonstrate that varying the water content within a reasonable range induced negligible changes in the compressive strengths of these concretes, when a constant paste content was used. A direct correlation between the w/b ratio and the amount of permeable voids in the concretes was not identified. The carbonation behaviour of these concretes changes prominently depending on the CO₂ concentration of exposure, meaning that comparable accelerated carbonation rates were observed at varying w/b ratios, conversely to observations under natural carbonation conditions where w/b was significant in defining the carbonation rate.

Keywords: Alkali-activated slag concretes, water content, mechanical strength, transport properties, durability

1.0 INTRODUCTION

Infrastructure is at the heart of the societal growth of any nation, and concrete is the primary material used for its development. Concretes are mainly produced with Portland cement (PC). One of the main strategies adopted to enhance the sustainability and performance of concrete has been the partial replacement of PC by supplementary cementitious materials (SCMs). The mostly widely used SCMs include blast furnace slags from the iron-making industry, fly ashes obtained from coal combustion processes, and natural materials such as calcined clays or natural pozzolans (Snellings *et al.*, 2012).

Although this approach offers significant carbon savings to the construction sector, major advances in the development of non-Portland cements have been achieved over the past decades. In general, most alternative binders can offer attractive advantages associated with their manufacturing process, which typically is less energy intensive than PC production, and in some instances, the raw materials needed for their production can be industrial by products or wastes with little or no commercial value (Juenger *et al.*, 2011). One of the most promising classes of alternative candidates is alkali-activated cements, which are produced by blending a poorly crystalline aluminosilicate powder and an alkaline solution, to form synthetic mineral-like binders (Shi *et al.*, 2011).

In particular, alkali activated slags (AAS) are gaining significant attention as materials with great potential for replacing Portland cement for production of concretes (Provis, 2017). Despite the advantageous mechanical and durability properties AAS concretes can develop when properly formulated and cured, the lack of standardised methodologies for their design is one of the factor affecting their adoption.

Over the past decades a significant number of studies have focused on the development and optimisation of AAS binders. However, notably fewer studies have assessed the influence of conventional concrete mix design parameters such as the amount of binder (Bernal *et al.*, 2011) or the water content on the performance of AAS concretes, as it is often assumed that these parameters will induce similar changes in properties to those expected in Portland cement based concretes.

The water content in concrete mixes is usually selected based on the workability required for casting. For Portland cement-based concretes, it is well known that higher contents of water in the mix lead to an increase in the porosity and consequently a reduction in mechanical performance (Hewlett, 1998). In the case of alkali-activated slag (AAS) concretes, an alkaline solution (referred to as the *alkali activator*), rather than water, is required to promote the chemical reactions leading to the

formation of the binding phases (Provis and Bernal, 2014) and its consequent hardening.

The workability and rheology of AAS are strongly dependent on mix design parameters including the type and amount of alkali activator (Puertas *et al.*, 2014, Collins and Sanjayan, 1999) and the particle size distribution of the slag used (Kashani *et al.*, 2013). Other parameters such as speed and duration of mixing (Palacios and Puertas, 2011), ambient conditions during the mixing and casting of fresh AAS, among others, can also influence the workability of these materials. Although increasing the amount of water is a common parameter used to adjust the workability of concretes, in the case of AAS this changes the alkali activator concentration and pore solution alkalinity, which can extend the setting time and modify the structure and amount of reaction products forming in these materials (Bernal *et al.*, 2015b).

A study in AAS pastes did not identify direct correlation between their water content and the kinetics of the alkali-activation reaction (Bernal *et al.*, 2015b), although an increased porosity has been identified in AAS pastes and mortars when increasing water content (Ismail *et al.*, 2011, Wang *et al.*, 1994). Despite this, it is largely unknown if a direct correlation between the mechanical performance and porosity of these materials can be drawn, and how variation in water content might influence the permeability of AAS concretes, and consequently also their durability performance when exposed to aggressive agents.

Carbon dioxide present in the air is one of the main threats to our cement-based built environment, as its diffusion through concretes, and its dissolution in the pore water present in these materials, can initiate acid-base reactions leading to degradation or corrosion processes that can compromise the integrity of structures. This degradation mechanism is referred to as carbonation, and mainly leads to decalcification of the strength-giving phases through formation of carbonate-rich products (Fernández-Bertos *et al.*, 2004; Sanjuán *et al.*, 2003; Hobbs, 2001).

The way in which carbonation proceeds in AAS differs from the existing understanding of PC-based systems due to their differences in chemistry and microstructure. The main differences are the absence of portlandite ($\text{Ca}(\text{OH})_2$) in AAS pastes and concretes, and the high alkalinity characteristic of these materials (Puertas *et al.*, 2004), which makes them more prone to undergo carbonation. In the past there was a general consensus that these materials appear less resistant than Portland cements (Bakharev *et al.*, 2001; Puertas *et al.*, 2006; Deja, 2002). However, over the last decade it has been demonstrated that the carbonation testing conditions, particularly CO_2 concentration, temperature and relative humidity have a significant impact in the

carbonation mechanism and extent of degradation of AAS systems (Bernal *et al.*, 2015a; Bernal *et al.*, 2014; Bernal *et al.*, 2012b). This is a consequence of the changes of the pore solution carbonation, modifying the type and amount of carbonation products forming.

In this study the influence of the water content in alkali-activated slag concretes was assessed. Compressive strength, water permeability properties as well as accelerated carbonation resistance were determined.

2.0 EXPERIMENTAL PROGRAMME

2.1 Materials

A commercial granulated blast furnace slag (GBFS) with a specific gravity of 2800 kg/m^3 and a d_{50} of $15 \mu\text{m}$ was used. The chemical composition of the slag is shown in Table 1.

Table 1. Composition of blast furnace slag (GBFS) from X-ray fluorescence analysis. LOI is loss on ignition at 1000°C

Component wt.% as oxide	CaO	Al_2O_3	MgO	SiO_2	Others	LOI
Slag	43.1	13.8	5.4	34.2	1.3	1.8

Commercial sodium metasilicate granules with a chemical composition of 50.5 wt.% Na_2O and 46.0 wt.% SiO_2 (balance H_2O) were dissolved in tap water and cooled for two hours before use as the activating solution.

Crushed gravel and sand were used as coarse and fine aggregates in the production of the concretes. The coarse aggregate was of 20 mm maximum size, with a specific gravity of 2830 kg/m^3 and water absorption of 1.10%. The specific gravity and water absorption of the sand were 2550 kg/m^3 and 0.90% respectively.

2.2 Sample preparation and tests conducted

Three sets of alkali-activated slag concretes were produced, with water/binder ratios of 0.40, 0.44 and 0.48. In this definition, the binder comprises anhydrous slag + solid activator. The concretes were produced using similar proportions of slag (400 kg/m^3 of fresh paste) as the main binder component, and were mixed in an electric pan mixer following the Australian Standard AS 1012 (Standards Australia, 1994) The concretes were cast in 100 mm diameter \times 200 mm height cylinder moulds, and vibrated until suitably consolidated. The concretes were then cured for 28 days in a water bath at ambient temperature ($20\text{-}23^\circ\text{C}$), until testing.

2.3 Compressive strength and water absorption

An ELE ADR Auto 1500 compression testing instrument was used for compressive strength testing of concrete cylinders according to the standard procedure ASTM C 39-10 (ASTM International, 2010), at a loading rate of 2.4 kN/sec, until failure. The results reported correspond to the average of three measurements.

Volume of permeable voids (VPV) was determined according to the standard test ASTM C 642-06 (ASTM international, 2006) drying the specimens at 100°C until reaching constant weight, strictly following the standard recommendations. The results reported correspond to measurements of 4 slices taken from two cylinders, for a total of 8 measurements.

Capillary sorptivity was assessed by applying the standard procedure EMPA-SIA 162/1 (Fagerlund, 1982), 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.

2.4 Carbonation testing

To induce accelerated carbonation, cylindrical concrete specimens were stored in a chamber with a CO₂ concentration of 1.0 ± 0.2%, temperature of 23 ± 2 °C, and relative humidity (RH) of 65 ± 5%. For the natural carbonation study, concrete specimens were stored in an indoor warehouse in Melbourne, Australia, with an urban environment consistent during the testing time. The accelerated and naturally carbonated specimens were exposed to CO₂ for up to 90 days. Carbonation depths were determined periodically by treating the surface of freshly cleaved samples with a 1 % solution of phenolphthalein in alcohol.

3.0 RESULTS AND DISCUSSION

3.1 Compressive strength

Concretes produced with w/b ratios of 0.40 and 0.44 (Table 2) presented comparable compressive strengths at 28 days of curing. Increasing the w/b ratio to 0.48 reduced the compressive strength by ~10 MPa compared to the concretes with lower w/b ratios. This indicates that changes in the water content in the concretes when formulated with w/b ratios lower than 0.44 are not causing significant changes in the degree of reaction achieved, at least up to 28 days of curing.

This observations differs from what has been identified in pastes with similar compositions to the concretes tested in this study during the first 48 hours of reaction (Bernal *et al.*, 2015b), where a direct

correlation between the w/b ratio and the kinetics of reaction was not identified. Pastes produced with a w/b of 0.44 reacted faster than those formulated with a w/b of 0.40, and the degree of reaction achieved when using w/b of 0.48 was comparable to that obtained when using lower water contents. This highlights that although the water content will influence how the reaction of these materials will proceed, this does not necessarily impact the mechanical performance AAS concretes might develop.

Table 2. 28-day compressive strength of AAS with different w/b ratios

Water/binder ratio	Compressive strength (MPa)
0.40	59.4
0.44	58.1
0.48	49.9

3.2 Volume of permeable voids of AAS concretes

A direct correlation between the water content in the concrete and the VPV is not identified (Fig. 1). Specimens formulated with w/b = 0.44 presented the lowest volume of permeable voids while the concrete with w/b ratios of 0.40 had slightly higher VPV values. Concretes with a w/b ratio of 0.48 reported the highest VPV. The differences in the VPV values are not considered sufficiently high to attribute compressive strength performance solely to increments in porosity.

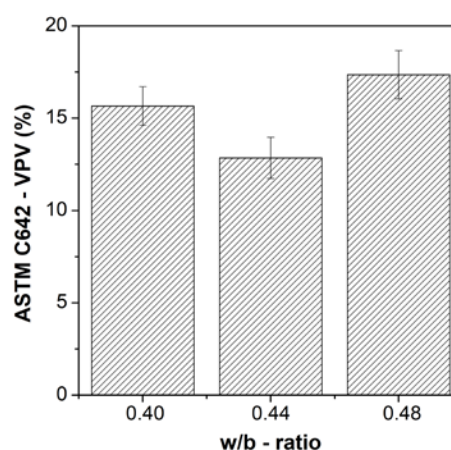


Fig. 1. 28-day volume of permeable voids of AAS with different w/b ratios

Comparing the compressive strength with the VPV values of the concretes tested indicates that these two properties are not directly related (Fig. 2.), conversely to what is typically identified in PC-based concretes. However, concretes produced with a w/b ratio of 0.48 did, as expected, show the lowest compressive strength and the highest VPV among the materials tested. This is consistent with the trends identified in pastes (Bernal *et al.*, 2015b) with similar compositions to the concretes tested in this study,

where w/b ratios beyond 0.44 induced delayed formation of reaction products, hindering compressive strength development, and promoted formation of more porous materials.

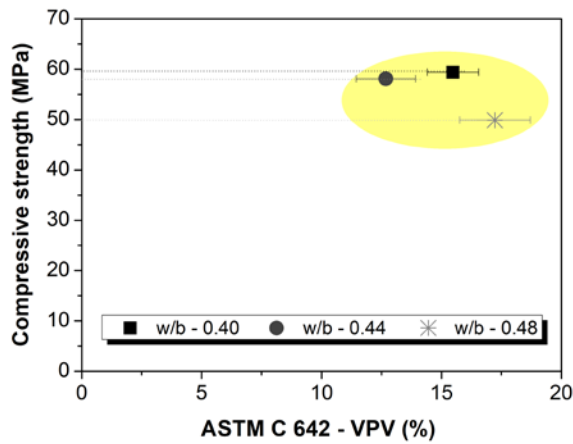


Fig. 2. Relationship between compressive strength and volume of permeable voids for 28-day cured alkali-activated slag concretes

According to the classification given in the ASTM C 642 standard, these concretes would not be classified as durable; however, the severe pre-conditioning stipulated by this testing protocol induced severe microcracking of the tested AAS concretes, increasing the permeability of the samples, causing the collection of results that most likely do not represent the real porosity of undamaged concrete specimens. In general VPV values are higher than those reported for other alkali-activated concretes (Bernal *et al.*, 2012a). This is mainly attributed to the differences in the procedure and temperatures adopted during sample pre-conditioning prior to testing.

3.3 Capillary sorptivity of AAS concretes

Water sorptivity curves of the produced concretes (Fig. 3) show that concretes formulated with a w/b ratio of 0.44 present the lowest total water penetration of the concretes tested, followed by concretes with w/b ratios of 0.40 and 0.48. These results are consistent with the VPV values recorded for these concretes (Fig. 1) where concretes with a w/b ratio of 0.44 presented lower VPV values than the others. All the concretes reached saturation at comparable testing times, which might be indicating a comparable pore network tortuosity (Bernal *et al.*, 2012a).

The capillary absorption coefficient (k ; initial slope of the sorptivity curves in Fig. 2) and resistance to water penetration (m , saturation time divided by the square of the penetration depth) are reported in Table 3.

Concretes with w/b ratios of 0.40 and 0.48 presented similar k and m values, indicating that the total capillary porosities of these concretes are similar, despite presenting significantly different VPV (Fig. 1),

which causes the uptake of larger amounts of water in concretes with w/b ratio of 0.48. Conversely, concretes with a w/b of 0.44 had a lower k value, indicating a more tortuous and refined pore network structure compared with the other concretes assessed; and a higher m value, consistent with the lower VPV (Fig. 1) of these samples.

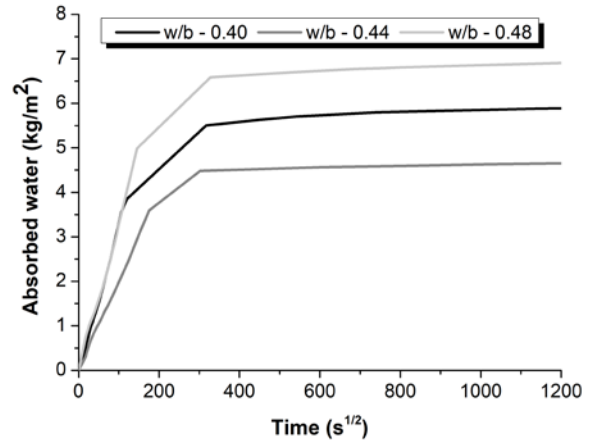


Fig. 3. Capillary sorptivity curves of 28-day cured alkali silicate-activated slag concretes

Table 3. Capillary absorption parameters of AAS concretes

Water/binder ratio	k (kg/m ² s ^{1/2})	m (× 10 ⁷ s/m ²)
0.40	0.031	1.88
0.44	0.020	2.63
0.48	0.033	1.88

3.4 Carbonation resistance

Under natural carbonation conditions (Fig. 4), concretes produced with a w/b ratio of 0.40 do not show observable carbonation during the first 40 days of storage, while specimens formulated with w/b ratios of 0.44 and 0.48 had comparable carbonation depths. Beyond this exposure time, all concretes were partially carbonated, and this was more noticeable as the w/b ratio increased. After 90 days of storage, the carbonation depths of all concretes were less than 4 mm. The carbonation values identified in these concretes are third of those reported for 7-year old naturally carbonated AAS concretes (Bernal *et al.*, 2014) formulated with different w/b ratios, and produced with a slag with much lower MgO content than the one used in this study.

Conversely, under accelerated carbonation conditions the carbonation depth increased at longer times of exposure, particularly when the w/b ratio of the concretes was higher. Differences between natural and accelerated carbonation depths are typically identified when testing AAS concretes, even when accounting for the change in carbonation rate that would be expected due to the higher CO₂ concentration (Bernal *et al.*, 2012b; Bernal *et al.*,

2015a). These outcomes can be mainly attributed to the mechanism governing carbonation of these materials. As carbonation will initially take place in the pore solution, which can be considered as a highly concentrated NaOH solution, variations in both temperature and/or CO₂ concentration lead to the formation of different sodium carbonate/ bicarbonate type products whose density, and therefore ability to plug pores when precipitating, is notably different (Bernal *et al.*, 2012b; Bernal *et al.*, 2013).

The carbonation results, either under natural or accelerated conditions do not correlate neither with the VPV (Fig. 1) nor with the sorptivity (Fig. 3) measurements for the concretes assessed, where a reduced permeability was identified in concretes with a w/b ratio of 0.44. This highlights that the carbonation reaction mechanism control is prevailing in these concretes over the direct effects of the diffusivity of CO₂, indicating that the microstructural differences induced by varying alkalinity of these concretes as water content increases, particularly the crystallinity of the reaction products forming (Bernal *et al.*, 2015b), are influencing the kinetics of carbonation of these materials. However, unlocking the correlation of the crystallinity of reaction products forming in AAS binders and their resistance to carbonation needs detailed investigation.

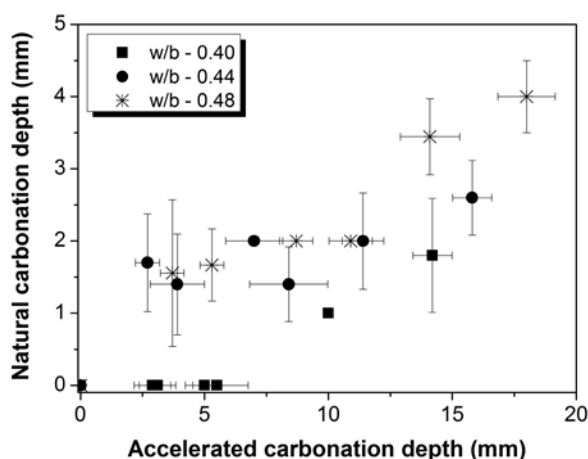


Fig. 4. Correlation between natural and accelerated carbonation of silicate-activated slag concretes

A linear correlation between natural and accelerated carbonated specimens was not identified (Fig. 4); instead, it seems that there is a 'skin' effect where the accelerated carbonation starts immediately, while the CO₂ entering the specimens under natural carbonation conditions takes a longer time to pass the surface layer of the concrete to induce a sufficiently measurable carbonation depth. It seems that the highly alkaline pore solution present in these materials, particularly at early times of curing, promotes the formation of this 'carbonation skin' at relatively short times of CO₂ exposure.

4.0 CONCLUSIONS

The water content in alkali-activated slag concretes strongly influences the mechanical strength and permeability of these concretes. Conversely to what is expected for conventional Portland based concretes, a direct correlation between water content of the concrete, compressive strength and porosity cannot be drawn for the AAS concretes assessed. This demonstrates that the changes in activating solution concentration induced by slight modification in the w/b ratio of AAS concretes can significantly impact how these materials will perform, particularly at an early age of curing.

There is not a direct correlation between natural and accelerated carbonation results of AAS concretes, and the water permeability measured in these concretes, elucidating the complexity of the carbonation process in these materials, and the need to understand in detail the competition between chemical reactions vs. gas transport mechanisms in the extent of carbonation of AAS materials.

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References

- ASTM International 2006. Standard test method for density, absorption, and voids in hardened concrete (ASTM C642-06). West Conshohocken, PA
- ASTM International 2010. Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens (ASTM C39/C39M - 10). West Conshohocken, PA.
- Bakharev T., Sanjayan, J. G. & Cheng, Y. B. 2001. Resistance of alkali-activated slag concrete to carbonation. *Cement and Concrete Research* 31:1277-1283.
- Bernal S. A., Mejía de Gutiérrez, R., Pedraza, A. L., Provis, J. L., Rodríguez, E. D. & Delvasto, S. 2011. Effect of binder content on the performance of alkali-activated slag concretes. *Cement and Concrete Research* 41:1-8.
- Bernal S. A., Mejía de Gutiérrez, R. & Provis, J. L. 2012a. Engineering and durability properties of concretes based on alkali-activated granulated blast furnace slag/metakaolin blends. *Construction and Building Materials* 33: 99-108.
- Bernal S. A., Provis, J. L., Brice, D. G., Kilcullen, A., Duxson, P. & Van Deventer, J. S. J. 2012b. Accelerated carbonation testing of alkali-activated binders significantly underestimate the real service life: The role of the pore solution. *Cement and Concrete Research* 42:1317-1326.

- Bernal S. A., Provis, J. L., Mejía de Gutiérrez, R. & Van Deventer, J. S. J. 2015a. Accelerated carbonation testing of alkali-activated slag/metakaolin blended concretes: effect of exposure conditions. *Materials and Structures* 48:653-669.
- Bernal S. A., Provis, J. L., Walkley, B., San Nicolas, R., Gehman, J. D., Brice, D. G., Kilcullen, A. R., Duxson, P. & Van Deventer, J. S. J. 2013. Gel nanostructure in alkali-activated binders based on slag and fly ash, and effects of accelerated carbonation. *Cement and Concrete Research* 53:127-144.
- Bernal S. A., San Nicolas, R., Provis, J. L., Mejía de Gutiérrez, R. & Van Deventer, J. S. J. 2014. Natural carbonation of aged alkali-activated slag concretes. *Materials and Structures* 47: 693-707.
- Bernal S. A., San Nicolas, R., Van Deventer, J. S. J. & Provis, J. L. 2015b. Water content modifies the structural development of sodium metasilicate-activated slag binders. *Journal of the Latin-American Association of Quality Control, Pathology and Recovery of Construction* 5:30-41.
- Collins F. & Sanjayan, J. G. 1999. Workability and mechanical properties of alkali-activated slag concrete. *Cement and Concrete Research* 29:455-458.
- Deja J. 2002. Carbonation aspects of alkali activated slag mortars and concretes. *Silicates Industriels* 67:37-42.
- Fagerlund G. 1982. On the capillarity of concrete. *Nordic Concrete Research* 1:6.1-6.20.
- Fernández-Bertos M., Simons, S. J. R., Hills, C. D. & Carey, P. J. 2004. A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO₂. *Journal of Hazardous Materials B112*: 193-205.
- Hewlett P. C. 1998. *Lea's Chemistry of Cement and Concrete*, 4th Ed., Oxford, UK, Elsevier.
- Hobbs D. W. 2001. Concrete deterioration: causes, diagnosis, and minimising risk. *International Materials Reviews* 46:117-144.
- Ismail I., Provis, J. L., Van Deventer, J. S. J. & Hamdan, S. The effect of water content on compressive strength of geopolymer mortars. AES-ATEMA' 2011 International Conference on Advances and Trends in Engineering Materials and their Applications, 4-8 Jul 2011 Milan, Italy. CD-ROM proceedings.
- Juenger M. C. G., Winnefeld, F., Provis, J. L. & Ideker, J. 2011. Advances in alternative cementitious binders. *Cement and Concrete Research* 41:1232-1243.
- Kashani A., Provis, J. L. & Van Deventer, J. S. J. Effect of ground granulated blast furnace slag particle size distribution on paste rheology: A preliminary model. AIP Conference, 2013. American Institute of Physics, 1094.
- Palacios M. & Puertas, F. 2011. Effectiveness of mixing time on hardened properties of waterglass-activated slag pastes and mortars. *ACI Materials Journal* 108:73-78.
- Provis J. L. 2017. Alkali-activated materials. *Cement and Concrete Research*. DOI: 10.1016/j.cemconres.2017.02.009
- Provis J. L. & Bernal, S. A. 2014. Geopolymers and related alkali-activated materials. *Annual Reviews of Materials Research* 44:299-327.
- Puertas F., Fernández-Jiménez, A. & Blanco-Varela, M. T. 2004. Pore solution in alkali-activated slag cement pastes. Relation to the composition and structure of calcium silicate hydrate. *Cement and Concrete Research* 34:139-148.
- Puertas F., Palacios, M. & Vázquez, T. 2006. Carbonation process of alkali-activated slag mortars. *Journal of Materials Science* 41:3071-3082.
- Puertas F., Varga, C. & Alonso, M. M. 2014. Rheology of alkali-activated slag pastes. Effect of the nature and concentration of the activating solution. *Cement and Concrete Composites* 53:279-288.
- Sanjuán M. A., Andrade, C. & Cheyrezy, M. 2003. Concrete carbonation test in natural and accelerated conditions. *Advances in Cement Research* 15:71 - 180.
- Shi C., Fernández-Jiménez, A. & Palomo, A. 2011. New cements for the 21st century: The pursuit of an alternative to Portland cement. *Cement and Concrete Research* 41:750-763.
- Snellings R., Mertens, G. & Elsen, J. 2012. Supplementary cementitious materials. *Reviews in Mineralogy and Geochemistry* 74:211-278.
- Standards Australia 1994. AS 1012: Methods of testing concrete.
- Wang S. D., Scrivener, K. L. & Pratt, P. L. 1994. Factors affecting the strength of alkali-activated slag. *Cement and Concrete Research* 24: 1033-1043.