This is a repository copy of *Alkali-activated slag cements produced with a blended sodium carbonate/sodium silicate activator*.

White Rose Research Online URL for this paper:
http://eprints.whiterose.ac.uk/135527/

Version: Accepted Version

Article:

Bernal, SA, San Nicolas, R, van Deventer, JSJ et al. (1 more author) (2016) Alkali-activated slag cements produced with a blended sodium carbonate/sodium silicate activator. Advances in Cement Research, 28 (4). pp. 262-273. ISSN 0951-7197

https://doi.org/10.1680/jadcr.15.00013

© 2016, ICE Publishing, all rights reserved. This is an author produced version of a paper published in Advances in Cement Research. Uploaded in accordance with the publisher's self-archiving policy.

Reuse

Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

eprints@whiterose.ac.uk
https://eprints.whiterose.ac.uk/

Alkali-activated slag cements produced with a blended sodium carbonate/silicate activator

Susan A. Bernal,[1] Rackel San Nicolas,[2] Jannie S.J. van Deventer,[3,4] John L. Provis[1]*

[1]Department of Materials Science and Engineering, The University of Sheffield, Sheffield S1 3JD, UK
[2] Department of Infrastructure Engineering, The University of Melbourne, Victoria 3010, Australia
[3]Department of Chemical & Biomolecular Engineering, The University of Melbourne, Victoria 3010, Australia
[4]Zeobond Pty Ltd, P.O. Box 210, Somerton, Victoria 3062, Australia

*Corresponding author. Email j.provis@sheffield.ac.uk, phone +44 114 222 5490, fax +44 114 222 5493

Abstract

In this study, an alkali-activated slag cement produced with a blend of sodium carbonate/sodium silicate activator has been characterised. This binder hardened within 12 h, and achieved a compressive strength of 20 MPa after 24 h of curing under ambient conditions, which is associated with the formation of an aluminium substituted calcium silicate hydrate as main reaction product. Carbonates including pirssonite, vaterite, aragonite and calcite were identified, along with the zeolites hydroxysodalite and analcime at early times of reaction. The partial substitution of sodium carbonate by sodium silicate reduces the concentration of CO_3^{2-} in the pore solution, increasing the alkalinity of the system compared to a solely carbonate-activated paste, accelerating the kinetics of reaction, and supplying additional silicate species to react with the calcium dissolving from the slag, as the reaction proceeds. These results demonstrate that this blend of activators can be used effectively for the production of high strength alkali-activated slag cements, with a microstructure comparable to what has been identified in aged Na_2CO_3-activated slag cements, but without the extended setting times reaction usually identified when using this salt as alkali activator.

Keywords: alkali-activated slag, near-neutral salts, microstructure, X-ray diffraction, nuclear magnetic resonance, scanning electron microscopy

1. Introduction

Alkali-activated slags are part of the tool-kit of Portland clinker-free alternative binders that have been developed over the past decades. These materials are produced through the chemical reaction between industrial by-products and an alkaline solution, promoting the formation of a hardened solid (Provis and Bernal, 2014). There is a general consensus that alkali-activated slag binders can exhibit advantageous technical properties, such as high temperature resistance (Guerrieri et al., 2010), resistance to sulphate (Ismail et al., 2013) and acid attack (Lloyd et al., 2012, Bernal et al., 2012b), meaning that they are suitable for use in various specialised applications, as well as for general-purpose concrete production. However, prediction of the performance of alkali-activated slag materials based simply upon mix design information is not straightforward, as there are many factors that can modify their microstructure and transport properties, such as the source, chemical composition, mineralogy and thermal history of the slag used, the type and concentration of the alkaline activator incorporated (Wang et al., 1995, Juenger et al., 2011), along with the mixing duration when producing the binder (Palacios and Puertas, 2011) and the curing conditions adopted (Bakharev et al., 1999).

The role of the alkaline activator in an activated slag binder system is to promote an increase in pH, which drives the initial dissolution of the precursors, and the consequent condensation reaction to form calcium aluminium silicate hydrate (C-A-S-H) type gels as main reaction product (Zhou et al., 1993, Shi, 2003, Song et al., 2000), and layered double hydroxides with a hydrotalcite-type structure, along with zeolites as secondary reaction products, depending on the composition of the slag used (Provis and Bernal, 2014, Bernal et al., 2013). The activators commonly used for the production of activated slag binders are sodium hydroxide (NaOH), sodium silicates ($Na_2O{\cdot}rSiO_2$), sodium carbonate (Na_2CO_3) and sodium sulphate (Na_2SO_4) (Wang et al., 1994, Shi et al., 2006), and the effectiveness of each has been mainly associated with the elevated pH and reactive species that each of these solutions can provide.

Sodium carbonate has been identified as a suitable possibility to achieve comparable pH in the pore solution of alkali-activated slag to that identified in Portland cements (Bai et al., 2011), and is significantly less expensive than most other possible activators. Sodium carbonate activation of blast furnace slag has been applied for several decades, especially in eastern Europe (Krivenko, 1994, Xu et al., 2008), as a more cost-effective and environmentally friendly alternative to the widely used activators for production of activated slag products; it is possible in many parts of the world to obtain Na_2CO_3 either as a secondary product from industrial processes, or by mining alkali carbonate deposits followed by moderate-temperature thermal treatment (Provis et al., 2014a, 2014b). More recently, Na_2CO_3-slag-fine limestone concretes have been observed to show very good early strength development, as well as calculated potential Greenhouse emission savings as high as 97% when compared to Portland cement (Sakulich et al., 2010).
However, Na_2CO_3 is a relatively weak alkali compared to the hydroxide or silicate activators which are more commonly used in alkali activation. For this reason, when using a sodium carbonate

activator in a slag-based binder, delayed formation of strength giving phases is often identified at early times of curing (Fernández-Jiménez and Puertas, 2001, Duran Atiş et al., 2009). At early age, formation of calcium and mixed sodium-calcium carbonates, as a consequence of the interaction of the CO_3^{2-} from the activator with the Ca^{2+} from the dissolved slag, is favoured instead of the development of calcium silicate hydrate gels (Bernal et al., 2015). In order to overcome the delayed hardening (which can take up to 5 days in some systems) and slower strength development of these materials, high temperature curing has usually been adopted, which limits the commercial application of these materials. In a recent study it was proposed (Bernal et al., 2015) that what might be required to overcome the delayed formation of strength giving phases in these systems is either:

(i) a mechanism by which the carbonate can be removed from solution at early age, leaving the slag to then react in a NaOH-rich environment, or
(ii) the addition of a second activator compound to modify the pore solution chemistry of the system, and supply species which are more prone to react with the progressively dissolving calcium from the slag than is the CO_3^{2-} supplied by the sodium carbonate activator.

In this study, we evaluate the effect of sodium silicate addition on the structural development of a sodium carbonate-activated slag. X-ray diffraction, ^{29}Si and ^{27}Al MAS NMR spectroscopy and scanning electron microscopy were used to determine the nature and chemistry of the reaction products formed, and the kinetics of reaction are assessed via isothermal calorimetry of fresh paste specimens. Compressive strength values of mortars corresponding to the pastes produced for the structural study are also reported.

2. Experimental methodology

2.1.Materials and sample preparation

As primary raw material a granulated blast furnace slag (GBFS) was used, with oxide composition as shown in Table 1. Its specific gravity is 2800 kg/m^3 and Blaine fineness 410 ± 10 m^2/kg. The particle size range, determined through laser diffraction, was 0.1-74 μm, with a d_{50} of 15 μm.

Table 1. Composition of GBFS used. LOI is loss on ignition at 1000°C

Component (mass % as oxide)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Others	LOI
GBFS	33.8	13.7	0.4	42.6	5.3	0.1	0.4	1.9	1.8

In order to produce the two activating solutions used, reagent grade sodium carbonate (Sigma-Aldrich) was dissolved in water until complete dissolution was reached. Simultaneously, a blend of NaOH pellets and a commercial silicate (PQ Grade D) solution was produced in order to achieve a sodium metasilicate solution with a molar ratio of SiO_2/Na_2O of 1.0 (i.e. a composition corresponding to dissolved Na_2SiO_3).

Paste specimens were formulated with a water/binder ratio of 0.40 and an activator (50 wt.% Na_2CO_3/50 wt.% Na_2SiO_3) content of 8 g per 100 g of slag. The activating solutions were mixed separately with the anhydrous slag, by first adding the sodium silicate, followed by the sodium carbonate. The paste was mixed in a Hobart N50 bench mixer at low speed for 10 min to achieve homogeneity. All paste specimens were cured in sealed centrifuge tubes at 23°C until testing. Mortar cubes, 50 mm in size, were used for compressive strength testing; these were formulated with a sand:binder ratio of 1:2.75, and a binder formulation matching the paste specimens.

Isothermal calorimetry experiments were conducted using a TAM Air isothermal calorimeter at a temperature of 25 ± 0.02°C. Fresh paste was mixed externally, weighed into an ampoule, and immediately placed in the calorimeter to record heat flow for the first 140 h of reaction. All values of heat release rate are normalised by total mass of paste.

2.2.Tests conducted on hardened specimens

The hardened paste specimens were analysed through:

- X-ray diffraction (XRD), using a Bruker D8 Advance instrument with Cu Kα radiation and a nickel filter. Data were collected with a step size of 0.020º, over a 2θ range of 5º to 70º.
- Magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy; ^{29}Si MAS NMR spectra were collected at 119.1 MHz on a Varian INOVA-600 (14.1 T) spectrometer using a probe for 4 mm o.d. zirconia rotors and a spinning speed of 10.0 kHz. The ^{29}Si MAS experiments employed a pulse width of 6 μs, a relaxation delay of 60 s and 4300-6500 scans. Solid-state ^{27}Al MAS NMR spectra were acquired at 156.3 MHz on the same instrument, with a pulse width of 6 μs and a relaxation delay of 2 s. All spectra were collected with a pulse angle of 51º. ^{29}Si and ^{27}Al chemical shifts were referenced to external samples of tetramethylsilane (TMS) and a 1.0 M aqueous solution of $AlCl_3.6H_2O$, respectively.
- Environmental scanning electron microscopy (ESEM), using an FEI Quanta instrument with a 15 kV accelerating voltage, a Link-Isis (Oxford Instruments) energy dispersive X-ray (EDX)

detector, and a working distance of 10 mm. Polished, uncoated samples were evaluated in low vacuum mode, using a backscatter detector for imaging.

- Compressive strength testing, using an ELE International Universal Tester, at a loading rate of 1.0 kN/s for the 50 mm mortar cubes.

3. Results and discussion

3.1. Isothermal calorimetry

The heat release rate of the sodium carbonate/silicate activated slag (Fig. 1) shows an initial pre-induction period in the first hour of reaction, corresponding to the wetting and start of dissolution of the slag particles, followed by an induction period where limited, but non-zero, heat release is detected during the subsequent 11 hours. This is associated with a progressive dissolution of the slag and initial condensation and precipitation of reaction products. A low intensity hump was identified after 3 h of reaction, which is most likely associated with the formation of carbonates. After 13 h a significant heat release is observed, consistent with the process described as the acceleration period in cementitious binders, reaching a maximum after 17 h, and the subsequent deceleration period is complete after 30 hours of reaction. The significant heat release observed in the acceleration and deceleration periods is assigned to the formation and precipitation of a large amount of reaction products.

The kinetics of reaction of these binders resemble what has been identified in sodium silicate activation of the same slag (Bernal et al., 2014), and in other systems with comparable slag chemistry (Ben Haha et al., 2011), where the pre-induction period was observed during the first hour after mixing, followed by short induction periods (<10 h in metasilicate activated slags with MgO contents lower than 8 wt.% (Bernal et al., 2014)). However, the results differ from those identified for a sodium carbonate activated slag (Bernal et al., 2015), where an induction period of over 62 hours was detected, and the acceleration-deceleration periods were observed after 4-9 days of curing. These results demonstrate that the inclusion of sodium silicate is effective in accelerating the kinetics of reaction of a sodium carbonate activated slag, which could be a consequence of the combined effects of reducing the fraction of carbonate in the systems (as less Na_2CO_3 activator is used), and the increased alkalinity of the system and higher concentration of Si species in the pore solution, supplied by the sodium metasilicate, at early stages of reaction.

<Fig 1>

Figure 1. (A)Heat release rate and (B) heat of reaction of an alkali silicate/carbonate activated slag binder. Heat release data for sodium silicate-only and sodium carbonate–only activated mortars from (Bernal et al., 2013, 2015)

3.2. X-ray diffraction

The X-ray diffractograms of the silicate modified sodium carbonate activated slag are shown in Figure 2. After 1 day of curing (which is immediately after the acceleration-deceleration peak in the calorimetry data, Figure 1), the main crystalline compounds present are the three polymorphs of calcium carbonate ($CaCO_3$): calcite (powder diffraction file, PDF #005-0586), vaterite (PDF #002-0261) and aragonite (PDF #04-013-9616), along with the Na-Ca carbonate phase pirssonite ($Na_2Ca(CO_3)_2 \cdot 2H_2O$, PDF# 002-0157), and hydroxysodalite ($Na_8Al_6Si_6O_{24}(OH)_2(H_2O)_2$, PDF# 04-011-3164). Calcium carbonate in various polymorphs has been identified in sodium carbonate-activated slag binders (Bernal et al., 2015, Fernández-Jiménez and Puertas, 2001), and its formation was associated with the preferential early age reaction between dissolved CO_3^{2-} present in the pore solution and the Ca^{2+} released by the partial dissolution of the slag (Bernal et al., 2015), comparable to what is expected to occur during the carbonation reaction of Ca-rich cementitious binders.

<Fig. 2>

Figure 2. X-ray diffractograms of an alkali silicate/carbonate activated slag as a function of the time of curing

It is noted that the intensity of the reflections assigned to the carbonate phases aragonite, vaterite and pirssonite increase monotonically up to 45 days of curing, followed by a significant decrease at advanced times of curing. Formation of aragonite or vaterite rather than calcite, in the early stages of the reaction, may be associated with an intermediate relative humidity reached within the sample (Dubina et al., 2013), or a high concentration of magnesium present in the pore solution at early times of curing. Magnesium has a significant influence on calcium carbonate precipitation, and can stabilise amorphous carbonates, aragonite and/or vaterite when its concentration is sufficiently high (Falini et al., 1996, Loste et al., 2003). As the alkali-activation reaction progresses, is expected that the concentration of Mg^{2+} in the pore solution will decrease with the formation of Mg-rich layered double hydroxides, and therefore minimising its effect in hindering calcite formation.

The addition of sodium silicate here favours the formation of pirssonite rather than the more hydrated double salt gaylussite ($Na_2Ca(CO_3)_2\cdot 5H_2O$), which was identified at early age when sodium carbonate was used as the sole activator (Bernal et al., 2015, Fernández-Jiménez and Puertas, 2001). Pirssonite and gaylussite have also been identified as reaction products in naturally carbonated and accelerated carbonated alkali-activated slag binders (Bernal et al., 2012a, Bernal et al., 2013), respectively, and the formation of pirssonite as a transient phase in the silicate-modified sodium carbonate-activated slag binder here is consistent with those findings.

The formation of zeolites at early age of reaction in sodium carbonate activated slag binders has been associated with the consumption of Ca^{2+} by CO_3^{2-} towards formation of carbonates, which leads to saturation of Si and Al species with respect to aluminosilicate zeolite type products in the NaOH-rich pore solution from the earliest stages of the reaction process (Bernal et al., 2015). In absence of sodium silicate, zeolite NaA was identified at early age in Na_2CO_3-activated slag binders, but was fully consumed at advanced times of curing (Bernal et al., 2015). The inclusion of sodium metasilicate favours the formation of hydroxysodalite rather than zeolite NaA; the reflections assigned to this phase vary in intensity between 1 and 7 days of curing, and the formation of analcime ($NaAlSi_2O_6$, PDF# 01-073-6448) is also observed. Both zeolites are fully consumed after 7 days of reaction. Sodalite type zeolites can be formed from zeolite Na-A (which is a closely related framework structure) under highly alkaline conditions (Deng et al., 2006, Chen et al., 2010), which suggests that the increased alkalinity, compared with that reached when using sodium carbonate as sole activator, is favouring the evolution towards sodalite structures in the silicate/carbonate activated system here.

Formation of a crystalline layered double hydroxide with a hydrotalcite type structure (resembling $Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$, PDF# 014-0191), along with a calcium aluminium silicate hydrate (C-A-S-H) (resembling a disordered, Al-substituted form of tobermorite-11Å, $Ca_5Si_6O_{18}\cdot 5H_2O$, PDF #045-1480), is identified after 3 days of curing. These phases have been reported as the main reaction products in NaOH and $Na_2O\cdot rSiO_2$ activated slag binders (Ben Haha et al., 2011, Bernal et al., 2013, Escalante-Garcia et al., 2003). The intensities of the reflections assigned to these phases increase substantially during the first 45 days of curing, with only minor variation at advanced age (180 days), consistent with the deceleration of the progressive activation process after the first months of reaction. The formation of heulandite, a Ca-rich zeolite which was identified in the sodium carbonate activated slag paste (Bernal et al., 2015), appears to be suppressed by the incorporation of sodium silicate in the system.

3.3.Nuclear magnetic resonance spectroscopy

The ^{29}Si MAS NMR spectra of the anhydrous slag and sodium carbonate/silicate-activated binders are shown in Figure 3A. After 1 day of curing, low intensity peaks centred at –80, -83 and -86 ppm, assigned to Q^1, Q^2(1Al) and Q^2 sites respectively and characteristic of the Al-substituted C-S-H type phase (Le Saoût et al., 2011, Bernal et al., 2014), are observed. This indicates that the partial replacement of sodium carbonate by sodium silicate is effectively favouring the formation of strength-giving phases during the first 24 h of reaction. It is noted (Figure 3A) that the intensity in the region between -60 and -80 ppm decreases up to 28 days of curing, consistent with the progressive reaction of the unreacted slag; however at advanced times of curing a slight increase in the intensity of the sites present in this region was identified. This is mainly associated with the formation of additional Q^1 sites as reaction progresses.

As reaction progresses, a significant increase in the intensity of these bands is identified. In all specimens, resonances at -89 and -93 ppm are also observed. These sites are typically assigned to Q^3(1Al) sites present in crosslinked tobermorites with Al(IV)-O-Si linkages (Fernández-Jiménez et al., 2003) and Q^3 sites, respectively. However, a structural model and interpretation of ^{29}Si MAS NMR results for alkali-activated slags has recently been proposed (Myers et al., 2013), suggesting that Q^3 and Q^3(1Al) sites could overlap with contributions of Q^4(3Al) and Q^4(4Al) sites from an aluminosilicate type gel forming in Al-rich binders, and these Q^4(3Al) and Q^4(4Al) sites will thus also contribute to the -89 and -93 ppm peaks (Myers et al., 2013, Bernal et al., 2014). According to this model, the contribution of Q^3 sites to the -93 ppm peak may be a minor one, as the majority of crosslinking sites in the tobermorite-type gel involve an aluminium bridging site, and so this peak is predominantly related to the Q^4 type aluminosilicate environments (Myers et al., 2015).

<Fig 3>

Figure 3. (A) ^{29}Si MAS NMR spectra as function of the time of curing, and (B) deconvolution of ^{29}Si MAS NMR spectra of 28-day cured of sodium silicate/carbonate-activated slag binders. The grey area corresponds to the remnant unreacted slag contribution.

It was suggested (Bernal et al., 2015) that the extraction of calcium from the slag glass, and the consequent formation of carbonate species, will be favoured at the alkalinity conditions reached in sodium carbonate activated slag systems (pH ~11), and consequently the Q^0 sites in the slag would be prone to preferential release upon reaction. However, recent studies (Snellings et al., 2014, Snellings, 2015) evaluating the surface characteristics of synthetic glasses within the system CaO-Al_2O_3-MgO-SiO_2 demonstrated that these glasses dissolve congruently in alkaline media (pH above

11), independent of the content of MgO. The partial substitution of sodium carbonate by sodium silicate promoted a higher alkalinity (activator pH = 13.1) than is achievable in a sodium carbonate activating solution, and therefore congruent dissolution of the slag is more plausible in the system studied here. Based on this, quantitative analysis of these spectra was carried out through the direct subtraction of the scaled contribution of the unreacted slag component from the spectra of reacted samples at different times of curing, as proposed by Le Saoût et al. (2011). A summary of the deconvolution results is shown in Table 2. An example of a deconvoluted ^{29}Si MAS NMR spectrum is shown in Figure 3B.

Table 2. Deconvolution results of ^{29}Si MAS NMR spectra of silicate/carbonate-activated slag binders as a function of the time of curing. Estimated uncertainty in site percentages is ± 2%

Time of curing (days)	**Unreacted slag (%)**	**Reaction products**						
		Q^0	**Q^1(I)**	**Q^1(II)**	**Q^2(1Al)**	**Q^2**	**Q^3(1Al)/ Q^4(4Al)**	**Q^3/ Q^4(3Al)**
		-74 ppm	**-78 ppm**	**-80 ppm**	**-83 ppm**	**-86 ppm**	**-89 ppm**	**-93 ppm**
1	54	3	12	7	12	8	4	0
3	34	5	16	11	17	11	5	1
7	33	6	15	12	18	10	5	1
28	31	5	15	13	19	11	5	1
45	30	6	17	11	17	9	8	2

When sodium silicate was used as the sole activator for slag at a similar dose to the mix designs used here, unreacted slag percentages of 25±2% and 21%±2% were calculated, after 14 days (Bernal et al., 2013) and 56 days (Bernal et al., 2014) respectively, through deconvolution of ^{29}Si MAS NMR spectra. The fraction of unreacted slag in sodium carbonate/silicate slag pastes is significantly higher, consistent with the delayed kinetics of reaction in this system. As the reaction progresses during curing, the slag continues reacting in the sodium carbonate/silicate slag pastes, and eventually approaches a similar extent of reaction at later age to that identified in sodium silicate activated slag binders.

Differences in the relative abundances of the silicon site environments are most evident when comparing the results of paste after 1 day and 3 days of curing, where a significant fraction of unreacted slag is reacting, promoting the formation of silicon sites assignable to C-(A)-S-H type gel forming in these materials. This agrees well with the high heat released by these binders (Figure 1) within the first 48 h of reaction. The relative fractions of the different sites remain much more similar from 7 to 45 d, indicating that the binder structure is largely established at 3 d, and the ongoing reaction continues to produce a larger quantity of similar reaction products, rather than showing a fundamental shift in the nature of the binder as it matures. It is worth noting that the fraction of the sites at -89 ppm is comparable in the sodium carbonate/silicate slag paste to that of sodium silicate activated pastes (-89 ppm fraction 3-7% (Bernal et al., 2014)), suggesting that the blended activator is promoting similar crosslinking of the reaction products than when using sodium silicate as sole activator.

Three distinct types of aluminium environments, Al(IV) (52-80 ppm), Al(V) (30-40 ppm) and Al(VI) (0-20 ppm) (Engelhardt and Michel, 1987), are identified in all of the ^{27}Al MAS NMR spectra (Figure 4). Sharpening in the tetrahedral Al band is observed after 1 day of curing, along with the appearance of a shoulder centred at 74 ppm, whose intensity increases with curing time. This band corresponds to the Al(IV) incorporated in bridging tetrahedra in the C-A-S-H (Andersen et al., 2003, Sun et al., 2006). These results are consistent with the ^{29}Si MAS NMR data, where formation of C-A-S-H type phases is identified after 1 day of curing, and differs from the trends identified in Na_2CO_3-activated slag cement (Bernal et al., 2015), where the distinctive peaks assigned to the strength-giving phase C-A-S-H were only observed after 7 days of curing. This is also in good agreement with the much later onset of the acceleration peak in the calorimetry data for the carbonate-only system (Figure 1).

In pastes cured for 7 days, asymmetric broadening of the band at 68 ppm is observed, along with the formation of a low intensity shoulder at ~58 ppm, consistent with the formation of Al-substituted tobermorites with low Ca/(Si+Al) ratio (Sun et al., 2006) and highly crosslinked C-A-S-H phases (Myers et al., 2013). Formation of a narrow peak centred at 8.7 ppm is also observed at early times of curing (1 day), and the intensity in this region significantly increases as the reaction progresses. This peak has been assigned to layered double hydroxide type phases in alkali-activated slag cements (Bernal et al., 2013), including hydrotalcite and/or AFm type phases, and the increase in intensity of this peak with curing duration is in good agreement with the observation of hydrotalcite by XRD (Figure 2). Hence, it can be stated that the addition of sodium silicate is accelerating the kinetics of reaction in this blended system, via preferential reaction of Si species supplied by the activator with the Ca from the dissolving slag, favouring formation of C-A-S-H phases within the first day of reaction.

<Fig 4>

Figure 4. ^{27}Al MAS NMR spectra of sodium silicate/carbonate-activated slag binders as function of the time of curing

3.4.Scanning electron microscopy

Backscattered electron (BSE) images of the paste evaluated at three different magnifications and two different curing durations (7 and 28 days) are shown in Figure 5. In the 7-day cured sample (Figure 5A) several distinctive features are identified, with varying greyscale intensities. Light grey angular particles correspond to remnant unreacted slag grains. These slag particles are embedded in a mostly continuous matrix, which contains some isolated dark grey regions which will be discussed in detail below, and large pores (black regions). Little difference is visually identifiable between the samples cured for 7 and 28 days (Figure 5B), although the XRD data in Figure 2 showed the consumption of the zeolitic phases during this time interval, which indicates that this process does not have a significant influence on the microstructure on the length scale observable by SEM. Conversely, at more advanced times of curing (90 days, Figure 5C) the dark grey and black regions are no longer identifiable, and instead the material is mainly composed of a dense and homogeneous matrix, encapsulating the remaining unreacted slag particles. Change in greyscale intensity in SEM imaging of cementitious binders can be attributed either to a change in the chemistry of the binding gel, or to changes in density (Ben Haha et al., 2011, Zhang et al., 2002, Kjellsen, 1996, Famy et al., 2002). To separate these effects, elemental maps of pastes cured for 7 and 90 days were collected, and are reported in Figure 5 and 6, respectively.

<Fig 5>

Figure 5. BSE images of sodium carbonate/silicate-activated slag binders after (A) 7, (B) 28 and (C) 90 days of curing, at three different magnifications per sample (denoted 0, 1 and 2)

In the 7 day-cured paste, two distinctive areas can be identified in the BSE image in Figure 6: a light grey homogenous matrix rich in Al, Si and Ca, consistent with a C-A-S-H type phase, as previously identified in these pastes via NMR (Figure 3), and a dark grey area similar to those noted in Figure 5A. This region has a lower content of Ca than the light grey region, and is enriched in Na, O, and C. In this region, little or no Al, Mg and Si are present, and so the elemental composition of the dark area is consistent with the presence of an Na-Ca carbonate type phase. XRD results for this early-age paste (Figure 2) showed the formation of pirssonite ($Na_2Ca(CO_3)_2\cdot 2H_2O$), and therefore it is likely that these areas correspond to this phase. In the paste cured for 90 days (Figure 7), corresponding Ca-Na carbonate areas were not identified (consistent with the reduction in pirssonite in the XRD data in Figure 2 at later ages); instead, a homogeneous matrix with Ca, Na, Al, and Si more evenly distributed is observed. This is consistent with the formation of a C-(N)-A-S-H type phase as the main binding product, as identified by other analytical techniques throughout this study.

<Fig 6>

Figure 6. BSE image and corresponding elemental maps of a sodium carbonate/silicate activated slag cured for 7 days

<Fig 7>

Figure 7. BSE image and corresponding elemental maps of a sodium carbonate/silicate activated slag cured for 90 days

3.5. Compressive strength

Mortars produced with the sodium carbonate/silicate activator developed a compressive strength of 19 MPa after 1 day of curing (Figure 8). Subsequent to this, a significant increase in compressive strength is also observed between 1 and 4 days of curing, so that the mortars reach a strength of 44 MPa after 7 days. This differs from what has been observed for sodium carbonate activated materials produced with the same slag used in this study (Bernal et al., 2015), where the material had not yet hardened after 1 day of curing, and after 4 and 7 days of curing the mortars achieved compressive strengths of 9 MPa and 33 MPa, respectively. Longer curing times promote further strength development, in agreement with the densification of the matrix observed by SEM (Figure 5). Mortars cured for 56 days reached 63 MPa, which is 20 MPa higher than is achieved when sodium carbonate is utilised as the sole activator (Bernal et al., 2015).

<Fig 8>

Figure 8. Compressive strength development of a sodium silicate/carbonate activated slag binder, compared with data for similar mix designs using silicate-only and carbonate-only activators. Compressive strength data of sodium carbonate activated slag mortars from (Bernal et al., 2015)

The earlier strength development in the carbonate/silicate activated slag mortars is associated with the reduced concentration of CO_3^{2-} in the system compared to the carbonate-only activator, as in the absence of dissolved silicates, the calcium released by slag dissolution is consumed via formation of carbonate phases instead of forming strength-giving binder gels. The higher alkalinity of the sodium silicate-containing solution accelerates the slag dissolution compared to the sodium carbonate-only system, and the Si species supplied by the sodium silicate component of the activator participate in formation of the strength-giving phase C-A-S-H within the first 24 h of reaction, as identified via XRD and solid-state NMR spectroscopy, and therefore favour high early strength development of these cements.

The compressive strength values of the sodium carbonate and sodium carbonate/silicate activated slag pastes are generally lower than those of the silicate-only system; however after 56 days of curing, the strength values of the carbonate/silicate activated paste are comparable to those of silicate activated pastes, although a reduced degree of reaction of the slag was identified in this mix, compared with the silicate only system.

4. Conclusions

This paper demonstrates that highly significant performance gains in alkali-carbonate activation of slags can be achieved through the addition of sodium silicate, particularly in terms of early-age reaction rate and strength. Setting and hardening occur within the first 24 h after mixing under ambient-temperature sealed curing, and a significant strength (19 MPa) is achieved at this point in time, which would be sufficient for demoulding or formwork removal. This route to the production of alkali-activated binders offers a reduced cost (both financial and environmental) compared with the use of a silicate-only activator, with but with performance which significantly exceeds that of a carbonate-only system. The addition of sodium silicate is promoting faster dissolution of the slag, as identified via isothermal calorimetry, as higher alkalinities are achieved compared with sodium carbonate activation. The carbonate ions are removed from the liquid phase in the hardening paste by reaction with the calcium released by the slag; this early-age formation of alkali/alkali-earth carbonates is accompanied by early formation of calcium (alumino-)silicate hydrate as a strength-giving product. The calcium carbonate phases formed at early age remain stable in the reaction product assemblage, while the alkali/alkali-earth carbonate double salts, as well as some zeolitic phases which incorporate the excess alumina supplied by the slag, are transient phases which are later converted to calcium (alumino-)silicate hydrate and hydrotalcite as further Ca and Mg are supplied by the ongoing reaction of the slag. The final binder microstructure is dense and relatively homogeneous, with a compressive strength exceeding 60 MPa after 56 days.

Acknowledgements

This work has been funded by the Australian Research Council, through a Linkage Project co-sponsored by Zeobond Pty Ltd, including partial funding through the Particulate Fluids Processing Centre. We wish to thank Adam Kilcullen and David Brice for producing the specimens tested, and Dr John D. Gehman for assistance with the NMR spectroscopy. The work of JLP and SAB received funding from the European Research Council under the European Union's Seventh Framework Programme (FP/2007-2013) / ERC Grant Agreement #335928 (GeopolyConc).

References

Andersen, M. D., Jakobsen, H. J. & Skibsted, J. (2003) Incorporation of aluminum in the calcium silicate hydrate (C−S−H) of hydrated Portland cements: A high-field ^{27}Al and ^{29}Si MAS NMR investigation. Inorganic Chemistry **42(7)**:2280-2287.

Bai, Y., Collier, N., Milestone, N. & Yang, C. (2011) The potential for using slags activated with near neutral salts as immobilisation matrices for nuclear wastes containing reactive metals. Journal of Nuclear Materials **413(3)**:183-192.

Bakharev, T., Sanjayan, J. G. & Cheng, Y. B. (1999) Effect of elevated temperature curing on properties of alkali-activated slag concrete. Cement and Concrete Research **29(10)**:1619-1625.

Ben Haha, M., Le Saout, G., Winnefeld, F. & Lothenbach, B. (2011) Influence of activator type on hydration kinetics, hydrate assemblage and microstructural development of alkali activated blast-furnace slags. Cement and Concrete Research **41(3)**:301-310.

Bernal, S. A., Provis, J. L., Brice, D. G., Kilcullen, A., Duxson, P. & Van Deventer, J. S. J. (2012a) Accelerated carbonation testing of alkali-activated binders significantly underestimate the real service life: The role of the pore solution. Cement and Concrete Research **42(10)**:1317-1326.

Bernal, S. A., Rodríguez, E. D., Mejía De Gutiérrez, R. & Provis, J. L. (2012b) Performance of alkali-activated slag mortars exposed to acids. Journal of Sustainable Cement-Based Materials **1(3)**:138-151.

Bernal, S. A., Provis, J. L., Walkley, B., San Nicolas, R., Gehman, J., Brice, D. G., Kilcullen, A., 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., Myers, R. J., Mejía De Gutiérrez, R., Puertas, F., Van Deventer, J. S. J. & Provis, J. L. (2014) MgO content of slag controls phase evolution and structural changes induced by accelerated carbonation in alkali-activated binders. Cement and Concrete Research **57**:33-43.

Bernal, S. A., Provis, J. L., Myers, R. J., San Nicolas, R. & Van Deventer, J. S. J. (2015) Role of carbonates in the chemical evolution of sodium carbonate-activated slag binders. Materials and Structures **48(3)**:517-529.

Chen, S., Wu, M. Q. & Zhang, S. R. (2010) Mineral phases and properties of alkali-activated metakaolin-slag hydroceramics for a disposal of simulated highly-alkaline wastes. Journal of Nuclear Materials **402(2-3)**:173-178.

Deng , Y., Harsh, J. B., Flury, M., Young, J. S. & Boyle, J. S. (2006) Mineral formation during simulated leaks of Hanford waste tanks. Applied Geochemistry **21**:1392-1409.

Dubina, E., Korat, L., Black, L., Strupi-Šuput, J. & Plank, J. (2013) Influence of water vapour and carbon dioxide on free lime during storage at 80°C, studied by Raman spectroscopy. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy **111(0)**:299-303.

Duran Atiş, C., Bilim, C., Çelik, Ö. & Karahan, O. (2009) Influence of activator on the strength and drying shrinkage of alkali-activated slag mortar. Construction and Building Materials **23(1)**:548-555.

Engelhardt, G. & Michel, D. (1987) High-Resolution Solid-State NMR of Silicates and Zeolites. Chichester, John Wiley & Sons.

Escalante-García, J., Fuentes, A. F., Gorokhovsky, A., Fraire-Luna, P. E. & Mendoza-Suarez, G. (2003) Hydration products and reactivity of blast-furnace slag activated by various alkalis. Journal of the American Ceramic Society **86(12)**:2148-2153.

Falini, G., Gazzano, M. & Ripamonti, A. (1996) Magnesium calcite crystallization from water-alcohol mixtures. Chemical Communications **(9)**:1037-1038.

Famy, C., Scrivener, K. L. & Crumbie, A. K. (2002) What causes differences of C-S-H gel grey levels in backscattered electron images? Cement and Concrete Research **32(9)**:1465-1471.

Fernández-Jiménez, A. & Puertas, F. (2001) Setting of alkali-activated slag cement. Influence of activator nature. Advances in Cement Research **13(3)**:115-121.

Fernández-Jiménez, A., Puertas, F., Sobrados, I. & Sanz, J. (2003) Structure of calcium silicate hydrates formed in alkaline-activated slag: Influence of the type of alkaline activator. Journal of the American Ceramic Society **86(8)**:1389-1394.

Guerrieri, M., Sanjayan, J. & Collins, F. (2010) Residual strength properties of sodium silicate alkali activated slag paste exposed to elevated temperatures. Materials and Structures **43(6)**:765-773.

Ismail, I., Bernal, S. A., Provis, J. L., Hamdan, S. & Van Deventer, J. S. J. (2013) Microstructural changes in alkali activated fly ash/slag geopolymers with sulfate exposure. Materials and Structures **46(3)**:361-373.

Juenger, M. C. G., Winnefeld, F., Provis, J. L. & Ideker, J. (2011) Advances in alternative cementitious binders. Cement and Concrete Research **41(12)**:1232-1243.

Kjellsen, K. O. (1996) Heat curing and post-heat curing regimes of high-performance concrete: Influence on microstructure and C-S-H composition. Cement and Concrete Research **26(2)**:295-307.

Krivenko, P. V. (1994) Alkaline cements. In Proceedings of the First International Conference on Alkaline Cements and Concretes. (Krivenko, P. V. (ed)) VIPOL Stock Company, Kiev, Ukraine, vol. 1, pp. 11-129.

Le Saoût, G., Ben Haha, M., Winnefeld, F. & Lothenbach, B. (2011) Hydration degree of alkali-activated slags: A ^{29}Si NMR study. Journal of the American Ceramic Society **94(12)**:4541-4547.

Lloyd, R. R., Provis, J. L. & Van Deventer, J. S. J. (2012) Acid resistance of inorganic polymer binders. 1. Corrosion rate. Materials and Structures **45**:1-14.

Loste, E., Wilson, R. M., Seshadri, R. & Meldrum, F. C. (2003) The role of magnesium in stabilising amorphous calcium carbonate and controlling calcite morphologies. Journal of Crystal Growth **254(1–2)**:206-218.

Myers, R. J., Bernal, S. A., Provis, J. L., Gehman, J. D. & Van Deventer, J. S. J. (2015) The role of Al in cross-linking of alkali-activated slag cements. Journal of the American Ceramic Society **98(3)**:996-1004.

Myers, R. J., Bernal, S. A., San Nicolas, R. & Provis, J. L. (2013) Generalized structural description of calcium-sodium aluminosilicate hydrate gels: the cross-linked substituted tobermorite model. Langmuir **29**(**17)**:5294-5306.

Palacios, M. & Puertas, F. (2011) Effectiveness of mixing time on hardened properties of waterglass-activated slag pastes and mortars. ACI Materials Journal **108(1)**:73-78.

Provis, J. L. & Bernal, S. A. (2014) Geopolymers and related alkali-activated materials. Annual Reviews of Materials Research **44**:299-327.

Provis, J. L., Brice, D. G., Buchwald, A., Duxson, P., Kavalerova, E., Krivenko, P. V., Shi, C., Van Deventer, J. S. J. & Wiercx, J. A. L. M. (2014a) Demonstration projects and applications in building and civil infrastructure. In Alkali-Activated Materials: State-of-the-Art Report, RILEM TC 224-AAM. (Provis, J. L., andVan Deventer, J. S. J. (eds)) Springer/RILEM, Dordrecht, pp. 309-338.

Provis, J. L., Duxson, P., Kavalerova, E., Krivenko, P. V., Pan, Z., Puertas, F. & Van Deventer, J. S. J. (2014b) Historical aspects and overview. In Alkali-Activated Materials: State-of-the-Art Report, RILEM TC 224-AAM. (Provis, J. L., andVan Deventer, J. S. J. (eds)) Springer/RILEM, Dordrecht, pp. 11-57.

Sakulich, A. R., Miller, S. & Barsoum, M. W. (2010) Chemical and microstructural characterization of 20-month-old alkali-activated slag cements. Journal of the American Ceramic Society **93(6)**:1741-1748.

Shi, C. (2003) On the state and role of alkalis during the activation of alkali-activated slag cement In: Grieve, G. & Owens, G. Proceedings of the 11th International Congress on the Chemistry of Cement. Durban, South Africa, Tech Books International, pp. 2097-2105.

Shi, C., Krivenko, P. V. & Roy, D. M. (2006) Alkali-Activated Cements and Concretes. Abingdon, UK, Taylor & Francis.

Snellings, R. (2015) Surface chemistry of calcium aluminosilicate glasses. Journal of the American Ceramic Society **8(1)**:303-314.

Snellings, R., Paulhiac, T. & Scrivener, K. (2014) The effect of Mg on slag reactivity in blended cements. Waste and Biomass Valorization **5(3)**:369-383.

Song, S., Sohn, D., Jennings, H. M. & Mason, T. O. (2000) Hydration of alkali-activated ground granulated blast furnace slag. Journal of Materials Science **35**:249-257.

Sun, G. K., Young, J. F. & Kirkpatrick, R. J. (2006) The role of Al in C-S-H: NMR, XRD, and compositional results for precipitated samples. Cement and Concrete Research **36(1)**:18-29.

Wang, S.-D., Pu, X.-C., Scrivener, K. L. & Pratt, P. L. (1995) Alkali-activated slag cement and concrete: a review of properties and problems. Advances in Cement Research **7(27)**:93-102.

Wang, S. D., Scrivener, K. L. & Pratt, P. L. (1994) Factors affecting the strength of alkali-activated slag. Cement and Concrete Research **24(6)**:1033-1043.

Xu, H., Provis, J. L., Van Deventer, J. S. J. & Krivenko, P. V. (2008) Characterization of aged slag concretes. ACI Materials Journal **105(2)**:131-139.

Zhang, Z., Olek, J. & Diamond, S. (2002) Studies on delayed ettringite formation in heat-cured mortars: II. Characteristics of cement that may be susceptible to DEF. Cement and Concrete Research **32(11)**:1737-1742.

Zhou, H., Wu, X., Xu, Z. & Tang, M. (1993) Kinetic study on hydration of alkali-activated slag. Cement and Concrete Research **23(6)**:1253-1258.