Cement & Concrete Composites 34 (2012) 131–139

Contents lists available at SciVerse ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Alkali activation of a slag at ambient and elevated temperatures

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ARTICLE INFO

Article history:
Received 24 August 2010
Received in revised form 26 May 2011
Accepted 17 August 2011
Available online 25 August 2011

Keywords:
Slag
Alkali activation
High temperature
Ambient
Caustic soda
Water glass

ABSTRACT

Strength development of alkali activated slag (AAS) mortars, activated using alkali hydroxide and sodium silicate, was investigated at room and elevated temperatures. Heat evolution at room temperature was measured using isothermal calorimetry. Important differences were observed between critical activation parameters. Heat cured specimens gain strength rapidly, humid oven conditions being favorable, but given sufficient time room temperature curing yields comparable strengths. Both activators are needed for high strength at room temperature, NaOH solution is more critical and its concentration greatly influences strength. At 80 °C however, sodium silicate is essential and even sufficient. KOH is more effective than NaOH at 80 °C, but not at room temperature. Lower water-to-slag ratios give higher strength at early ages. AAS hydration evolves less heat than Portland cement hydration. Time to significant strength gain of mixtures can be predicted using their time and heat evolution at setting. Twenty eight-day strength of AAS mortars is roughly related to total evolved heat and increases nearly linearly with the amount of NaOH activator for fixed water glass content.

1. Introduction

Attempts at activating ground granulated blast furnace slag using alkalis go back more than 70 years [1,2]. Recently, due to the potential environmental and energetic benefits of replacing Portland cement-based concrete (PCC) with concretes incorporating activated industrial wastes as the sole binder for some construction applications, there has been a renewed interest in alkali-activated slag (AAS) systems. The hydration, mechanical properties, and durability of AAS have been studied extensively [3–10]. Shi et al. [2] present a detailed summary of such work, based on which it becomes clear that with sufficient knowledge about the properties of the particular slag being used, and proper choice of activating chemical and curing conditions, AAS mortars and concretes with mechanical properties and durability comparable to or better than those of PCC can be made.

Slags, being by-products, can show great variation in their chemical and physical properties. Depending on how they are cooled, their glassy content in particular can significantly affect their potential for use in AAS systems. The dependence of mechanical property development on the physical and chemical properties of slag has also been demonstrated for blended cement pastes. Heat evolution during blended cement hydration was found to be correlated to strength and useful as an indicator of the reactivity of a slag [11]. In addition, alkaline activators demonstrate selectivity i.e. the effect that an activator has on strength development may be different for slags of different origins [12]. For this reason, the use of AAS mortars and concretes in any region is closely tied to the level of experience with local slags. Roy [13] concluded that greater confidence will be gained in the manufacture and use of alkali-activated cements as a more extensive database of research findings is available to enhance the predictability of performance. Many previous studies investigated the behavior of particular slags at either room temperature or at elevated temperatures. Relatively few studies compare in detail the activation of AAS systems at both.

In this study, the effectiveness of alkaline activation of a slag from Turkey was investigated at ambient and elevated temperatures, using mortar and paste mixtures. Each mixture paste contained only ground slag as the powder binder and various combinations of three activators: Sodium silicate, sodium hydroxide, and potassium hydroxide solutions. Through a comparison of mechanical properties and isothermal calorimetry, favorable activation parameters were found for each curing scenario and an explanation of the observed differences is provided. Results in agreement and in conflict with published studies in literature are presented indicating that activation conditions suggested in other studies are not all suitable for this slag. Most significantly, it is found that the addition of sodium silicate alone is essential and sufficient for adequate strength gain at elevated temperatures, whereas both activators are needed for mixtures cured at room temperature. Due to their low heats of reaction, AAS mixtures can be a good alternative to Portland cement mixtures, for mass concrete applications.

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doi:10.1016/j.cemconcomp.2011.08.003

Table 1
Oxide analysis of the slag used.

Oxide (%)	Slag
SiO_2	39.90
Al_2O_3	11.13
Fe_2O_3	0.26
CaO	34.56
MgO	9.37
SO_3	0.09
K_2O	1.18
Na_2O	0.35
Blaine fineness (cm^2/g)	4228
Specific gravity	3.06

2. Experimental

2.1. Materials

The slag used was received, from Kardemir Iron and Steel Plant, in Karabük, Turkey, in powder form. The as received oxide composition and physical properties of the slag are given in Table 1.

The alkaline activators used were laboratory-grade >97% pure NaOH pellets, >85% pure KOH pellets and liquid sodium silicate. The alkalihydroxide pellets were dissolved in water to obtain the various molarity mixtures used for the different activation attempts. The sodium silicate, $Na_2O\cdot xSiO_2\cdot nH_2O$, where x represents the degree of polymerization and n represents the moles of water, was a 40–42° Baume solution with a solids content of 37.5% (thus containing 62.5% water) and a SiO_2/Na_2O weight ratio of 3.2. From here on, water glass (WG) is used to refer to the sodium silicate solution. For two-activator mixtures, the activators were mixed together and allowed to cool to room temperature prior to mixing with the slag. After an initial mixing of the slag with the activator solution mixture, CEN standard sand was added, the mixture mixed again, diluted water added to adjust flowability, and the whole mixture mixed once again.

2.2. Methods

2.2.1. Measurement of strength

The mixing and preparation of the specimens used to investigate strength development was done according to EN 196-1 [14] with the exception that the water-to-binder ratio was not 0.50 but slightly lower. The total water content of the mixtures was selected to give AAS mortars with similar flow properties as a typical EN 196-1 Portland cement (PC) mortar. $4 \times 4 \times 16\ cm^3$ prism specimens were cast. The motivation for choosing this sample size is that it is the European standard for PC mortars and strength results obtained can be compared with results of PC mixtures with similar flowability. Some previous studies have used smaller or larger size specimens to measure strength. This can give misleading results, particularly when oven curing is applied, and requires precaution.

A control (base mixture) was selected based on recommendations in Rangan [15]. The proportions of this mixture are given in Table 2. The influence of varying proportioning and activation parameters were investigated by comparison to this base mixture. Among the parameters varied were the length of time the elevated temperature samples were kept at room temperature prior to the application of oven curing, curing temperature, oven humidity conditions, oven curing time, age of specimen, activator concentration, activator-to-binder ratio, and water-to-binder ratio. The later-age oven-cured test samples were kept at room temperature following the corresponding heat-application interval. The ambient temperature specimens were left at room temperature for the whole curing time, demolding taking place after 24 h. All samples were tested up to age ~10 weeks. Table 2 summarizes the different activation and curing scenarios studied for strength development.

2.2.2. Measurement of heat evolution

An eight channel isothermal microcalorimeter with precision of ±20 μW was used to monitor heats of hydration/reaction. A subset of the mixtures used for investigation of strength development (described in Table 2) was tested. A total of eight 5 g paste samples with slag-to-activator ratios identical to the paste phase of the chosen mortar samples were used. Table 3 lists these mixtures. A measured amount of dry, ground slag calculated to have a specific heat capacity approximately equal to that of the paste was used as the heat reference. The activator solutions were mixed by hand with the slag and the pastes were immediately placed in the calorimeter. The heat evolution of the pastes at 23 °C was tested until the heat signature appeared nearly stable for each mixture. Since the sample size was quite small, the measurements were done twice for each mixture to check that the pastes were adequately mixed. The two heat signatures were nearly identical for each paste.

3. Results and discussion

The influence of varying mixture proportions and activation parameters on mortar strength, microstructural development and heat evolution signature is presented in this section.

3.1. Influence of curing temperature

The effect that dry oven curing at three different temperatures above room temperature has on microstructural development and subsequent strength gain of the base mixture is shown in Fig. 1a. The three curves show different curing times. Fig. 1b shows

Table 2
Summary of mixture proportions and curing conditions of mortars used to evaluate rates and amounts of strength development.

	Elevated temperature cured samples	Ambient temperature cured samples	Base mixture
Slag content (kg/m^3)	~225	~225	~225
Concentration of NaOH or KOH solution (M)	0, 1–16	0, 1–16	8
MOH solution/Waterglass	2.5	2.5	2.5
Amount of MOH solids (wt.% of slag)	0, 0.5, 0.85, 1.16, 1.46, 1.75, 2.63, 3.63, 4.46	0, 0.5, 0.85, 1.16, 1.46, 1.75, 2.63, 3.63, 4.46	2.63
Waterglass/Slag	0, 0.063, 0.125, 0.25, 0.38	0, 0.063, 0.125, 0.25, 0.38	0.25
Total water/Slag	~0.38, 0.46, 0.53	~0.38, 0.46, 0.53	~0.46
Total water/Total solids	~0.34, 0.41, 0.47	~0.34, 0.41, 0.47	~0.41
Time at ambient prior to oven curing (h)	8–48	–	–
Oven curing time (d)	1, 2, 4	–	–
Oven curing temperature	60, 80, 95 °C	–	–
Oven curing condition	Dry, humid	–	–

Table 3
Pastes tested using isothermal calorimetry.

	1	2	3	4	5	6	7	8
Slag content (kg/m^3)	~225	~225	~225	~225	~225	~225	~225	~225
Molarity of NaOH solution	2	5	8	16	8	8	0	8
NaOH solution/Waterglass	2.5	2.5	2.5	2.5	2.5	2.5	0	–
Waterglass/Slag	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0
Total water/slag	~0.46	~0.46	~0.46	~0.46	~0.38	~0.53	~0.46	~0.46
Total water/total solids	~0.41	~0.41	~0.41	~0.41	~0.34	~0.47	~0.41	~0.41

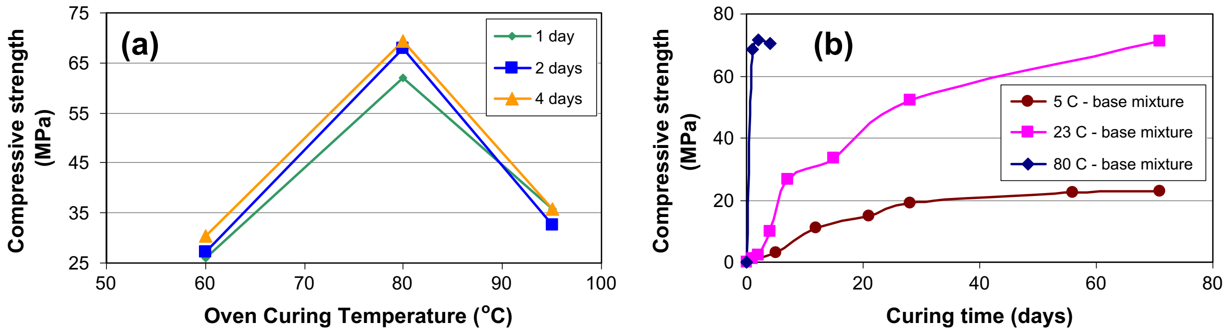

Fig. 1. The effect of: (a) three different elevated curing temperatures on compressive strength and (b) curing temperature on compressive strength.

the strength gain over time of the same mixture for three different, greatly contrasting temperatures.

For comparison with the results shown in Fig. 1a, the compressive strength of the base mixture cured at room temperature (23 °C ± 2 °C) is 1 MPa at age 1 day, and increases to ~10 MPa at 4 days. So, it is obvious that elevated temperature curing has a beneficial effect on strength. However, there is a threshold curing temperature at which strength peaks, about 80 °C for this slag and activator combination, above which strength gained is lower. Chindaprasirt et al. [16] observed similar behavior activating a fly ash with alkalis. Fig. 1b suggests that the same strength as that gained using elevated temperature curing can be attained at room temperature, given sufficient time. At the very low temperature of 5 °C however, the ultimate strength is limited to about a third of that reached at room temperature or above which is consistent with results of other studies [17].

3.2. Influence of pre-oven curing time and oven humidity condition

As seen in Fig. 2, the length of time the specimens are kept at ambient temperature prior to oven curing does not have a noticeable effect of the strength achieved after oven curing, up to 2 days, conflicting with the findings of Bakharev et al. [18], who observed a substantial increase in the strength of samples subjected to ambient pre-oven curing. The compressive strength of the base mixture after 2 days at room temperature is less than 2.5 MPa indicating that very little reaction has occurred. In fact, the accelerated hydration heat evolution rate peak for this mixture, corresponding to substantial strength gain, occurs after 48 h (shown later in Fig. 7). It is likely that longer pre-oven curing times, during which substantial hydration and other chemical reactions can taken place, would have an effect on the strength after oven curing.

The presence of humidity in the curing oven has a measurable effect on strength development. Specimens placed in a humid oven at 80 °C after 2 days of room temperature curing achieved ~15% greater strength than specimens in a dry oven at the same temperature. This is due to the quicker loss of water from within the samples in the dry oven. While the humid oven samples continue to gain a significant amount of strength from 2 to 4 days, the increase in strength of the dry oven samples is minor.

3.3. Influence of alkali hydroxide type and concentration

Fig. 3 compares the influence on compressive strength of using NaOH solution as the caustic activator with that of using KOH solution. The mixtures contain identical amounts of water glass (25% by mass of the ground slag).

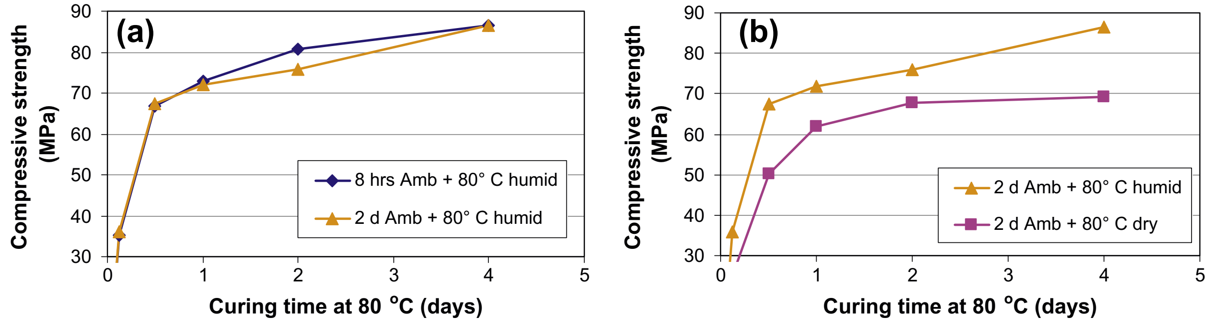

Fig. 2. The effect of pre-oven curing time and oven humidity conditions on strength.

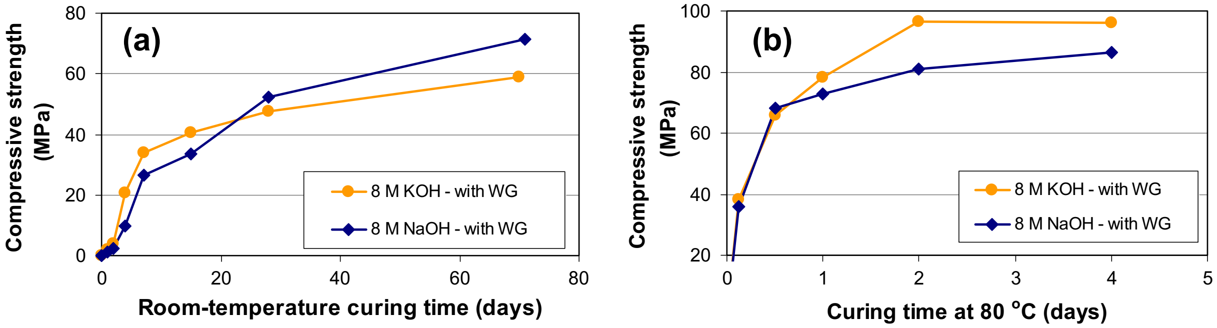

Fig. 3. The effect of alkali hydroxide type on strength: (a) at room and (b) elevated temperature.

At the chosen concentration of 8 M, KOH gives 10–15% higher strength than NaOH at elevated temperatures, as seen in Fig. 3b. One reason for this can be that at the same molarity, KOH solution contains a greater amount of solids than NaOH solution, therefore the mortars have higher activating solids-to-total slag ratio. However, the case at room temperature is different. In Fig. 3a, it is seen that the KOH-activated mortar has greater strength up to three weeks, after which the NaOH-activated solution surpasses it. NaOH is often preferred over KOH as an activator due in part to its lower cost.

Fig. 4 shows the influence of changing the sodium hydroxide solution concentration on compressive strength. The total NaOH solution (dry pellets and water) is identical for each mixture. The remainder of the proportions is like in the base mixture. The amount of water added to the mixture is adjusted for each mortar to keep the W/S constant.

Based on literature [5,19], it is generally expected that mortars activated using higher concentrations of NaOH solutions give higher compressive strengths. For the room temperature specimens in Fig. 4a, this is indeed the case. The rate of strength gain at early ages and the ultimate strength achieved are affected greatly by activator concentration, to the extent that the 16 M NaOH-activated mortar has nearly three times the strength of the 2 M NaOH-activated mortar, at 56 days. The mortar containing no NaOH (and only water glass) ultimately gains minimal strength, only ~3 MPa.

The situation is once again quite different for the elevated temperature cured samples shown in Fig. 4b. The mortar using 16 M NaOH solution gives the highest strength at all curing ages, however, many of the other concentrations yield similar strength results. In fact, the mortar made with only 1 M NaOH solution gives the second highest strength. The strength order of some of the mortars changes from 1 day of oven curing to 2 days and 4 days and there appears to be no specific relation between activator concentration and strength. This is probably due to the amount of water glass activator present in all mixtures in Fig. 4b being equal. Water glass content is more significant than the NaOH activator content for oven-cured mortars, as will be explained in the following section.

3.4. Influence of water glass content

Fig. 5 shows the influence of varying the total water glass content on compressive strength gained at room temperature and at 80 °C. The mortars labeled “only…WG” do not contain any NaOH solution. “No WG” contains only 8 M NaOH solution as activator.

In the case of room temperature curing (Fig. 5a), water glass does not seem to contribute to strength gain, and therefore its addition mainly works to dilute the NaOH solution. Since the concentrated NaOH solution attacks the ground slag particle surfaces and frees ions for reaction, the addition of no water glass gives the highest overall NaOH concentration and strength. When no NaOH is used but only water glass is added, the ultimate strength is only ~3 MPa. When oven curing is applied, the reverse trend is observed and water glass addition seems to be more beneficial to strength gain than NaOH addition. As seen in Fig. 5b, the addition of high amounts of water glass without the use of NaOH gives 90–100 MPa after 1 day of curing at 80 °C, while the use of only NaOH solution gives relatively much lower strength, 15–20 MPa. Increasing the added water glass amount initially does little to improve strength but beyond a certain threshold, increases strength dramatically, nearly proportionally with the content added. An explanation for this is that the solubility of essential ions present in the slag particles is sufficiently high at 80 °C, and therefore the essential ingredients for formation of C–S–H and potential geopolymerization. 170.4 g of water glass is about 38% by weight of the powder slag used. 113.6 g is about 25% and is used in the base mixture.

3.5. Influence of water-to-slag ratio

Fig. 6 shows the influence of changing W/S on strength of the mortars.

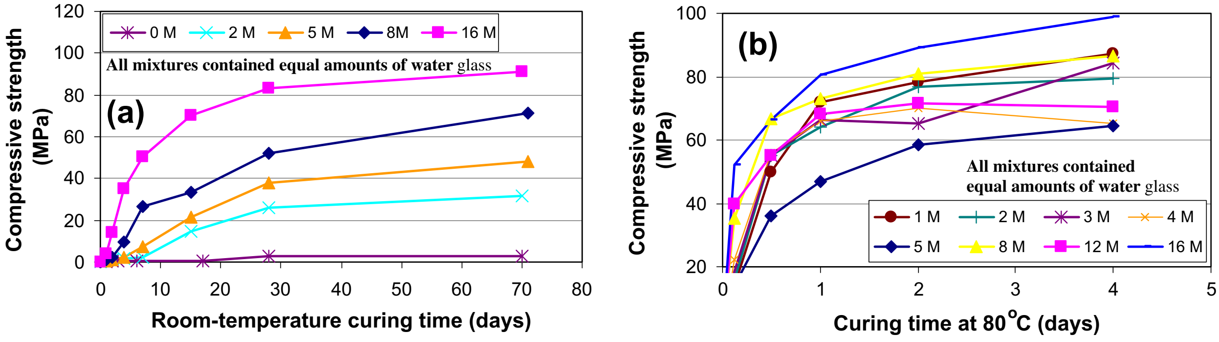

Fig. 4. The effect of NaOH concentration at: (a) room-temperature and (b) elevated temperature.

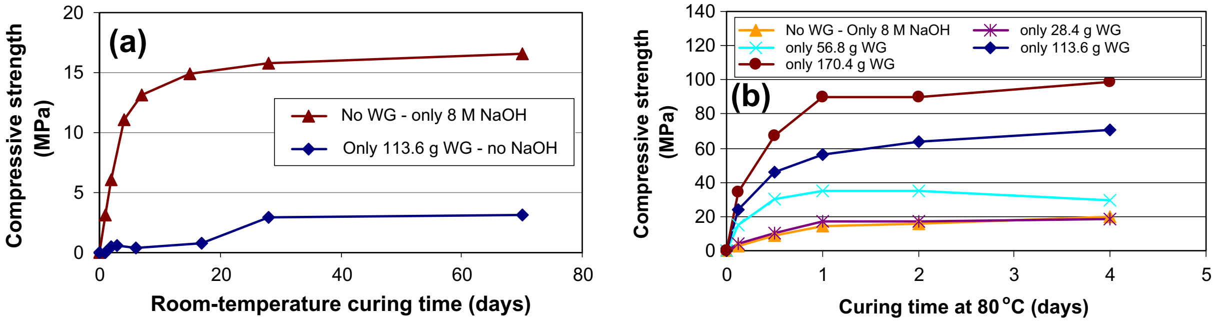

Fig. 5. The effect of water glass concentration on strength at: (a) ambient and (b) elevated temperature.

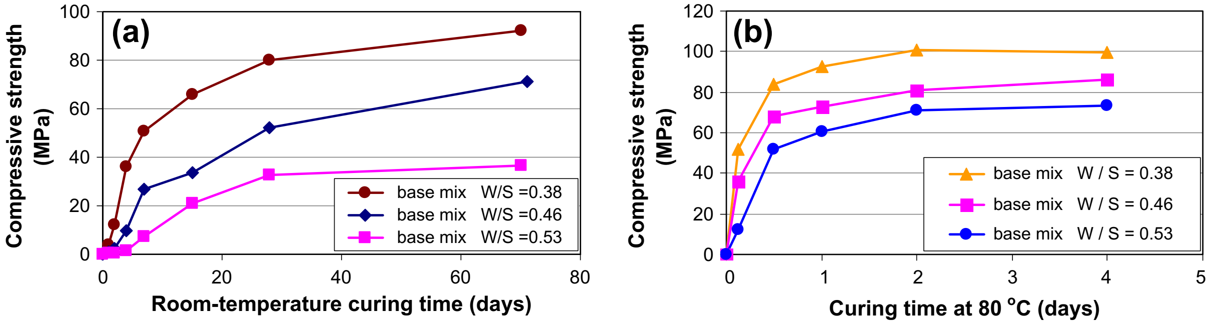

Fig. 6. The effect of W/S on compressive strength: (a) at room-temperature and (b) at elevated temperatures.

Similar to PC mortars, large changes in total water content with respect to total binder content cause measurable fluctuations in strength. At room-temperature, the ultimate strength of the mortar with a W/S of 0.38 is about 150% higher than that with a W/S of 0.53. In addition, the W/S ratio significantly affects the rate of strength gain. While the base mixture and the high W/S mortar have negligible strength in the first 5 or 6 days, the low W/S mortar achieves ~12 MPa after 1 day and surpasses 25 MPa at 3 days. The strength achieved by this mixture up to a certain age is closely related to W/S. In fact, a linear regression of either 7- or 28-day room-temperature strength on W/S of the mixtures yields $r^2 > 0.99$. The range of W/C is limited (and there are only three data pairs) and this is the case for this two-activator mixture but is expected to be similar for other cases as well. The relationship for earlier ages is weaker since water glass lengthens the induction period. The influence is less in the case of curing at 80 °C, but the strength of the mortar with a low W/S of 0.38 is still about 50% higher than the one with a W/S of 0.53. In PC mortars increasing water-to-cement ratio mainly increases the distance between cement particles and the amount of water-filled porosity. In AAS mortars, the extra water additionally dilutes the chemical activators. Wang et al. [20] found that for a given activator type and concentration, there exists a range for activator solution-to-slag ratio below which strength increases with increasing solution-to-slag ratio, since this also increases total alkaline activator solids content, above which strength decreases with increasing solution-to-slag ratio due to an increase in pore volume, and in which strength is little affected because these two effects are more or less balanced. However, changes in W/S can also alter the nature (by different amounts at different temperatures) of the water glass activator by altering the composition of silicate anions. This is discussed further in the interpretation of heat evolution of pastes with the same activators but different W/S.

3.6. Influence of activator composition and water-to-slag ratio on heat evolution

Fig. 7a shows the influence of increasing concentrations of NaOH solution on the heat evolution of pastes containing identical amounts of water glass (mixtures 1–4 in Table 3). Two peaks are

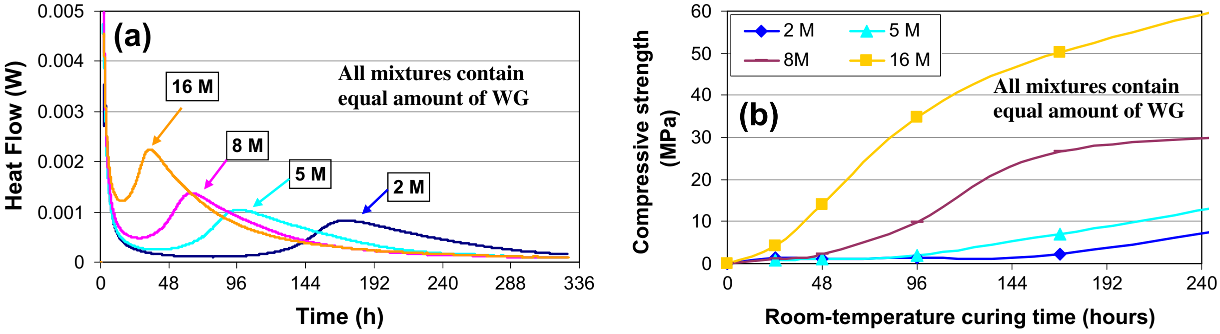

Fig. 7. The effect of NaOH solution concentration on: (a) heat evolution and (b) early-age strength development.

observed for each paste, a narrow one within a few hours after the start of mixing and the other at 40–170 h. Shi and Day [21] refer to these as initial and accelerated hydration peaks, respectively.

Since these pastes contain two activators, their heat signatures are a combination of those reported in [21] for slags activated with NaOH alone (Type II), and water glass alone (Type III). The two initial pre-induction peaks for only-water glass activation are combined into a single peak. The initial peak is attributed to wetting and dissolution of the slag, so increases in height for mixtures with greater concentration. The total percentage of Na_2O (mass% of total slag) in the 2 M, 5 M, 8 M, 16 M mixtures is 3.0%, 3.7%, 4.4%, and 5.8%, respectively. The 2 M mixture, with the lowest concentration and pH, gives the lowest initial peak. For all eight pastes tested in this work, the height of the second peak is lower than that of the initial peak.

In agreement with the behavior shown in Fig. 4a, NaOH solution concentration directly influences the rate of reaction. As the concentration of NaOH increases, the increasing concentration of OH^- leads to the breaking of a greater amount of Ca–O, and Mg–O bonds, faster. This is seen in Fig. 7a as the second heat evolution peak appearing at earlier ages for the higher concentration pastes. In addition, the second peak is higher for higher-activator concentration samples, indicating more reaction taking place. In fact, the relationship between NaOH concentration and height of the second peak is almost perfectly linear ($r^2 \sim 0.99$). As NaOH concentration decreases, the heat behavior resembles that of a mixture activated with water glass only.

Fig. 7b is a close-up of the first 10 days in Fig. 4a, that shows the influence of NaOH activator concentration on early-age strength gain. Analyzing Fig. 7a and b together, it can be seen that the time of the second heat evolution peak corresponds to the onset of significant strength development i.e. when the slope of the strength-time curve of the mortars increases noticeably. These times are roughly 30 h, 65 h, 100 h, and 170 h, for the 16 M, 8 M, 5 M, and 2 M NaOH solution mixtures, respectively. The first peak corresponds to the setting time of the pastes [17]. Unlike with PC hydration, in AAS systems activated with both NaOH and water glass there exists a double curvature strength-time curve at room temperature. The rate of strength gain is initially slow as the dissolution of the phases to react is awaited, followed by an increase in rate. For higher-concentration activators, the dissolution is more rapid and more effective, since the dissolution of anhydrous slag is dependent on solution pH [21]. A greater amount of dissolved slag also results an earlier and steeper strength-time slope change. It should be noted however, that a recent study determined that the rate of reaction of slag activated with only water glass is limited by nucleation and growth, rather than the rate of dissolution of the slag [22].

Fig. 8a compares pastes that contain only the NaOH solution activator or only the water glass activator with the base mixture which contains both activators. Again, the start of the rapid increase in strength seen in Fig. 5a corresponds roughly to the time of the second heat flow peak, for all three mixtures.

It was seen in Fig. 5a that at room temperature NaOH contributes more to strength than water glass. Fig. 8a confirms this finding with the paste containing only NaOH having an earlier and more pronounced peak than the base mixture and particularly the mixture containing only water glass. In fact, the 8 M NaOH only mixture (∼2% Na_2O) gave the earliest and highest heat peak for both the first and second peaks. This is in accordance with the observations of Fernandez-Jimenez and Puertas [23]. The 8 M NaOH only mixture has a Na_2O concentration of ∼2%. Shi and Day [24] report a second peak at ∼3 h with a height equivalent to ∼3.3 mW/g for a slag activated with NaOH (2% Na_2O) at 25 °C. The accelerated hydration peak observed in this study is lower (∼0.6 mW/g), and occurs at a significantly later time (∼15 h). The peak is also more diffuse. This could be due to differences between the two slags. For example, CaO content of that slag was similar but its MgO content was higher (∼15%), which would increase the amount of dissolved cations available for reaction at any given early age. The nature of the hydration products could change as well, such as magnesium aluminate hydrates or hydrotalcite forming instead of part of the calcium aluminate hydrates [21]. The induction period (time between the two peaks) appears to be very short (only a few hours similar to those of PC systems) for the mixture containing only 8 M NaOH as activator. Fernandez-Jimenez et al. [25] reported that slag activated with only NaOH had the highest degree of hydration at short time, higher than those of mixtures containing both NaOH and water glass. They added that in AAS systems using only NaOH solution as activator, the reaction was controlled by reactions happening on the surface of the particles or by dissolution of the reactants whereas in systems using both NaOH solution and water glass, the reaction is controlled by the diffusion of the reactants through a layer of reaction products, hence the accelerated hydration peak is delayed. The paste activated with only water glass shows the longest induction period, 8–9 days. The high silica modulus (∼3.2) of the water glass used in this study could be linked to this long induction period with polymerization of some $[SiO4]^{4-}$ from the water glass limiting the amount of Ca^{2+} which can react. The $[SiO4]^{4-}$ which reacts with dissolved Ca^{2+} results a form of C–S–H, contributing to the initial peak. The Na_2O dosage of the water glass only paste was ∼2.4%. Shi and Day [24] observed an accelerated hydration peak with a height of ∼2.2 mW/g, at ∼36 h for their slag activated with water glass (2% Na_2O). The second peak height and time observed in this study are ∼0.2 mW/g and ∼260 h, respectively. Again, the reaction observed here occurs much later and evolves less heat. Reasons for this difference could be compositional differences between the slags and also, the concentration of the water glass used. Krizan and Zivanovic [26] found that the induction period became longer as the modulus of the activator used increased.

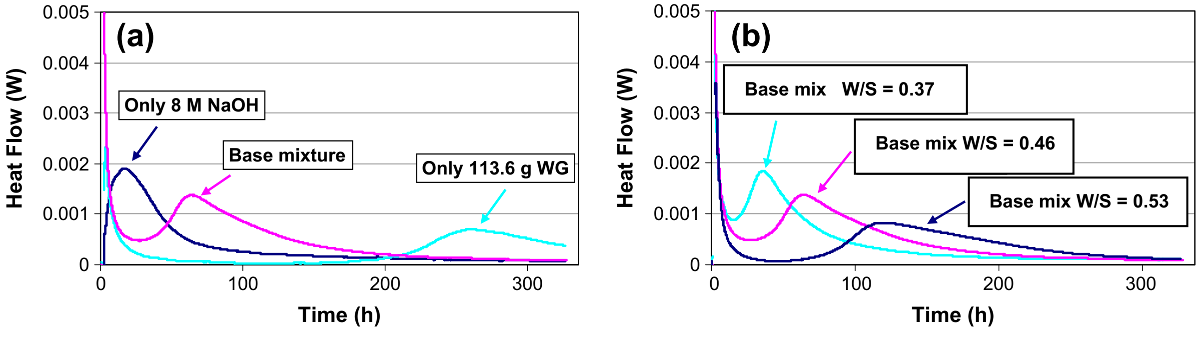

Fig. 8. The effect on heat evolution of: (a) different alkaline activators and (b) varying W/S.

Fig. 8b shows that the effect of increasing W/S on heat evolution of the two-activator base mixture is more similar to that of Type III mixtures [24] than to that of Type II mixtures i.e. a later and less pronounced accelerated hydration peak is observed. Also, the high-W/S peak is more diffuse than the sharp low-W/S peak. The height of the secondary peak is lowered by ~31% in increasing W/S from 0.37 to 0.46 and from 0.46 to 0.53. The W/S = 0.53 base mixture starts showing a clear induction period. This increase in water content does not change the total% Na_2O in the combination of activators but reduces the concentration of the 8 M NaOH solution, thus reducing its ability to break off Ca^{2+} from the slag particles. The silicate anion distribution in the water glass is also dependent, among other things, on concentration. The decrease in concentration of the water glass due to increased water content results in a delayed secondary peak.

The eight paste mixtures given in Table 3 evolved 50–70 calories per gram of anhydrous slag. The paste containing only NaOH as activator (mixture 8 in Table 3) gave off the least heat and the paste containing only water glass (mixture 7) gave off the second lowest amount of heat. This is probably because these two activators contained the lowest amounts (~2 and ~2.4%, respectively) of Na_2O. Shi and Day [24] report a large increase in the cumulative heat evolved for a slag activated with water glass only, as Na_2O content changes from 4% to 6%. For the pastes containing identical amounts of water glass (mixtures 1–4 in Table 3), the ones with more concentrated NaOH solutions gave off greater amounts of heat. For the base mixture, containing both activators (mixture 3), the cumulative heat evolved is less than the summation of the heats evolved by the separate activation of the slag with each of the activators. This is noteworthy because it occurs despite a large increase in the total Na_2O content. For example, based on the differences in the cumulative heat of hydration Shi and Day [24] observed for activation with 4% Na_2O- and 6% Na_2O-containing water glass only, a larger difference could be expected between the total heat of the water glass-only mixture and the base mixture.

These amounts of heat are all lower than the amount given off by typical PC mixtures. A more important point to compare is the rate of heat evolution. While nearly half of the total heat evolution (25–50 cal/g) takes place in the first 3 days for PC systems, the maximum heat evolved in any 3-day period for these AAS systems is less than 15 calories per gram of slag. AAS mortars and concretes appear quite attractive, in terms of heat behavior, for use in mass concrete applications. The slow strength gain at early ages relative to PC systems could also be acceptable, perhaps even an advantage, for such applications.

Certain other less evident observations can be made about the room temperature heat evolution signatures of the eight pastes. Fig. 9a shows that a linear relationship exists between the times of occurrence of the first peak and the second peak of each mixture. Sooner setting/dissolution signals earlier strength gain for a mixture. There also exists an inverse relationship, as shown in Fig. 9b, between the time of the first peak and its magnitude i.e. the heat flow rate at that time. More interestingly, the magnitude of the first peak is also inversely related to the time of occurrence of the second peak, as seen in Fig. 9c. Therefore, the less pronounced the first heat evolution peak of the AAS system is, the later will its substantial strength gain begin. This inverse relation is even stronger ($r^2 \sim 0.95$) if only pastes that contain identical amounts of water glass and have the same W/S (mixtures 1–4 and 8 in Table 3), are considered.

Using the relations in Fig. 9, it may be possible to predict some strength gain properties for mixtures with different proportions made using this slag (and perhaps those chemically and physically similar). There exists also a moderate linear relationship between the total specific heat evolved up to 28 days and the compressive strength at that age, as shown in Fig. 9d. As expected, pastes giving off more heat achieve greater strengths. The relationship between heat evolved and strength achieved weakens for shorter hydration time spans like 7 days and 24 h. This is partly due to the large difference in the times of the secondary peaks in NaOH-only and waterglass-only systems. However, if only pastes that contain identical amounts of water glass and that have the same W/S (mixtures 1–4 and 8 in Table 3) are considered, a linear regression of the 28-day compressive strength on the 28-day cumulative heat of the remaining pastes gives $r^2 \sim 0.92$. The activators in these

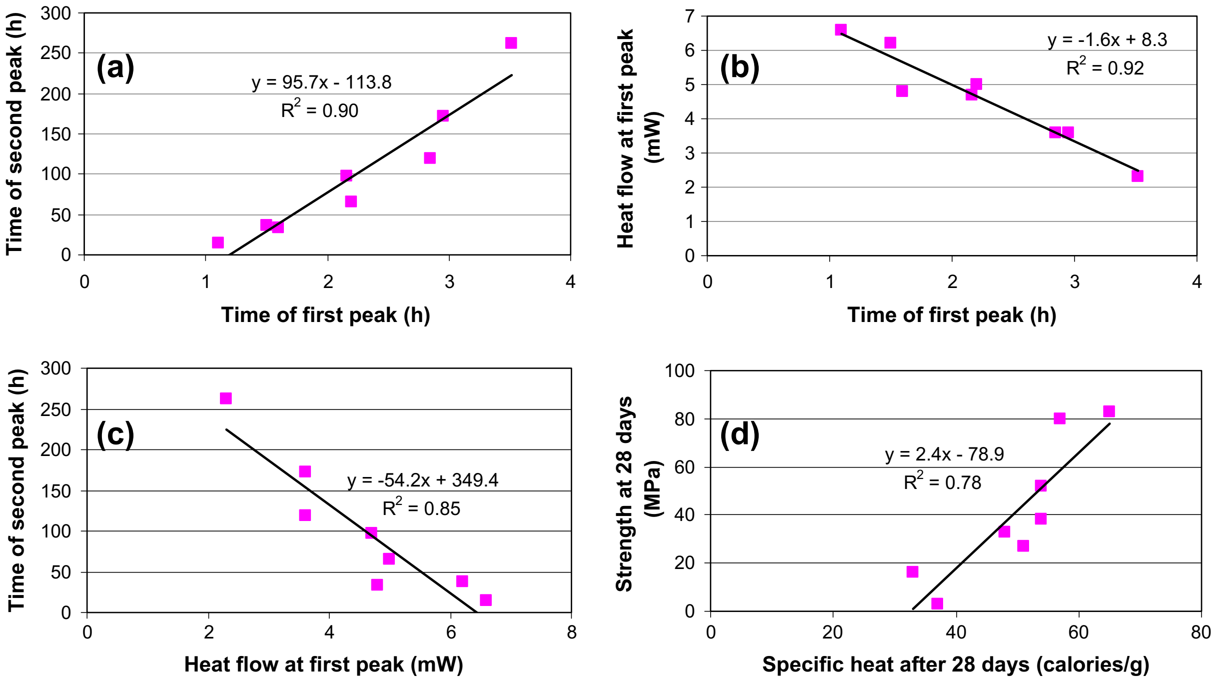

Fig. 9. Relations between: (a) time of the setting and beginning of significant strength gain, (b) the time of setting and rate of heat flow at setting, (c) the rate of heat flow at setting and the beginning of significant strength gain and (d) the heat evolved up to 28 days and the strength gain in that period; of the AAS pastes.

pastes contain identical amounts of water glass and since the contribution of water glass to heat evolved happens mostly at later times, NaOH concentration is what largely influences this heat-strength relationship. Changing W/S ratio has a similar affect to dilution or further concentration of the NaOH activator which changes the time of the heat peaks but does not upset this relationship for a time span of 28 days. One could also expect a relation between the total % Na_2O content (by mass of total slag) of the activator and strength gain up to 28 days. This linear relation has $r^2 \sim 0.77$ for all eight pastes in Table 3. If only pastes that contain identical amounts of water glass and have the same W/S are considered, then $r^2 \sim 0.99$. So, the 28-day compressive strength of a mixture with a fixed W/S increases nearly linearly with increasing NaOH content. The usefulness of the relations in Fig. 9 and the other observations for combined NaOH solution and water glass activation of slags needs to be checked using slags with different properties.

4. Conclusions

This study investigated the effect of various alkali activation parameters on the strength gain and heat evolution of mortar and paste mixtures containing ground granulated blast furnace slag as the sole powder binder. The following conclusions were drawn:

(a) AAS mortars cured at elevated temperatures can achieve admirable compressive strengths, significantly higher than PC mortars, very rapidly. There appears to be a critical curing temperature at which strength gain is maximized. AAS mortars cured at room temperature for a sufficiently long time can attain equal or greater strengths than mortars cured at 80 °C, however their early-age strengths are much lower. Even AAS mortars cured at 5 °C for several weeks can gain strengths comparable to those of Portland cement mortars.

(b) Pre-curing of mortars at room temperature up to 2 days prior to elevated temperature curing does not affect the strength gained since little hydration occurs during this time.

(c) The humidity condition in the curing oven noticeably affects mechanical property development. Humid conditions are more beneficial than dry conditions since moisture retention is required for hydration.

(d) For AAS mortars containing water glass and cured at 80 °C, KOH is a more effective activator than NaOH. At room temperature however, the use of KOH gave higher strengths than using an equal molarity NaOH only in the first few weeks, after which the trend was reversed.

(e) NaOH solution is more beneficial to strength gain than water glass solution for mortars cured at room temperature. Concentration of NaOH solution directly influences rate of strength gain and ultimate strength for room temperature-cured mixtures since it affects slag dissolution amount and rate. However, for mortars cured at 80 °C, water glass activator is essential, in fact NaOH solution is not needed for strength gain, since slag dissolution is sufficiently high at this temperature.

(f) Water-to-slag ratio has a large influence on strength gain at both elevated temperatures and at room temperature. Added water not only dilutes the activating alkali hydroxide but can also change the nature of the water glass used. For room temperature-cured AAS, rate of strength gain at early ages and ultimate strength are significantly greater for lower W/S.

(g) At room temperature, mixtures containing only NaOH solution as the alkaline activator give earlier rate of heat evolution vs. time peaks. Mixtures with only water glass activator give much later peaks. Mixtures using both activators show intermediate heat evolution rate peaks but achieve much greater compressive strength than either single-activator mixture.

(h) For the different mixtures made using this slag, the time of setting (first peak) can be related to the time at which substantial strength gain begins (second peak). The beginning of substantial strength gain for each mixture can also be roughly predicted based on the rate of heat evolution for that mixture at the time of setting.

(i) The total heat evolved by AAS pastes is lower than that evolved by hydration of PC pastes. The heat per any 3-day period is also much lower making AAS preferable for use in mass concrete applications. The strength gained up to 28 days is roughly related to the total amount of heat evolved until that age. Mixtures evolving greater amounts of heat achieve greater strengths. 28-day strength of mixtures with identical amounts of water glass and W/S increases linearly with increasing NaOH content.

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