ROLE OF ACTIVATOR TYPE AND DOSAGE ON THE REACTION KINETICS OF ALKALI-ACTIVATED SLAG PASTES

Berhan S. Gebregziabiher[1] and Sulapha Peethamparan[*2]

[1]Graduate Student, Department of Civil and Environmental Engineering, Clarkson University, Potsdam, NY 13699, USA, Email: gebregbs@clarkson.edu

[2*]Corresponding Author, Assistant Professor, Department of Civil and Environmental Engineering, Clarkson University, Potsdam, NY 13699, USA. Email: speetham@clarkson.edu; Phone: 001-315-268-4435; Fax: 001-315-268-7985

ABSTRACT

The early age reaction kinetics of alkali-activated slag binder systems at ambient and elevated temperatures is discussed. The influence of the dosage of sodium hydroxide and sodium silicate hydrate activators on the reaction kinetics was evaluated using isothermal calorimetry. The sodium hydroxide activated slag pastes exhibited a relatively faster reaction rate during the early hours of reaction under the ambient condition, which increased with increase in NaOH concentration. The duration of the induction period was only a few minutes in 5 and 8M NaOH-activated paste, and completely disappeared when the concentration increased to 12M. The NSH-activated systems, in general, displayed longer induction periods followed by acceleration and deceleration periods. Increasing the silica modulus from 1.5 to 2.5 caused significant reduction in the duration of the induction period. Elevated temperature curing, as expected, increased the heat evolution and changed the reaction kinetics of each alkali-activated slag paste.

Key words: alkali activated slag, sodium hydroxide, sodium silicate hydrate, Isothermal conduction calorimetry, reaction kinetics

INTRODUCTION

Alkali-activated binders formulated using industrial by-products such as ground granulated blast furnace slag (GGBFS) and fly ash are emerging as promising green binders for concrete (Wang, 1995; Lothenbach, 2011). Many studies have detailed the advantages of using alkali-activated slag binders in concrete and have discussed the early age and hardened properties of such concrete (Wang, 1995; Fernandez-Jimenez, 1999; Bernal, 2010).

GGBFS is a cementitious material that exhibits latent hydraulic properties. The hydration of slag in water is impeded mainly due to the formation of an impermeable coating of alumino-silicate on the surface of slag grains within the first few minutes of exposure to water. Due to the impermeability of this coating, further hydration of slag in water is prevented until the impermeable coating is removed from the surface. A highly alkaline environment (pH>13) is found to dissolve this coating, thereby enhancing the dissolution and subsequent hydration of slag. Therefore, raising the PH of the system by introducing external chemicals is an important step for activating the slag grains. In alkali-activated systems, the activating solution can easily dissolve the coating on the surface of the slag to initiate further reaction. The extent of reaction of GGBFS in the activated system mainly depends on the type and dosage of activator and the environmental conditions during curing (i.e., temperature) (Shi, 1995; Krizan, 2002; Altan, 2012; Bakharev, 1999; Aydın, 2012).

Many studies have reported the properties of activated slag systems formulated using different types of chemical activators (Krizan, 2002; Sajedi, 2010; Brough, 2002). In these studies, the type and concentration of the alkali activators was found to affect the systems' hydration kinetics, in terms of degree of reaction and various hydration processes. The hydration kinetics governs microstructural development, formation of products, pore size distribution and strength development. Alkali activators commonly used to make these cement free binders are sodium hydroxide solution and sodium silicate hydrate (waterglass) solution. The main reaction products found in activated systems are reported to be C-S-H and hydrotalcite-like ($Mg_6Al_2(CO_3)(OH)_{16}.4(H_2O)$) chemical products (Wang, 1995; Ben Haha, 2011). Heat treatment of alkali-activated slag specimens is believed to provide improved early strength, better pore size distribution, reduced shrinkage at later age and appreciable volumetric stability (Altan, 2012; Bakharev, 1999; Aydın, 2012).

The purpose of this research is to evaluate the influence of the type and dosage of two commonly used activators and the curing temperature on the early age reaction kinetics of alkali-activated slag binder systems. The hydration kinetics was studied by measuring the exothermic heat evolved during the activation process using a TAM Air isothermal conduction calorimeter.

MATERIALS AND EXPERIMENTAL METHODS

Materials

A grade 100, ASTM C 989 compliant, ground granulated blast furnace slag was used as the starting material in this study. The oxide chemical composition of the slag used for the experiments was 36% SiO_2, 10.5% Al_2O_3, 39.8% CaO, 7.93% MgO, 0.27% Na_2O, 2.11% SO_3, 0.16% K_2O and 0.67% Fe_2O_3. The Si/Al, the Blaine surface area and loss on ignition was 3.428, 340 m^2/kg and 3% respectively. The particle size distribution determined using a laser particle size analyzer showed that 80% of the particles had a size lower than 10 µm with an average particle size of 7.5 µm. The X-ray diffraction pattern obtained (not presented in this paper) for the slag powder shows a diffused XRD pattern (a hump) in between 25° and 35° (2θ), which is a typical characteristic of amorphous material.

The alkali activators used for the experiments were commercially available sodium hydroxide (NaOH) in pellet form and sodium silicate hydrate (NSH) in solution form, commonly known as *waterglass*. Required quantities of NaOH were dissolved in deionized water to make 5, 8 and 12M solutions. NSH activator was used for formulating solutions with two different silica moduli (Na_2O/SiO_2, SM), 1.5 and 2.5. The Na_2O percentage was kept constant at 2.5% by mass of slag.

Experimental Methods

The exothermal heat of reaction from the activated slag paste was measured using a TAM Air isothermal conduction calorimeter under 25 ^{0}C and 50 ^{0}C isothermal conditions. All the activated paste samples investigated in this study were prepared at a solution-to-slag ratio of 0.5. The heat evolved during the activation process was collected from the moment the activating solution was added to the slag up to a period of four days. The activating solution and the solid (slag, or the starting material) were stored separately and equilibrated at the required isothermal conditions (25^0C or 50^0C). The solution was then injected and mixed with the slag. TAM Air in-situ ampules were used for all of the calorimetric experiments. The heat of reaction and cumulative heat evolved were obtained and used for the analysis.

RESULTS AND DISCUSSION

Heat of Reaction (Reaction Kinetics)

The hydration curves of ordinary Portland cement (OPC) are known to have five distinctive regions; namely, a rapid initial process (dissolution of ions and initial hydration), a dormant period (induction-low heat evolution and slow dissolution of silicates), acceleration period (silicate hydration), retardation period (sulfate depletion and slowing down of the silicate hydration process) and steady state (slow process of hydration-ongoing and continuous) stage. Compared to OPC, GGBFS hydrates very slowly, as can be seen in the hydration curves obtained for a cement paste with 50% and 100% slag replacement shown in Fig.1. The CaO content of slag is much lower than that of OPC, and the hydration process does not produce calcium hydroxide as a byproduct. Instead, C-S-H with lower calcium to silica ratio along with hydrotalcite –like ($Mg_6Al_2 (CO_3)(OH)_{16}.4(H_2O)$) products, traces of ettringite $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$ or monosulfate ($Ca_4Al_2O_6(SO_4).14H_2O$) are formed. However, the reactions are slow enough that no measureable heat is evolved over a period of 48 hours, indicating the absence of formation of products as seen in Fig. 1.

When slag is used as an SCM, the OPC functions as an activator by raising the pH of the pore solution sufficiently for the dissolution of the impermeable coating formed on the surface of the slag particles to take place. A significant amount of heat is released in the system containing 50 % GGBFS as shown in Fig. 1(b), indicating the hydration of the slag in the system. If slag is used as the sole source of binding material, then a strong alkali activator is required for the formation of the binding gel.
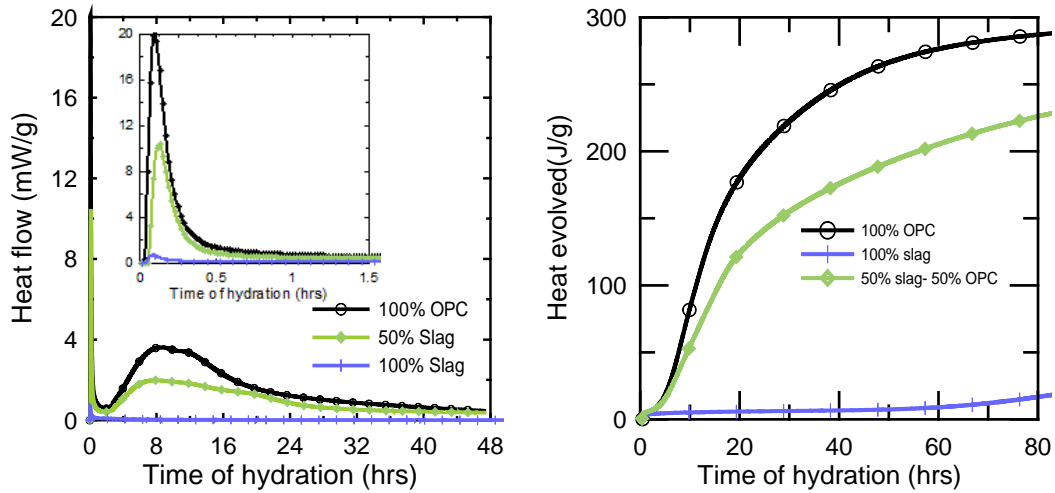
Figure 1. Hydration curves (heat flow and cumulative heat evolved) for 100% OPC, 50-50 % slag-OPC and 100% slag pastes at 25°C with w/b =0.5

Fig. 2 shows the influence of NaOH dosage on the reaction kinetics, i.e., the heat flow curve, for a period of 24 hours at 25 and 50 °C isothermal conditions. Fig. 2(b) shows the very early age reaction kinetics within the first 2 hours. The distinctive processes identified in a normal cement hydration curve such as dissolution/wetting, induction, acceleration and deceleration stages existed in the 5M and 8M NaOH-activated systems but the duration of each of the stages was very short compared to a typical OPC paste with the same water-to-solid ratio (Fig. 1). The acceleration stage peak occurred at about 30 and 45 minutes after adding the activating solution to the slag for 8M and 5M NaOH-activated pastes, respectively. The deceleration period for both pastes ended at about six hours, at which time the reactions entered the steady state stage for both the 5M and the 8M sodium hydroxide-activated systems. For the 12M NaOH-activated system, only one major peak occurred immediately after adding the activating solution to the slag. No distinct dissolution, induction, or acceleration stages were noted and the deceleration stage was relatively long, approximately 18 hours. The reaction reached a steady state, or diffusion controlled state, at the end of 18 hours. No other peaks were registered after 18 hours. Even though the included data is only for 24 hours the experiments were continued for four days to check for the occurrence of other peaks in the course of the reaction.

The elevated temperature curing, as expected, resulted in acceleration of the reaction kinetics. The calorimetric heat curves for 5, 8 and 12 M NaOH-activated pastes did not exhibit dissolution and induction periods. The acceleration stage peak occurred at about 30 minutes of reaction. The complete reaction was stabilized, or became diffusion controlled, after 2 hours. The peak heat released was three to four times greater than that which resulted from samples cured in 25°C isothermal conditions
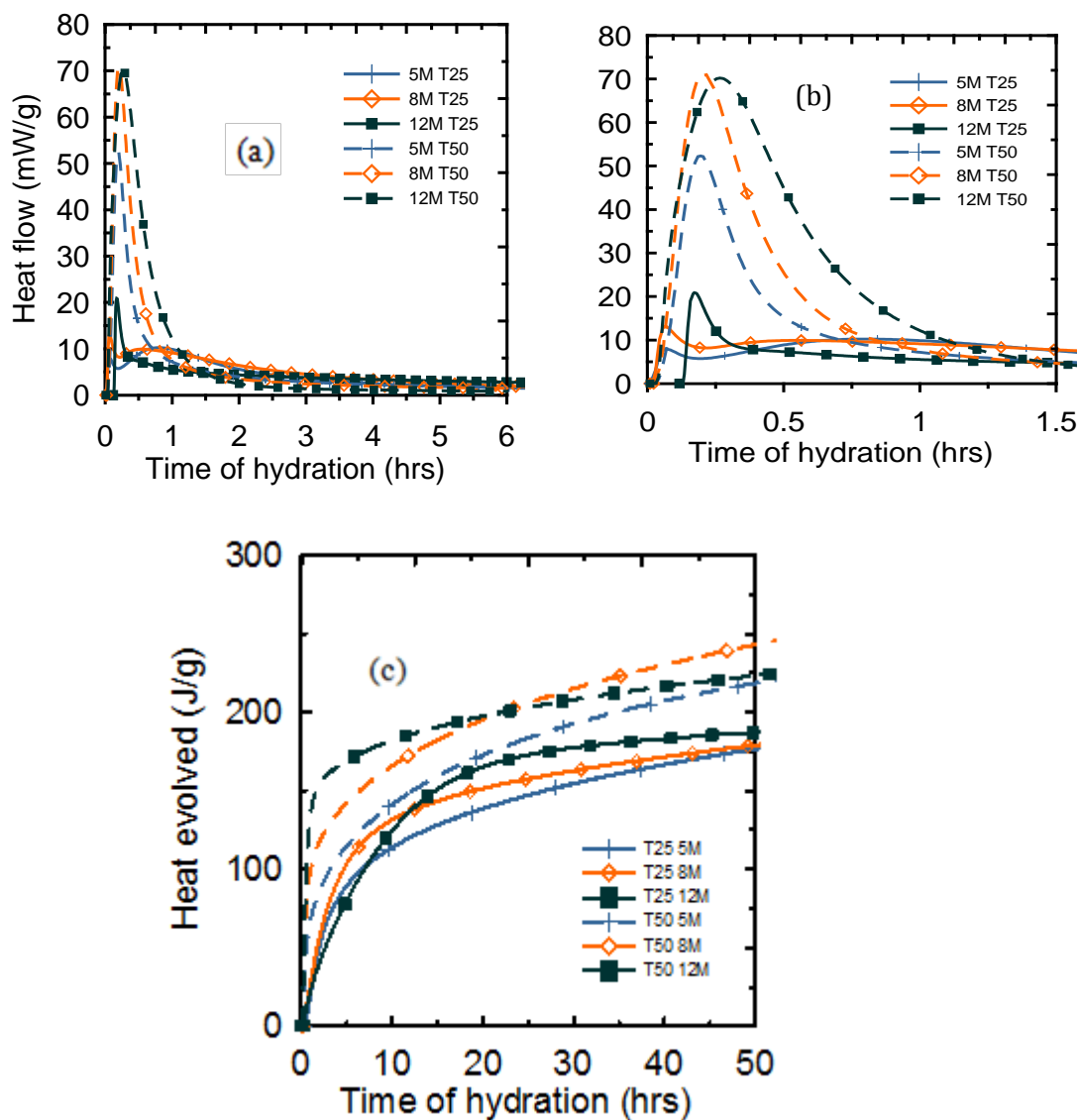
Figure 2. Hydration kinetics of activated slag with 5, 8, and 12 M sodium hydroxide solution (a) isothermal hydration curves at 25°C and 50°C (b) magnified view of the very early hours reaction kinetics and (c) total heat evolved at 25ºC and 50ºC

Figure 2 (c) shows the cumulative heat evolution at 25 and 50 ºC isothermal conditions. The elevated temperature curing (50 ºC), as expected, resulted in higher cumulative heat evolution for 5, 8 and 12 M NaOH-activated slag pastes compared to that of those cured in the 25 ºC isothermal condition. For 12 M solution-activated pastes, the total heat evolved during the initial hours was the highest when the reaction took place at 50 ºC. However, the rate then slowed down after 20 hours, whereas for 5 and 8 M sodium hydroxide-activated systems, the rate

(slope) remained fairly constant even after 50 hours. This trend was also seen in the case of ambient (25 $^{\circ}$C) cured samples. A complimentary result was observed in the compressive strength developed in these mixtures. These results agree with the observation made from the compressive strength test results (not reported here), that a longer curing period did not have a significant effect on the compressive strength development in 12 M NaOH activated system at ambient curing condition, while the strength increased progressively for 5 and 8 M-activated slag.

Hydration Kinetics of NSH-activated Slag systems

Hydration curves of NSH-activated slag systems are presented in Fig. 3. The heat flow curve for both the 1.5 SM and 2.5 SM NSH activated slag exhibited an exothermic heat peak immediately after mixing the activator and slag, followed by a very long induction period at 25 $^{\circ}$C isothermal condition (Figure 3(a) and (b)). As can be seen in the heat flow curves, the induction period for the slag activated with 1.5 SM NSH ended only at the end of ~35 hours and was followed by 8-10 hour-long acceleration and deceleration periods. The system reached a steady state diffusion controlled stage only after ~70 hours. In contrast, slag pastes activated with 2.5 SM NSH exhibited two induction periods and three exothermic peaks in the calorimetric heat curve. The first exothermic peak occurred immediately after mixing followed by a 15-hour-long induction period. This 15-hour induction period was followed by a small exothermic reaction, a second dormant period of ~10 hours and a broader major exothermic peak, in that order. The NSH activators were formulated by keeping the amount of Na_2O = 2.5% by mass of the slag and changing the amount of SiO_2 in the solution as needed. This difference in SiO_2 content had a dominating effect on the reaction kinetics and the degree of reaction. At elevated temperature, the peaks occur at an earlier period of time, as shown in Fig. 3(c). The occurrence of the peaks are shifted to about 24 hours earlier in slag activated with both 1.5 and 2.5 silica moduli NSH. Both systems exhibited large heat release compared to ambient cured samples. As a result, the total heat evolved is also increased significantly due to the elevated temperature curing.
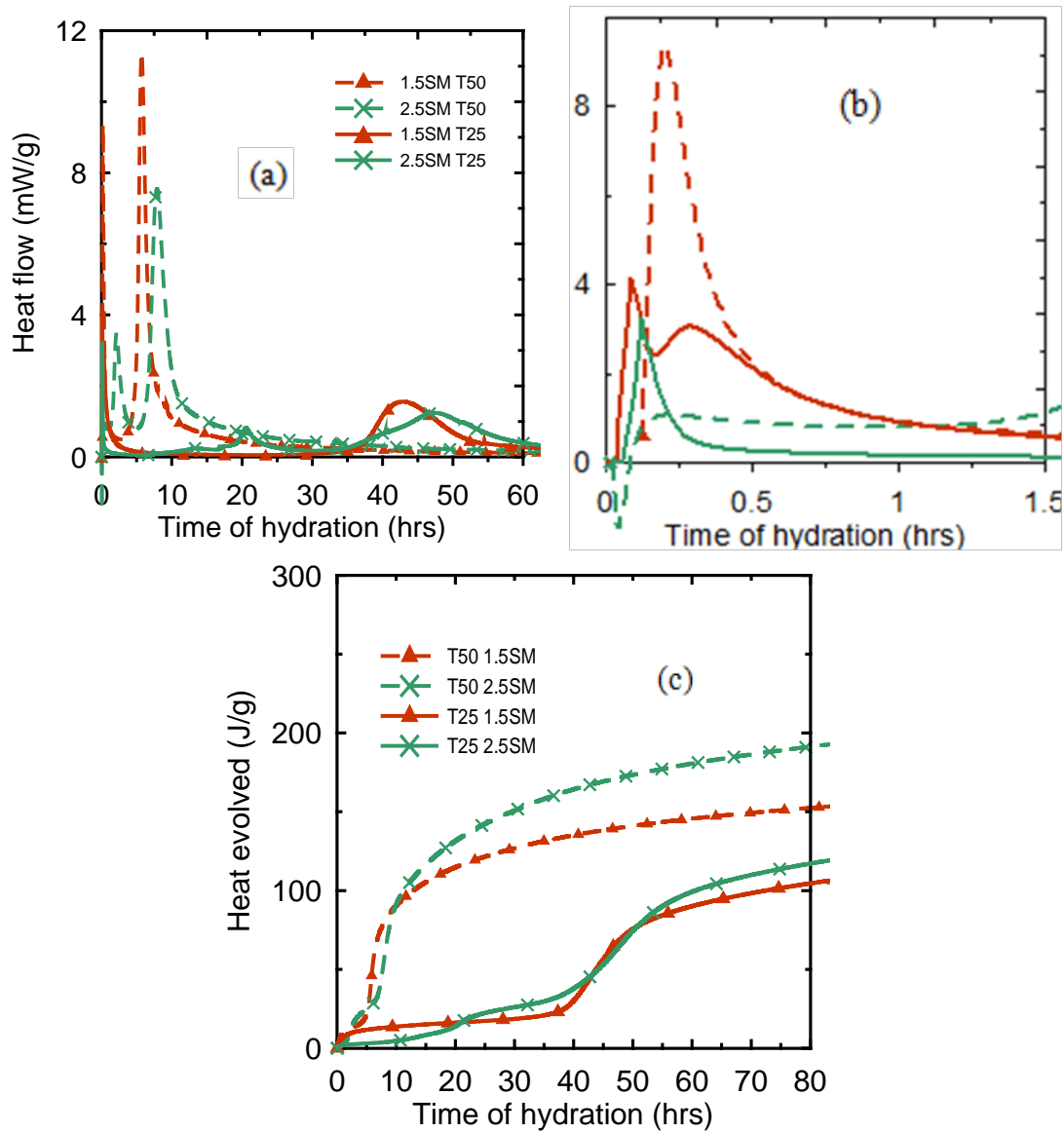
Figure 3. Slag activated with sodium silicate solutions (Na$_2$O%=2.5, SiO$_2$/Na$_2$O=1.5&2.5): (a) isothermal hydration curve at 25ºC and 5025ºC (b) magnified view of the very early hours reaction kinetics and (c) total heat evolved at 25ºC and 50 ºC

DISCUSSION

The results presented in previous sections show that the hydration kinetics of the activated slag system is very different from that of a typical hydration curve obtained for an OPC system or OPC system containing slag as an SCM. The heat of hydration curves of normal OPC systems were obtained by a TAM Air conduction calorimeter where the mixing was carried out ex-situ. A typical elapsed time before starting the heat evolution measurement in a TAM Air Calorimeter is 45 minutes in a normal cementitious system. However, using ex-situ mixing would significantly underestimate the heat of hydration in the case of the alkali activated slag system. The major stages in the hydration curve would be lost in that case. Hence, the in-situ measurement of heat of hydration is more appropriate for the evaluation of the activated system. We acknowledge the introduction of a small increase in the heat due to the manual stirring of the sample in in-situ measurement, but the many advantages associated with this method and the amount of information obtained outweigh this small error.

The hydration kinetics curve obtained for the different systems, even for a solution-to-slag ratio of 0.5, show a smaller induction period of the order of a few minutes, which may be a limiting factor for using these binders in real applications because of their very short setting times. Proper delaying of the setting time will be a challenge for sodium hydroxide-activated systems. Our laboratory experience shows that most of the commercially available decelerators for OPC systems will not be effective in these alkali-activated systems. On the other hand, the induction period in sodium silicate activated systems is very long, almost 35 and 20 hours in 1.5 and 2.5 SM sodium silicate activated slag systems, respectively. This longer induction period will also limit the use of these binders in the field if proper methods to accelerate the reaction kinetics at the early stages are not introduced. As reported in the results, the higher curing temperature in this case is advantageous for reducing the long induction period to within the practically applicable range.

CONCLUSION

The influence of two types of activating solutions and their concentration on the reaction kinetics of alkali-activated slag paste was evaluated under ambient and elevated temperature curing conditions. The in-situ isothermal conduction calorimetric data shows the strong influence of activator type on the reaction kinetics. Activating slag with NaOH initiated the spontaneous reaction process with a very small induction period at ambient temperature, whereas the activation of slag with sodium silicate solution resulted in very long induction period. The concentration of the solution also has a very significant effect, with higher dosage of the sodium hydroxide or higher SM of sodium silicate solution resulting in higher heat evolution and shorter reaction stages, for example the induction period. The elevated temperature curing resulted in the acceleration of the entire process and hence shortening of various stages of reaction observed in 25 $^{\circ}$C ambient cured samples. The higher temperature, in some cases, changed the reaction kinetics, exemplified by the disappearance of the induction period in the sodium hydroxide activated system.

ACKNOWLEDGMENT

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