



## Temperature and activator effect on early-age reaction kinetics of alkali-activated slag binders



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### HIGHLIGHTS

- The effects of activators and temperature on activation kinetics are investigated.
- Elevated temperature and increased activator alkalinity greatly accelerate hydration.
- Increased silica retards hydration but improves later-age strength.
- The main product is C-S-H with varying levels of hydrotalcite.

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### ABSTRACT

The early-age reaction kinetics of alkali-activated ground granulated blast-furnace slag (GGBFS) binders as determined by in-situ isothermal calorimetry are discussed in this paper. Particular attention is paid to the effects of activator type (sodium hydroxide and sodium silicate) and concentration, as well as curing temperature (23 °C and 50 °C). The mechanical strength development, microstructure, and product phase composition are also discussed to provide context for the phenomena observed in the kinetics results. It is shown for both activators that elevated temperature curing greatly accelerates hydration, resulting in more rapid product formation and strength development. High-molarity sodium hydroxide activators are shown to accelerate early hydration at ambient temperature, but tend to present a barrier to advanced hydration thereby limiting the later-age strength. Elevated temperature curing is shown to remove this barrier to advanced hydration by improving solubility and diffusivity. Hydration of sodium silicate-activated slag is comparatively slow, resulting in the delayed formation of very dense products with higher mechanical strength. Increasing sodium oxide tends to accelerate hydration, resulting in improved early- and later-age strength, while increasing the silica tends to retard the reaction, resulting in slower, more complete hydration as well as improved mechanical strength.

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### 1. Introduction

Alkali-activated industrial byproducts, and in particular ground granulated blast-furnace slag (GGBFS, hereafter *slag*), have received much attention in recent literature as potential sustainable alternatives to portland cement binders for concrete. The production of portland cement is one of the world's leading sources of carbon dioxide emissions and is a major barrier to the production of sustainable concrete mixtures. The partial replacement of portland cement with beneficiated industrial byproducts like fly ashes and slag has long been employed with noteworthy improvements to the rheology, strength, durability, and heat of hydration [1–7].

Despite its benefits when used in conjunction with portland cement, slag shows only latent hydraulic properties when used as the sole binder. While successful replacements of up to 70% of portland cement with slag have been routinely demonstrated, replacement is often limited to about 40% in North America [7].

In pure water, slag rapidly develops a glassy shell on the grain surface, acting as a barrier to advanced hydration. When used in conjunction with portland cement, the high alkalinity of the pore solution breaks down this barrier, promoting further hydration. When slag is used as the sole binder, an alkaline activating agent like sodium hydroxide or sodium silicate is necessary to promote advanced hydration [8–11]. The resulting binders are predominantly composed of sodium and calcium aluminosilicate hydrates (C-A-S-H and N-A-S-H), as well as some hydrotalcite-like products [12–15]. A cornucopia of studies in the past decades have shown alkali-activated slag binders and concretes to be strong, durable,

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and environmentally-friendly, with 10–50% lower associated CO<sub>2</sub> emissions than comparable portland cement formulations [16,17].

The behavior of alkali-activated aluminosilicates is highly dependent on the type and concentration of the alkaline activator and on the curing temperature [18–21]. Elevated-temperature curing greatly accelerates the formation of the microstructure and the development of mechanical strength [22–26]. Sodium silicate-activated slag systems tend to gain strength much more slowly than sodium hydroxide-activated slag, but with significant improvements in later-age strength [13,15,21,27,28]. Increased mechanical strength is attributed to increased silica or sodium oxide in sodium silicate-activated slag. Meanwhile, sodium hydroxide-activated slag sets and gains strength very rapidly [12,20]. This early product formation, however, is accompanied by the formation of a dense reaction ring surrounding incompletely-reacted slag grains and limiting continued diffusion and product formation [15,28]. As such, increased concentration of the sodium hydroxide activator often does not improve mechanical strength.

Several studies have reported in detail on the composition of the hydration products in alkali-activated slag cured at both ambient and elevated temperatures. These studies have concluded that the product phases are generally C-S-H, C-A-S-H, and N-A-S-H, the crystallinity of which increases with age [13,29–31]. Several of these studies have suggested that the composition of the product phases is similar at both ambient and elevated curing temperatures [29,30].

A few early kinetics studies compared the hydration of sodium silicate-activated slag with that of portland cement, concluding that both systems underwent the same basic stages of hydration, viz. wetting, induction, acceleration, deceleration, and steady-state, but that the mechanisms of hydration during these stages were distinct [32–34]. The wetting period in sodium-silicate activated slag is marked by the rapid early formation of C-A-S-H and N-A-S-H gels, and the acceleration period is marked by the later diffusion-limited reaction of larger slag grains [32,34]. Krizan and Zivanovic [35] showed the effect of silica on the kinetics of sodium silicate-activated slag, citing an increase in both the magnitude of the initial heat evolution peak and in the duration of the acceleration period. In addition, Haha et al. [36] discussed the effect of activator type on the hydration kinetics of activated slag, concluding that the high initial rate of reaction in sodium hydroxide-activated slag limited the later-age decrease in coarse porosity, and therefore limited the later-age strength as compared to sodium silicate-activated slag. Much more recently, Gebregziabher et al. [28] discussed the specific effects of the molarity of sodium hydroxide activators and the silica modulus (relative concentration of silica to sodium oxide) of sodium silicate activators on the hydration kinetics of alkali-activated slag binders cured at ambient temperature. That study showed spontaneous hydration in sodium hydroxide-activated slag, with significant product formation and microstructural development within the first few hours. Increased activator molarity showed a pronounced accelerating effect on the reaction, but did not significantly alter the later-age strength or microstructure [28,36]. Sodium silicate-activated slag, on the other hand, reacted in a slower and more controlled manner. Silica was shown to have a retarding effect on the reaction, allowing for the formation of denser products with higher later-age strength [28]. These observations were consistent with those of Krizan and Zivanovic [35].

Despite the availability of several studies on the reaction kinetics of alkali-activated slag, several important questions remain unanswered. First, it has been well established that curing at elevated temperatures results in much more rapid strength and microstructural development in alkali-activated binders. However, these effects have not been quantitatively evaluated by means of

kinetic studies. Additionally, while the effects of activator type and concentration on the hydration kinetics have been discussed to some extent, these discussions have neglected the effect of sodium oxide concentration of sodium silicate activators, focusing instead on the effect of silica in those systems. The present study seeks to address these gaps in knowledge in order to further the understanding of how the activator and temperature affects the rate and degree of hydration in alkali-activated slag binders.

## 2. Material and methods

### 2.1. Materials

The raw binder is an ASTM C 989-compliant grade-100 ground granulated blast-furnace slag (slag) sourced from a reputable commercial supplier. The oxide composition as determined by X-ray fluorescent spectroscopy (XRF) is 39.8% CaO, 36% SiO<sub>2</sub>, 10.5% Al<sub>2</sub>O<sub>3</sub>, 7.93% MgO, 2.11% SO<sub>3</sub>, and less than 1% of Fe<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, and K<sub>2</sub>O. The Blaine surface area is 340 m<sup>2</sup>/kg and the loss on ignition is 3%. The particle size distribution as determined by laser diffraction particle size analysis indicates a median particle size of 7.5 μm, with 80% of particle smaller than 10 μm. The X-ray diffraction analysis of the unreacted binder shows a diffuse diffraction pattern typical of an amorphous glassy material.

The alkaline activating agents are aqueous solutions of sodium hydroxide (NaOH) and sodium silicate (SS) (Na<sub>2</sub>O + *m*-SiO<sub>2</sub>, where *m* is the silica modulus). The former are prepared by dissolving reagent-grade sodium hydroxide pellets in deionized water and allowing sufficient time for heat dissipation. The latter are prepared by diluting a pre-mixed reagent-grade sodium metasilicate solution (*m* = 2.5) with deionized water. The silica modulus *m* is altered using additions of sodium hydroxide, forming what is actually a compound solution of sodium hydroxide and sodium silicate. The sodium oxide equivalent is determined according to stoichiometry. The mixture details are presented in Table 1. The mass ratio of solution to binder (*s/b*) is 0.40 throughout.

### 2.2. Experimental methods

The methods and procedures related to this work are described exhaustively by Deir et al. [15,28] and Gebregziabher et al. [28]; they are discussed only briefly here. Paste mixtures were mixed in a standard laboratory mixer in accordance with the specifications of ASTM C305. Fresh pastes were cast into the appropriate molds, consolidated on a vibrating table, sealed in plastic, and placed in the specified curing environment. Specimens were either cylindrical, measuring 25 mm in diameter and 50 mm in length, or cubic, measuring 50 mm in each dimension. Cylindrical specimens were used for SEM analyses, and cubic specimens were used for strength evaluation. Specimens were either moist-cured at ambient temperature or heat-cured at elevated temperature. The former was at 23 ± 2 °C and in excess of 95% RH and the latter at 50 ± 0.1 °C. Moist-cured specimens were demolded after 24 h when possible; a few slowly-setting mixtures were demolded after 72 h. Heat-cured specimens remained sealed within the molds to prevent moisture loss during curing.

Compressive strength of paste cubes was determined in accordance with the specifications of ASTM C109 after demolding and 7, 14, 28, and 56 d curing for moist-cured specimens and after 24, 48 and 72 h curing for heat-cured specimens. Microstructural features were observed by backscattered scanning electron microscopy of epoxy-impregnated, polished, and sputter-coated segments sawn from cured cylindrical paste specimens. Specimens were sputter-coated with gold and palladium. Carbon tape was used to maintain conductivity through the sample holder. The elemental composition of the pastes was determined by electron dispersive X-ray spectroscopy (EDS) in conjunction with electron microscopy. More

**Table 1**  
Activator compositions.

ID	Molarity (M)	
<i>Sodium hydroxide</i>		
5 M	5	
8 M	8	
12 M	12	
ID	<i>m</i>	%Na <sub>2</sub> O
<i>Sodium silicate</i>		
S1	1.5	2.5
S2	1.5	5.0
S3	1.5	7.0
S4	2.5	2.5

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