



Understanding the role of silicate concentration on the early-age reaction kinetics of a calcium containing geopolymeric binder

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HIGHLIGHTS

- Faster hardening in the calcium binders activated by silicates than by hydroxides.
- Formation of C-S-H/C-A-S-H in hydroxide binder, C-S-H and K-A-S-H in silicate binder.
- Calorimetry peak of silicate binder delayed with less polymerized silicate activator.
- Products on precursor surface in hydroxide binder, within pore space in silicate binder.

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ABSTRACT

Understanding the effects of silicate concentration of activator solution is critical for developing cost effective geopolymeric binders, and controlling their setting and hardening behavior. However, in calcium containing geopolymers, effects of silicate concentration of activator solution on the amount and nature of reaction products at different ages are still unclear. In this study, we examined class F fly ash and slag binders activated by both silicate and hydroxide solutions. Faster hardening from ultrasonic wave reflection and faster reaction from calorimetry were seen in the binder activated by silicates than that by hydroxides. Subtraction of infrared spectra, aided by selective chemical treatments, indicated the main reaction peak in calorimetry curves correlates with formation of calcium silicate hydrate/calcium aluminosilicate hydrate (C-S-H/C-A-S-H) of the same Ca/Si ratio in the hydroxide activated binder but formation of both C-S-H gel and potassium aluminosilicate hydrate (K-A-S-H) gel in the silicate activated binder. In additional tests, the main reaction peak of the silicate activated binder was delayed as silicates in the activator solution became less polymerized, further confirming contribution of K-A-S-H formation towards the main heat peak in calorimetry curve. Scanning electron micrographs showed products grew from surface into pore space in the hydroxide activated binder but within interstitial space in the silicate activated binder.

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1. Introduction

Geopolymers are aluminosilicate gels produced when activating solutions including alkaline hydroxides or silicates are added to aluminosilicate precursors such as metakaolin, slag or fly ash [1–3]. The potential for commercializing geopolymers as an alternative binder for concrete is driving extensive research on their mechanical performance, reaction mechanisms, durability and testing protocols [2,4]. However, typical geopolymers are expensive compared to portland cements [5], and the amount of common precursors such as fly ashes and slags is believed to be

insufficient to fully replace cements [6]. Reducing the cost and exploring readily-available precursors with controlled quality appear to be two major challenges.

Both cost reduction and use of new precursor materials call for changes in the mix, which usually alters the concentration of aqueous silicates available for reaction during the early-age reaction. To reduce the cost, attempts have been made to decrease the alkaline content (e.g., K_2O/Na_2O) in the activator solution [7–9]. A promising way to further cut cost is to reduce the silicates in the activator solution, as the cost per unit weight of solid alkaline silicates is generally higher than alkali hydroxides [5]. Use of new precursors, such as zeolites and other minerals [10–12] with variation in their compositions, especially amount of reactive silica and SiO_2/Al_2O_3 ratios, would also change the amount of aqueous silicates for

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early-age reaction, a change that influences the properties and performance of the geopolymer binder [13–15]. This discussion leads us to a fundamental question about how concentration of aqueous silicates would change the structural development of geopolymer mix at early ages. This question is even more critical for complex geopolymeric binders made with calcium containing precursors. Knowing exactly which products form during the hardening stage and where they form are necessary to determine ways to control setting and hardening behaviors. Early-age structural evolutions also affect the long-term performance. Therefore, the first step of our study aimed at comparing the early-age structural evolution process between alkali-silicate activated and alkali-hydroxide activated geopolymers made with calcium containing precursors.

Silicate concentration in the activating solution has been shown to substantially affect early-age structural evolution in geopolymers without any calcium. In alkali-silicate solutions, monomers and dimers of silicates are the main species at low silicate concentration, percent of dimers increases as silicate content increases and a large amount of cyclic trimers are present as silicate content further increases [1,16]. Higher percent of dimers are found to promote their condensation with aluminates, but the cyclic trimers are reported to retard the reaction. Also mixes with smaller silicates and aluminosilicates tend to reorganize more readily even before the gel hardens and thus are more likely to crystallize compared to mixes containing a higher amount of larger cyclic species [16]. Evidently, both the kinetics of the reaction and the extent of crystallization are affected by the silicate concentration. Generally during the reaction, Al-rich gel, also called gel I, forms, followed by a gel with higher Si content, also called gel II [17], probably because Si-O-Al bonds are relatively easier to form than Si-O-Si bonds under such alkalinity [18]. The transition from gel I to gel II is usually observed when mixes are activated by hydroxide or low-silicate solutions [2], while high amount of silicates may overlap with aluminosilicates in common spectroscopic characterizations and therefore complicate the interpretation [19]. Additionally, silicate concentration in the activating solution is also found to affect microstructural porosity [20], final strength [18,20], and location where (close or away from precursor surfaces) gel forms [21–23].

The addition of calcium has also been shown to substantially affect early-age structural evolution. Setting is substantially accelerated by calcium as seen and reviewed in our previous studies [8,9,24]. Few mechanisms for this acceleration have been proposed including formation of calcium silicate hydrate/calcium aluminosilicate hydrate (C-S-H/C-A-S-H), enhanced dissolution, and presence of additional nucleation sites to promote geopolymer formation [25–27].

Combination of both the factors, that is variable silicate concentration and calcium addition, affects the structural evolution of geopolymeric binders in a more complicated way and would need further investigation. The strength of high-calcium fly ash geopolymers is found to depend on both alkali and silicate content of the activating solutions [28]. Generally, addition of higher amount of silicates to the activating solution would lower the pH [1]. Setting is found to be caused predominately by precipitation of calcium-containing hydrates at low pH, while mainly by geopolymer gel at relatively high pH [29,30]. At even higher pH (>14), precipitation of nano-sized particulates of $\text{Ca}(\text{OH})_2$ is observed in hydroxide activated mixes [31], but is less likely in silicate activated mixes because the calcium would be complexed with silicates [2]. However, none of these studies have directly probed structural evolution of products with time as identifying different phases from the overlapping spectra from common characterizations techniques is challenging. Our recent studies quantified the structures at different ages for both metakaolin and fly ash geopolymers with

calcium [9,24], however, did not include the effects of varying silicate concentrations.

Our objectives in this study were to directly identify and quantify structures of reaction products, i.e., calcium-containing hydrates and geopolymers, at different ages, and correlate them with hardening behaviors for calcium-containing geopolymer binders with varying silicate concentrations. We examined the user-friendly mix (i.e., class F fly ash and slag activated by very low alkaline solution [8,9]) when activated by solutions both with and without external silicates. We compared hardening, reaction kinetics, microstructure, amount and nanostructure of calcium-containing hydrates and dissolution extent of fly ash for the two mixes, and we found both the amount and structure of the reaction products differ with the two solution types. We then further investigated the effects on structural evolution by varying the state of silicate polymerization in the activator solution while keeping the solution composition constant. The fundamental understanding of the role silicate concentration and polymerization play when mixed with a calcium containing precursor will pave the way to lower the cost and to explore new precursors for geopolymeric binders, and also will offer new ways to control the early-age reaction kinetics.

2. Experimental methods

Fly ash-slag mix made with 75% fly ash (supplied by Boral Material Technologies) and 25% slag (from Lafarge Corporation) was activated either by potassium hydroxide (KOH) or a combination of KOH and potassium silicate (KOH-KSiI) solutions. The compositions of slag and fly ash are presented in Table 1, and the same raw materials were used and their XRD patterns were presented in our earlier study [8]. Both the amount of K_2O in activator solution and water to binder ratio were kept constant between the two mixes. Potassium hydroxide solution of molarity 1.9 M (1.86 M to be exact) was used for hydroxide activated binders and potassium silicate solutions with $\text{SiO}_2/\text{K}_2\text{O}$ molar ratio of 1.25 was used for silicate activated binders unless otherwise stated. During sample preparation, the dry powders were mixed for 30 s followed by mixing with the activating solution for 3.5 min. The same procedure was followed and described in more detail in our previous study [8].

Reaction kinetics was monitored using Thermometric 3114/3236 TAM Air Isothermal Conduction Calorimeter (ICC) at 22 °C. Data collected during the first 45 min was ignored as it might be affected by friction while placing samples inside the instrument. The hardening process was monitored using S-wave ultrasonic wave reflection (UWR) and Proctor penetration methods, as described in our previous studies [8,32]. The fracture surface of the samples was analyzed using JEOL JSM-6060 LV scanning electron microscopy (SEM) instrument in secondary electron imaging (SEI) mode. Prior to characterization using SEM, the samples were treated with (50/50 by volume) methanol-acetone mixture, same solvent that was used for metakaolin geopolymers

Table 1
Composition of fly ash and slag.

Composition	Fly ash	Slag
SiO_2	60.17	35.70
Al_2O_3	21.91	11.21
CaO	1.81	39.40
Na_2O	0.81	0.26
K_2O	2.13	0.48
MgO	1.28	10.74
Fe_2O_3	7.57	0.42
SO_3	0.17	0.58

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