



The interrelationship between surface chemistry and rheology in alkali activated slag paste



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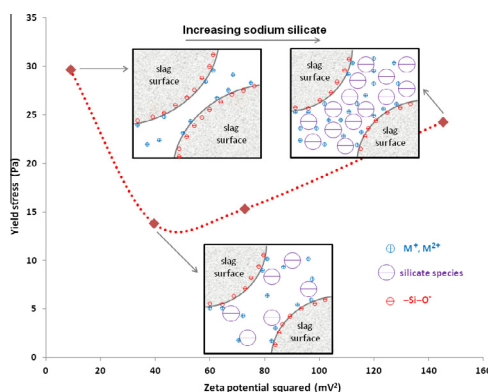
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HIGHLIGHTS

- Surface chemistry controls rheology in alkali-activated slag cements.
- Particle–particle interactions and gelation influenced by activator nature.
- Yield stress depends on square of zeta potential.
- Silicate and hydroxide activators differ notably in behavior.
- Influence of pH on fresh paste chemistry is indirect.

GRAPHICAL ABSTRACT



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ABSTRACT

Ground granulated blast furnace slag can react with an alkaline activating solution to form a cement-like binder based on a calcium–sodium aluminosilicate gel, which is a potential alternative to Portland cement in many applications. This study provides new information regarding the effect of activator type and dosage on rheology by monitoring changes in pH, particle surface charge (zeta potential), and heat evolution in the early stages of the reaction process. Sodium and potassium hydroxide silicate solutions, at two different M_2O (M: Na, K) dosages, are used here as activators. Alkali hydroxide activators cause a significant increase in the yield stress of an activated slag paste, especially at higher dosages as reactions take place rapidly, while within the same timeframe, the yield stress of the silicate activated slag remains unchanged. The results imply a direct relationship between a higher reaction rate with the formation of solid products (causing both spatial blockage effects and consumption of free water), and a rapid yield stress increase. However, the dependence of reaction rate on pH for different alkali-activated pastes is, at most, indirect. All activators induce a highly alkaline pH and a concentrated electrolyte solution environment in the fluid paste. As a result of complexation of poorly-hydrated ions on the surfaces of the particles, the magnitude of the zeta potential increases. A direct relationship is observed between the dosage of the activators and zeta potential. A zeta potential further from neutrality generally reduces yield stress by increasing the magnitude of double layer repulsive forces, with the exception of a higher dosage of silicate activator, which shows an indication of some attractive double layer forces.

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1. Introduction

Ground granulated blast furnace slag (GGBFS) is the by-product of reduction of iron oxides to metallic iron in a blast furnace, and when quenched forms a glassy calcium–magnesium aluminosilicate which granulates and is ground to form a fine powder. GGBFS is often combined with Portland cement as a supplementary cementitious material to reduce cost and attributed CO₂ emissions and to enhance mechanical and durability properties [1]. However, slag can also react as a sole precursor in an alkaline environment to form a cement-like binder [2], which is predominantly composed of a calcium–sodium aluminosilicate gel [3]. The commonly used alkali activators include alkali metal hydroxides, silicates and carbonates [2]. Among these activators, sodium silicate provides benefits regarding the ultimate strength of the alkali activated slag (AAS) binder, which can be similar to that of a good quality Portland cement depending on the activator modulus (molar ratio SiO₂/Na₂O) and dosage [4]; however, its setting rate is not as fast as when alkali hydroxides are used [5,6].

A key aim of many studies discussing and characterizing reaction products in AAS [7–10] has been to clarify the reaction mechanisms which are involved in the setting and hardening process. Upon contact with an alkaline solution, slag undergoes partial dissolution [11], with an exothermic reaction process [12–14] resulting in hardening if the water/solids ratio is sufficiently low. Isothermal calorimetry is used to monitor heat flow changes during alkali-activation reactions, and shows distinguishable differences as a function of alkali activator type and dosage, both in terms of the magnitude and duration of heat release [14–17]. It is also used as a tool to monitor reaction rate based on normalized heat flow curve versus time for Portland cement and blended cements [18,19].

The fluidity of an AAS paste can be monitored through changes in rheological properties such as yield stress and apparent viscosity. A low yield stress paste is generally considered desirable, as it reduces the energy required for pumping a concrete mix, and enhances the ability to fill voids when placing concrete. In addition, concretes are usually premixed for a specific time before placement, so it is also important to avoid much yield stress increase during the early age reaction.

A rapid early reaction leading to thickening and solidification of a cement paste affects the workability and fluidity of the binder in transportation and placement. This is controlled in Portland cements by the use of organic plasticizing admixtures [20,21], which has enabled the development of concretes which are workable (or pumpable), and yet show high early strength. These admixtures are designed to control surface interactions, and so can reduce the yield stress of the mix, reduce the likelihood of a sudden yield stress increase during the reaction process, and control the rate of thickening [22].

However, chemical admixtures are not effective in all different environments of cementitious materials, and need to be tailor designed case by case. For example, the typical plasticizers used in cement do not plasticize as effectively in alkali activated binders [23,24]. The development of admixtures for alkali-activated systems is still ongoing [25,26], and requires a much more detailed understanding of the surface chemistry of slag particles within the complex reacting environment of a fresh AAS paste. The work presented in this paper is targeted toward building this understanding.

Compared to the chemistry of a Portland cement, the addition of an alkali activator provides a higher pH and different electrolyte environment in the fresh binder paste, leading to differences in surface charges of particles and thus also in the electrostatic interactions between particles. However, the surface chemistry of alkali

activated binders, and particularly its interrelationship with rheology, is not well understood. This paper provides new insight into the effects of activator type and dosage on the rheological properties of an alkali activated slag paste. Yield stress is measured and related to the reactions taking place in this complex particle–fluid system. Zeta potential measurement is used to monitor the changes in electric double layer forces under different pH and electrolyte environments, which determine the sites and signs of the charges on particle surfaces [27]. Measurement of electric double layer forces by means of zeta potential provides insight into key parameters which determine yield stress [28]. The study results in an important new understanding of the relationship between the yield stress and the zeta potential of the activated slag paste.

2. Materials and methods

2.1. Materials

Ground granulated blast furnace slag, with chemical composition as displayed in Table 1, and anhydrous sodium metasilicate powder (Na₂O 50.9 wt.% and SiO₂ 49.1 wt.%) were provided by Zeobond Pty. Ltd., Australia. AR-grade NaOH and KOH (Sigma–Aldrich, Australia) were used. All activators were dissolved in MilliQ-grade purified water before mixing with slag to avoid any interference due to solid activator particle dissolution in the heat flow measurements, or the influence of additional particles on the paste solids fraction (and thus rheology). Dosages of 2.25×10^{-4} and 4.5×10^{-4} moles M₂O per gram of slag were used, and specified on a molar basis to give the same amount of alkali ions for different activators at each dosage (for instance, 2.25×10^{-4} mole M₂O per gram slag is equivalent to 1.80 g NaOH, 2.52 g KOH, and 2.75 g Na₂SiO₃ per 100 g slag). The samples were formulated by mixing slag with the activator solution at a water to slag weight ratio of 0.45. One sample was formulated without an activator but with the same water to binder ratio as a reference. After hand mixing to combine the components, the paste was mechanically mixed for 2 min or 10 min at 500 rpm before calorimetry and rheology measurements, respectively.

2.2. Rheological tests

The rheological behavior of each AAS sample was measured using a Haake VT550 rheometer with a four-blade vane with a length of 50.1 mm and diameter of 15.3 mm, in a sample volume sufficient to simulate an infinite medium [29]. A direct yield stress measurement at a low rotational rate (0.2 rpm) was used because of the accuracy and reproducibility of the measured data [30], and the yield stress was calculated from the applied torque based on the geometry of the vane and the rotation rate according to [30]. Before each measurement, the paste was mixed by hand to avoid settling of particles and to provide a homogenous paste, left to rest for 30 s to dissipate residual stresses induced by mixing, before the 0.2 rpm rotational rate was applied. The first yield stress measurement was taken 12 min after combination of the slag and the activator (this includes 10 min of mixing and 2 min for the residual stress relaxation after high shear mixing). Five consecutive measurements were then taken at intervals of 2 min. The apparent viscosity at a range of higher shear strains was also measured, immediately after yield stress measurement, for each sample in 15 consecutive steps (Fig. 1) and without mixing between measurements.

Table 1
Chemical composition of the slag used, as determined by XRF. LOI is loss on ignition at 1000 °C and d₉₀ was determined using a Malvern Mastersizer instrument.

Oxide component	wt.%
SiO ₂	33.1
TiO ₂	0.6
Al ₂ O ₃	15.0
Fe ₂ O ₃	0.6
MnO	0.3
MgO	5.9
CaO	41.8
Na ₂ O	0
K ₂ O	0.3
SO ₃	2.3
LOI	−0.4
d ₉₀ (μm)	39.8

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