Effects of activator characteristics on the reaction product formation in slag binders activated using alkali silicate powder and NaOH

Deepak Ravikumar [a], Narayanan Neithalath [b,*]

[a] Department of Civil and Environmental Engineering, Clarkson University, Potsdam, NY 13699, United States
[b] School of Sustainable Engineering and Built Environment, Arizona State University, Tempe, AZ 85286, United States

ARTICLE INFO

ABSTRACT

The influence of different levels of alkalinity, expressed using the Na_2O-to-source material ratio (n) and activator SiO_2-to-Na_2O ratio (M_s), on the compressive strength development of, and reaction product formation in sodium silicate and NaOH powder activated slag binder systems is discussed. Higher n value mixtures are found to exhibit higher early and later age compressive strengths. An increase in M_s results in reduced early age and slightly increased later age strengths. Compositional coefficients, which are functions of n and M_s are proposed, that relate to the early and later age strengths of the activated slag binders as well as to the shift in the FTIR spectra. The reaction product formation in these systems as a function of the total alkalinity is explained using the shifts of the dominant peak in the FTIR spectra. Fundamental changes in reaction products of powder activated binders as a function of alkalinity is observed. The deductions from the peak shifts are substantiated using the FTIR spectra of the pastes before and after salicylic acid–methanol (SAM) attack.

1. Introduction

Concerns related to greenhouse gas emissions and energy and resource consumption in Portland cement manufacturing has resulted in significant interest on the use of waste and by-product materials as the primary ingredient of structural binders. High volume cement replacement material usage in concrete and the use of cement-less binders are among the prominent strategies that are becoming increasingly accepted to further the cause of materials-related sustainability in the built environment. Cement-less binders generally are alkali-activated systems that use an alkaline activator, typically sodium hydroxide or sodium silicate [1–3], along with a silica-and-alumina rich precursor material to form a final product with properties comparable to that of ordinary Portland cement concrete. Among the precursor materials used, fly ash and ground granulated blast furnace slag have been the prominent ones because of their favorable chemistry (higher amounts of reactive silica and/or alumina species [1–6]) and abundant availability in many parts of the world. Also, since they are extensively used as partial cement replacement materials in concrete, they have been well characterized with respect to their performance in structural concretes.

Alkali activation of slag has been the subject of many studies [7–17]. Caustic alkalis or alkali compounds whose anions can react with Ca^{2+} to form compounds less soluble than calcium hydroxide can act as activators for slag [12,13]. The use of sodium silicate based activators ($Na_2SiO_3 \cdot xH_2O$ + NaOH) has been found to be ideal to produce desired mechanical properties [3,9,14]. The major reaction product formed as a result of alkali activation of slag is C–S–H gel, which is similar to that formed from Portland cement hydration, but typically with a lower Ca/Si ratio [15–17]. The influence of several parameters relating to the source material and the activator that can potentially influence the reaction kinetics as well as the mechanical and durability properties of the final product has been reported [1,7,14,18]. High amounts of alkalis in the activating medium have been reported to result in early strength gain of activated slag systems [19].

Alkali silicate solutions of varying moduli are generally used as the activating agents. However, the applicability of powder activators, in lieu of the commonly used liquid activators, also need to be evaluated in alkali activated slag binder systems so as to alleviate the concerns related to handling of caustic materials, and facilitate ease of handling. This potentially changes the reaction kinetics, the nature of the C–S–H gel formed, especially with respect to the Ca/Si ratio and the level of polymerization of silicates, and could result in the formation of other reaction products that have a bearing on the mechanical and durability properties of the material. This aspect is considered in this study, where the early and later age reaction

* Corresponding author. Tel.: +1 480 965 6023; fax: +1 480 965 0557.
E-mail address: Narayanan.Neithalath@asu.edu (N. Neithalath).

products in alkali silicate powder (anhydrous) activated slag binders proportioned using different levels of total alkali loading and activator moduli are analyzed using Fourier-Transform Infrared spectroscopy (FTIR), and related to the mechanical property development and the reaction product stability in such systems. While it is recognized that the powder activated binders do not develop compressive strengths as high as those of waterglass activated mixtures, primarily due to the effects of reduced silica dissolution, strengths in the 30 MPa range, which is the most common strength range for general purpose concrete applications, can be consistently achieved.

2. Experimental program

2.1. Materials

To prepare alkali activated slag pastes and concretes in this study, Type 100 ground granulated blast furnace slag (GGBFS) conforming to ASTM C 989 was used as the starting material. The chemical composition of the starting material is as follows SiO_2 – 36%, Al_2O_3 – 10.5%, CaO – 39.8%, Fe_2O_3 – 0.67%, MgO – 7.93%, Na_2O – 0.27%, SO_3 – 2.1% and loss on ignition – 3%. The silica-to-alumina (SiO_2/Al_2O_3) mass ratio of slag is 3.4, and the basicity coefficient of slag, defined as $(CaO + MgO)/(SiO_2 + Al_2O_3)$, is 1.03. The particle size distribution of slag is such that 95% is finer than 35 μm and the d_{50} is ~10 μm. The X-ray diffraction (XRD) pattern of slag showed that it is amorphous. Combinations of anhydrous sodium silicate powder (>99% sodium silicate and <1% crystalline silica) having a SiO_2-to-Na_2O ratio (or the modulus, M_s) of 1.95, and analytic reagent-grade sodium hydroxide (NaOH) beads were used as the activating agents in this study. The sodium silicate powder has a median particle size of 25 μm and a pH of 12.6 (for a 50% w/v slurry in water). NaOH addition facilitated changing the activator M_s to desired values.

2.2. Mixture proportions

The concrete mixtures were proportioned with approximately 50% of slag + water by volume. River sand was used as the fine aggregate and pea gravel with a nominal maximum size of 4.75 mm was used as the coarse aggregate. The parameters relating to the activator that were chosen to be studied are the Na_2O-to-slag ratio (n) and the SiO_2-to-Na_2O ratio (M_s). The ratio n provides the total amount of Na_2O in the mixture whereas the ratio M_s dictates the proportion of NaOH and sodium silicate powders in the activator. The n values used in this study were 0.05, 0.15 and 0.25, and M_s (mass-based) values ranged from 0.60 to 1.50 in increments of 0.30 (molar-based M_s ranged from 0.62 to 1.55; note that the molar and mass SiO_2-to-Na_2O ratios of sodium silicates are very close since the ratio of molecular masses of SiO_2 and Na_2O is 0.97). For example, if a mixture with an n value of 0.15 and a mass-based M_s of 1.2 is required, for every 1000 g of slag, 150 g of Na_2O and 180 g of SiO_2 is required. Since sodium silicate powder is the only source of silica from the activator, 180 g of SiO_2 can be obtained from 272 g of sodium silicate powder which has a M_s of 1.95. The sodium silicate powder would also provide 92 g of Na_2O. The remaining 58 g of Na_2O (150–92 g) is then obtained by the addition of NaOH. The calculated amounts of the two powder activators were blended with the required amount of slag before mixing. Water-to-powder ratio (w/p) of 0.40 was used for all the mixtures in this study. The powder consisted of slag, sodium silicate and NaOH.

It was observed that paste mixtures proportioned using the desired n and M_s values showed adequate workability (mini-slump flow values in the range of 95–120 mm) even though the higher

alkalinity mixtures tend to lose their flowability very quickly, and thus necessitated quick placing and consolidation in the molds. No attempt was made in this study to retard the setting of these binder mixtures, even though such an approach would be necessary for practical applications. The powder was mixed with the aggregates for approximately 30 s after which water was added. The contents were further mixed for 2 min to obtain a uniform mixture. The mixture was then filled in cube molds of 50 mm size and consolidated. Both the paste and concrete specimens were removed from the molds after 24 h, and subjected to moist curing at 23 ± 2 °C and RH > 98%. For the paste specimens to be used for electrical conductivity and Fourier Transform Infrared (FTIR) spectra analysis, samples were prepared by mixing slag and the activating powder so as to obtain the desired n and M_s values, along with the required water in a blender for 2 min. 50 mm × 50 mm × 150 mm prismatic specimens with stainless steel plate electrodes at the ends were used for electrical conductivity determination at various ages. The pastes for the FTIR analysis were mixed in sealed containers.

2.3. Test methods

The compressive strengths of the activated paste or concrete cubes at several ages were determined in accordance with ASTM C 109. Electrical impedance spectroscopy [20,21] was used to determine the electrical conductivity of the activated pastes as a function of time after mixing. Semi-adiabatic calorimetry was used to determine the temperature rise in pastes during early stages of activation.

The samples for FTIR spectroscopy were prepared by mixing approximately 1 mg of sample obtained from carefully sealed specimens, with 300 mg of KBr. The spectra of the precursor materials and the hydrated products at desired ages of curing were obtained using an ATI Mattson FTIR spectroscope in the wavenumber range of 4000–400 cm^{-1} at a resolution of 1 cm^{-1}. Fig. 1 shows the FTIR spectra of the precursor materials, i.e., slag and sodium silicate. The predominant bands in both the spectra correspond to the asymmetric stretching vibration of the Si–O–Si units.

A selective dissolution procedure using salicylic acid and methanol (SAM), also called Takashima's attack [22], was employed on the pastes hydrated for 28 days. This process involved exposing the alkali activated paste to a mixture of salicylic acid dissolved in methanol (1:20). The calcium bearing phases dissolve in this medium, whereas those without calcium form an insoluble
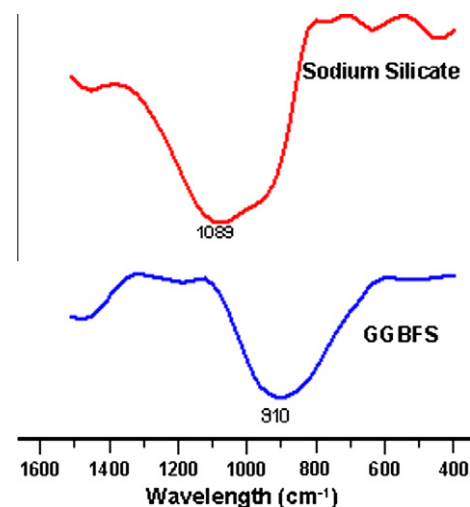

Fig. 1. FTIR spectra of starting materials (slag and sodium silicate powder).