Cement & Concrete Composites 44 (2013) 58–68

Contents lists available at SciVerse ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

An electrical impedance investigation into the chloride ion transport resistance of alkali silicate powder activated slag concretes

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

[a] Solidia Technologies, Piscataway, NJ, United States
[b] School of Sustainable Engineering and the Built Environment, Arizona State University, Tempe, AZ 85287, United States

A R T I C L E I N F O

Article history:
Received 14 October 2012
Received in revised form 24 May 2013
Accepted 7 June 2013
Available online 14 June 2013

Keywords:
Alkali activated slag
Powder activator
Rapid chloride permeability
Non-steady state migration
Electrical impedance
Pore structure
Circuit models

A B S T R A C T

The chloride transport resistance of alkali silicate powder activated slag concretes is evaluated. Two different Na_2O-to-source material ratios (n) and two SiO_2-to-Na_2O ratios of the activator (M_s) are used on concretes proportioned using two slag contents (300 kg/m^3 and 400 kg/m^3). Rapid chloride permeability (RCP) and non-steady state migration (NSSM) tests are used to evaluate the chloride transport behavior. Alkali silicate powder activated concretes demonstrate comparable or better chloride transport resistance than OPC concretes when evaluated using RCP and NSSM tests. The relationships between the activator parameter, $n \cdot M_s$, and the critical pore sizes (d_c) or the RCP and NSSM values demonstrate similar trends showing the influence of d_c in determining the ionic transport response. Electrical impedance spectroscopy (EIS) is used to relate the material response before and after the transport tests, and equivalent circuit models are used to extract the parameters that relate to the pore structure. EIS coupled with circuit modeling clearly brings out the differences between the RCP and NSSM test on their influences in the microstructure of alkali activated slag concretes.

1. Introduction

The need to reduce the consumption of portland cement because of its adverse environmental and energy-related impacts necessitates measures to develop alternate binding materials for concrete production. This has resulted in a variety of methodologies that either minimize or eliminate the use of ordinary portland cement (OPC) in concretes. The use of cement replacement materials such as fly ash and ground granulated blast furnace slag in high volumes in portland cement concrete has been established, as is the use of binders that do not contain any portland cement [1–3]. The latter category of binders is typically produced by activation of waste/by-product materials such as fly ash or slag by alkaline hydroxides or silicates.

Alkali activation of slag has been a subject of several reported studies [4–9]. The activating agent used typically is a sodium silicate-based solution ($Na_2SiO_3 \cdot xH_2O + NaOH$). It is well known that alkali activation of slag produces C–S–H gel as the main reaction product. 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 [1,10–15]. A majority of the studies on alkali activated slags have been carried out using waterglass solution as the activator. This presents issues with handling because of the caustic nature of the alkalis. Hence, in this study, powder sodium silicate and sodium hydroxide are used as activating agents. This is also expected to help in the development of blended binder-activator systems which can be handled easily, and will develop its properties just by the addition of water. While the strength of such binder systems is generally lower than those activated by waterglass solutions, by proper proportioning procedures, compressive strengths in the range of 30–35 MPa can be achieved [16], which is sufficient for most of the common concrete applications. Detailed studies on the reaction kinetics and product formation in alkali silicate powder activated systems have been reported recently by the authors [16,17].

The pore structure of alkali activated slag concretes have been studied [18,19] and it is reported that these concretes have beneficial pore structure features when compared to OPC concretes. However, the use of a highly alkaline activating agent results in a higher pore solution conductivity. A combination of these two factors influence the transport of ionic species such as chlorides through alkali activated slag concretes. This paper investigates the chloride ion transport in alkali silicate powder activated slag concretes using two common accelerated chloride transport tests – the rapid chloride permeability (RCP; conforming to ASTM C 1202) and non-steady state migration (NSSM; conforming to NT Build 492) tests. The influence of pore structure on chloride ion

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* Corresponding author. Tel.: +1 480 965 6023; fax: +1 480 965 0557.
E-mail addresses: dravikumar@solidiatech.com (D. Ravikumar), Narayanan.Neithalath@asu.edu (N. Neithalath).

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http://dx.doi.org/10.1016/j.cemconcomp.2013.06.002

transport is quantified, and the changes in pore structure as a result of these accelerated chloride transport tests are estimated through the use of electrical impedance spectroscopy and associated equivalent electrical circuit modeling.

2. Experimental program

2.1. Materials and mixture proportions

Type 100 ground granulated blast furnace slag conforming to ASTM C 989 was used as the binding material in this study. The chemical composition of slag is shown in Table 1. The particle size distribution of slag is such that 95% is finer than 35 μm and the d_{50} is $\sim$10 μm. 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 are 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 lower values in order to obtain 28-day compressive strengths in the range of 20–30 MPa. The M_s (mass-based) values thus chosen are 0.60 and 1.50, and the corresponding molar-based M_s values are 0.62 and 1.55. The n values (Na_2O-to-slag ratio) used are 0.05 and 0.15. An example of the activator quantity determination is provided below. If a mixture with an n value of 0.05 and a mass-based M_s of 1.5 is required, for every 1000 g of slag, 50 g of Na_2O and 75 g of SiO_2 is required. Since sodium silicate powder is the only source of silica from the activator, 75 g of SiO_2 can be obtained from 114 g of sodium silicate powder which has an M_s of 1.95. The sodium silicate powder would also provide 39 g of Na_2O. The remaining 11 g of Na_2O (50–39 g) is then obtained by the addition of NaOH.

Several activated slag concretes were proportioned as part of this study. Concretes containing two different slag contents (300 kg/m^3 and 400 kg/m^3) were proportioned and activated using powder sodium silicate and NaOH. The effective water-to-powder ratio for the mixtures was maintained at 0.40. The powder consists of the slag, powder sodium silicate and NaOH. River sand was used as the fine aggregate and pea gravel with a nominal maximum size of 9.5 mm was used as the coarse aggregate. The moisture absorption of the aggregates was accounted for in the mixture proportioning. The mixture proportions are shown in Table 2. The specimens made using these mixture proportions were used for compressive strength and chloride transport studies after specified durations of curing in a moist chamber. Activated mortar samples with a paste volume fraction of 50% were used for the compressive strength tests and paste specimens were proportioned for the microstructural tests using the same water-to-powder ratio as used for the concretes. All the paste, mortar, and concrete specimens were removed from the molds after 24 h and moist cured in a humidity chamber (>97%RH) until the time of testing.

2.2. Test methods

The experimental technqiues used include the methods for accelerated determination of chloride transport paramertes, electrical impedance spectroscopy (EIS) before and after the chloride transport tests, and pore structure determination using mercury intrusion porosimetry (MIP). In addition, compressive strength of mortar specimens determined in accordance with ASTM C 109, and Fourier Transform Infrared (FTIR) Spectroscopy were used to bring out the difference in the properties and reaction products when powder or liquid forms of sodium silictae were used as activators.

Table 1
Chemical composition of slag.

SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O	K_2O	SO_3	LOI
36.0%	10.5%	39.8%	0.67%	7.93%	0.27%	0.80%	2.1%	3.0%

2.2.1. Chloride transport test methods

Rapid chloride permeability (RCP) test in accordance with ASTM C 1202 and non-steady state migration (NSSM) test in accordance with NT Build 492 were carried out on 50 mm thick discs cut from 200 mm long cylindrical concrete specimens. For the RCP test, the specimens were conditioned by vacuum saturation, and enclosed in a cell flanked by reservoirs that contain 0.3 N NaOH solution on one side and 3% NaCl solution on the other. A 60 V potential difference was applied between the electrodes placed on both faces of the specimen, for a duration of 6 h. The total charge passed (in coulombs) at the end of 6 h of testing is reported as the RCP value. For the NSSM test, the specimens were preconditioned by vacuum saturation with $Ca(OH)_2$ solution. The catholyte and anolyte solutions used were 2 N NaCl and 0.3 N NaOH respectively. An initial voltage of 30 V was applied, and initial current recorded. The applied voltage and test duration were chosen based on the initial current. The test duration was maintained at 24 h and the voltage at 30 V for all the cases. After the test duration, the specimens were axially split and sprayed with a 0.1 M silver nitrate solution. The depth of chloride penetration was measured based on the precipitation of white silver chloride. The non-steady state migration coefficient (D_{nssm}) in m^2/s is given as:

$$D_{nssm} = \frac{RT}{zFE}\frac{x_d - \alpha\sqrt{x_d}}{t} \tag{1}$$

$$\alpha = 2\sqrt{\frac{RT}{zFE}}erf^{-1}\left(1 - \frac{2c_d}{c_0}\right) \tag{2}$$

$E = (U-2)/L$, where U is the absolute voltage (V), L is the specimen thickness in m, z is the valence of the chloride ion, F is the Faraday constant, R is the molar gas constant, T is the average value of initial and final temperatures in K, x_d is the average value of the penetration depth in m, t is the test duration in seconds, c_d is the chloride concentration at which silver nitrate changes to silver chloride (0.07 N), and c_0 is the chloride concentration of the catholyte solution (2 N). The value of c_d chosen for this study is the one generally used for OPC concretes. However, the calculations for D_{nssm} were repeated with c_d values of 0.05 and 0.1, but this resulted in insignificant changes to the D_{nssm} value. Hence a c_d of 0.07 itself is used in this study. While the use of RCP test for alkali activated slag concretes have been reported [20,21], the use of NSSM test for these systems is not reported, and further studies are needed to ascertain if the values of the constants used for OPC systems can be applied to alkali activated concretes also. This assumes more significance given our understanding of the limitations of the RCP test. In this paper, the NSSM coefficients are used as relative indicators of the transport properties of different mixtures, and hence the methodology adopted is considered to be adequate.

2.2.2. Electrical impedance spectroscopy (EIS)

Electrical impedance spectroscopy (EIS) was employed on specimens before and after they were subjected to the RCP and NSSM tests. EIS measurements were conducted in this study using a Solartron 1260™ impedance/gain-phase analyzer that was interfaced with a personal computer for data acquisition. The test set up is shown in Fig. 1a. The frequency of the EIS measurements ranged from 10 Hz to 1 MHz using a 250 mV AC signal, with 10 measurements per decade. The effective specimen conductivity (σ_{eff}) was determined from the bulk resistance (R_b) obtained from EIS. A typical Nyquist plot, which relates the real and imaginary imped-