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Influence of the slag content on the chloride and sulfuric acid resistances of alkali-activated fly ash/slag paste

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A B S T R A C T

This study aims to investigate the influence of the slag content on the chloride and sulfuric acid resistances of alkali-activated fly ash/slag (AFS) paste. A series of tests were conducted to examine the effects of reaction products and their contents on the chloride and sulfuric acid resistance capabilities. It was shown from the tests that the deterioration of the AFS binder due to a sulfuric acid attack was caused by 1) the corrosion by means of SO_4^{2-} penetration through the surface of the AFS binder, which is associated with permeable voids and a rate of water absorption and 2) the corrosion of the reaction products resulting from the different degrees of resistance to sulfuric attack between the C-(A)-S-H and the N-A-S-H. Variation of the slag content led to differences in the reaction product content of the AFS binder, clearly affecting the chloride-binding capacity and the resistance to chloride penetration.

1. Introduction

Alkali-activated binders have been investigated by many researchers over the past decade. In particular, alkali-activated, two-source binders, which consist of fly ash/slag or metakaolin/slag, have been studied recently in an effort to improve the performance of alkali-activated, one-source binder. There are two main types of reaction products, N-A-S-H and C-A-S-H, in alkali-activated, two-source binders [1,34]. The main product of alkali-activated binders with a fly ash content of 50 wt% and a slag content of 50 wt% was a N-C-A-S-H gel with a chemical composition intermediate between C-A-S-H and N-A-S-H [1]. Since the nature of the gel in alkali-activated, two-source binders is highly dependent on the fly ash/slag ratio, the mechanical properties and the durability of two-source binders should be investigated in view of the mixture ratio of the raw materials.

Acid resistance is one of the important performance parameters for structural materials when they are applied in aggressive environments such as urban sewer structures [2]. Alkali-activated slag (AAS) was reported to have better durability compared to ordinary Portland cement (OPC), with one study finding that AAS concrete showed a strength reduction of about 33% as compared to the 47% reduction of OPC in an acid environment (pH 4) after a time of one year [2]. The high resistance of AAS to an acid attack was attributed to the low Ca content (40% CaO) of the slag compared to Portland cement (~65% CaO) and to the presence of glassy slag, which is practically insoluble in an acid solution [2,3]. Likewise, alkali-activated fly ash binder also showed better performance in some aggressive environments compared to OPC concretes [4,5], resulting from a more stable cross-linked aluminosilicate gel which formed in the binder [2]. Allahverdi et al. [6] suggested the corrosion mechanism of geopolymer paste at a relatively high concentration of sulfuric acid (pH = 1); the first step is an ion exchange reaction between the charge compensating cations of the framework, and the second step is a reaction between the exchanged calcium and the sulfate anion, resulting in the formation of gypsum crystals inside the corroding layer. In alkali-activated, two-source binders, it was found that the binders underwent surface corrosion due to an acid attack [7]. The presence of calcium in the binder and a high alkali concentration resulted in high resistance to an acid attack due to the decreased mass transport rate through the tortuous pore structures of the binders [7].

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Alkali-activated fly ash binders may be a favorable alternative in the manufacturing of acid resistant concrete since it consists mostly of aluminosilicate rather than calcium silicate hydrate [8]. On the other hand, the resistance of an alkali-activated, two-source binder to an acid attack may be more complicated as the reaction products in the binders are C-A-S-H and N-A-S-H and possibly the hybrid C-N-A-S-H [1]. Very few studies of the acid resistance of alkali-activated, two source binders have been conducted thus far, and the relationship between the reaction products and the acid resistance capability still needs to be elucidated.

Chloride resistance is another important factor with regard to the durability of concrete. Although chlorides are not significantly harmful to concrete, chlorides may cause corrosion of an embedded reinforcement through a depassivation process, leading to serious damage to the concrete [9,10]. Ismail et al. [10] found in their study of the chloride penetration of alkali-activated slag/fly ash binder (fly ash contents at 0%, 25%, 50%, and 75% of the total binder) that an addition of fly ash in slag binder caused an increase in the porosity and chloride permeability due to the formation of more porous sodium aluminosilicate (N–A–S–H) type gels. Their study showed better chloride resistance in alkali-activated slag dominated by C–A–S–H gels compared to alkali-activated fly ash [10]. The addition of metakaolin to the slag binder also led to a reduction in the chloride permeability compared to an alkali-activated slag binder, showing that the addition of metakaolin as a secondary aluminosilicate precursor contributes to the refinement of the pore network and accordingly a reduction in the absorptivity [11].

Studies of chloride resistance in alkali-activated, two-source binders are very limited, and the relationship between the reaction products and the chloride resistance capability needs to be elucidated. This study is thus to investigate the influence of the slag content on the chloride and acid resistances of the AFS paste. A series of tests related to the chloride and sulfuric acid resistance capabilities were conducted and the effects of reaction products and their contents on the chloride and acid resistance capabilities were discussed. Chloride penetration depth and sulfuric acid-resistant reaction product were quantitatively evaluated through a steady-state chloride penetration test and NMR analysis, respectively.

2. Materials and mix proportion

In this study, Class F fly ash and blast furnace slag (BFS) were used as binder materials. For comparison, ordinary Portland cement (OPC) samples were manufactured. The Class F fly ash (classified according to ASTM C 618) and blast furnace slag were obtained from a power plant and from a steel plant both located in South Korea, respectively. Their chemical compositions are listed in Table 1.

A sodium silicate liquid solution ($SiO_2/Na_2O = 1.0$) was prepared as an alkali-activator. It was made by mixing a NaOH solution with a concentration of 4 mol/L and water glass (Korean industrial standards (KS) Grade-3; SiO_2 (29%), Na_2O (10%), H_2O (61%), specific gravity 1.38 g/mL) in accordance with the procedure developed by Lee and Lee [33]. The NaOH solution with a concentration of 4 mol/L was prepared by adding solid NaOH with a purity level of 98% to distilled water.

The alkali-activated paste prepared was cast into 50 mm cubic molds. All of the samples were cured at a temperature of 20 °C and at a relative humidity of 50% in a room with a constant temperature and humidity. After one day, all of the samples were removed from their molds and stored in the conditioning room until the day of testing.

Sample names (S0, S10, S30, and S50) are denoted with specific codes. The label 'S' represent blast furnace slag, and the numbers, '0', '10', '30', and '50' indicate the percentage of slag amount in the AFS binder by weight, respectively. For comparison, an OPC sample was manufactured using ordinary Portland cement with a water to cement ratio of 0.4.

Table 1
Chemical composition of the binder materials.

Oxide (wt. %)	Fly ash (FA)	Blast furnace slag (BFS)
CaO	4.41	42.47
SiO_2	67.26	35.17
Al_2O_3	14.76	13.93
Fe_2O_3	4.07	0.58
SO_3	–	2.03
MgO	1.29	4.12
Na_2O	2.04	0.15
K_2O	1.39	0.46
LOI	3.57	0.18

3. Experimental details

3.1. Sulfuric acid test

The sulfuric acid test was conducted as follows. After 28 days of curing, the samples were immersed in a 10% sulfuric acid solution (H_2SO_4) for 28 days and for 56 days to investigate the resistance of the AFS binder to an acid attack. The solution was refreshed once a week.

X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, and ^{29}Si MAS NMR spectrometry were utilized to investigate the microstructures of the AFS samples immersed in the sulfuric acid solution. Mass changes, water absorption rates, volume of permeable voids, and compressive strength were also measured to investigate the physical changes of the AFS samples.

The powdered samples were taken from the middle of the AFS samples by mechanical grinding. The XRD data were recorded on a Rigaku D/MAX-2500 machine using Cu Kα radiation at a scanning rate of 2°/min from 2° to 160° in the 2° mode. The powdered samples were also analyzed by Fourier transform infrared (FT-IR) spectroscopy (Model FT-IR 4100, JASCO, Japan).

A ^{29}Si MAS NMR spectrometer (Varian NMR system, WB500) was used to compare the solid-state NMR spectra of the AFS samples immersed and not immersed in sulfuric acid solution. The ^{29}Si resonance frequency was 99.31 MHz and the spinning rate was 3 kHz. The spectra were acquired using a pulse length of 2.0 μs, and a relaxation delay of 20s was chosen. Tetramethylsilane (TMS) was used as reference for the ^{29}Si NMR spectra. The reaction product contents (N-A-S-H and C-A-S-H) of the sample immersed in the sulfuric acid solution were evaluated through a NMR analysis. The method used to determine N-A-S-H and C-A-S-H can be found in Lee and Lee [12]. This was helpful to understand the resistance of the reaction products against the acid attack.

The mass change was measured to investigate the degradation of the samples resulting from the formation of a new phase after sulfuric attack. The compressive strength was measured to compare the difference between the samples immersed and not immersed in sulfuric acid solution. Each value was measured three times, and the average value of these three measurements was used as the final value.

3.2. Chloride penetration test

A steady-state chloride penetration test was conducted in accordance with a previously published method [13], as follows. After 28 days of curing, the side and top surfaces of 50-mm cubic