Inhibiting efflorescence formation on fly ash–based geopolymer via silane surface modification

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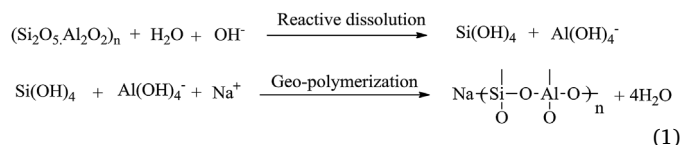
ABSTRACT

Efflorescence can be a critical issue for the application of alkali-activated fly ash–based geopolymer products, especially when the products are in a moist environment. In this study, a new method was explored to inhibit efflorescence of fly ash–based geopolymer via silane surface modifications. After the modification, the surface of the geopolymer was transformed from hydrophilic to hydrophobic, with a water contact angle of 144.1°, and the capillary absorption and diffusion of water were significantly suppressed; and as a consequence, the soluble alkali ion leaching was reduced. Analysis by Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction, and size-exclusion chromatography demonstrated that the selected silane is attached successfully onto the surface of the fly ash–based geopolymer via chemical bonding instead of via physical absorption. A possible reaction mechanism for the silane surface modification of the fly ash–based geopolymer is proposed.

1. Introduction

Ordinary Portland cement (OPC) is the most widely used binder material in construction technology; however, cement production accounts for approximately 5–8% of all man-made CO_2 emissions [1]. To reduce the cement industry's environmental impact, researchers have been motivated to explore new cementitious materials as partial or complete replacements for OPC. In recent years, geopolymer, which can be synthesized via chemical activation (geopolymerization) of aluminosilicate raw materials, has drawn increasing attention. Geopolymer essentially consists of repeating units of alluminosilicate (–Si–O–Al–O–) [2,3]. Fly ash, the by-product of coal fuel combustion, is now being widely used in the preparation of geopolymer binder because of its high content of silica and alumina and worldwide availability [4,5].

Geopolymer synthesis is the process of forming an amorphous three-dimensional network structure [3,6], usually by alkali activation of silica and alumina. Compared to the hydration of OPC, the formation of a geopolymer matrix experiences a reactive dissolution and geopolymerization process, as shown in Eq. (1), assuming sodium oxide is used as the alkali activator.
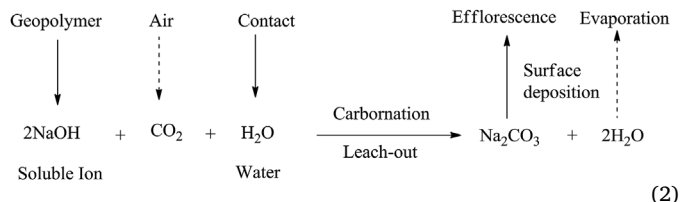
$$(Si_2O_5.Al_2O_2)_n + H_2O + OH^- \xrightarrow{\text{Reactive dissolution}} Si(OH)_4 + Al(OH)_4^-$$

$$Si(OH)_4 + Al(OH)_4^- + Na^+ \xrightarrow{\text{Geo-polymerization}} Na\left(\overset{\overset{|}{O}}{\underset{}{Si}}-O-\overset{\overset{|}{O}}{\underset{}{Al}}-O\right)_n + 4H_2O \quad (1)$$

The selection of an appropriate alkali activator is essential for the activation of fly ash to release free $[SiO_4]^-$ and $[AlO_4]^-$ tetrahedral units [7]. The concentration of the alkali activator had a very important influence on the properties of geopolymer binders because it determines the reaction extent and the densification of the microstructure [8,9]. However, high loading of Na_2O and weak complexation of alkali metal ions with an aluminosilicate framework leads inevitably to severe efflorescence on the geopolymer materials [10–13], especially when moisture transfer occurs in the material. A substantial amount of research has been conducted to reveal the mechanisms for efflorescence in geopolymer as well as other type of alkali activated cement (AAC) materials and to model the process [14–16]. The efflorescence in AAC materials is usually more violent than that in OPC [17], especially when a structure made of AAC materials is in contact with damp soil at its base. Such severe efflorescence not only affects aesthetics of the structure, but also inevitably causes deteriorating consequences of its

long-term stability [9,16,18,20]. Based on previous studies, the efflorescence products on the surface of sodium alkali–activated fly ash–based geopolymer are mainly sodium carbonate ($Na_2CO_3 \cdot nH_2O$) [20,21]. Thus, the efflorescence process in such geopolymer can be simplified as Eq. (2):

$$
\begin{array}{ccc}
\text{Geopolymer} & \text{Air} & \text{Contact} \\
\downarrow & \vdots & \downarrow \\
2NaOH & + \quad CO_2 \quad + & H_2O \\
\text{Soluble Ion} & & \text{Water}
\end{array}
\xrightarrow[\text{Leach-out}]{\text{Carbornation}}
\begin{array}{c}
\text{Efflorescence} \quad \text{Evaporation} \\
\text{Surface} \\
\text{deposition} \\
Na_2CO_3 \quad + \quad 2H_2O
\end{array}
$$

(2)

The mechanism of efflorescence is a combined leaching and carbonation process. Soluble alkali metal ions move outward by diffusion, enriching the surface with the soluble ions and forming crystalline precipitates as the water evaporates. The process also involves the precipitation of a carbonated product like sodium carbonate. Therefore, the two main factors that affect efflorescence on alkali-activated geopolymer materials are the soluble ion content and water. It is widely accepted that efflorescence occurs more quickly and dramatically on geopolymer in a wet environment than in a dry environment [14,15,19]. Water plays a key role in efflorescence on geopolymer materials because it is the carrier of soluble alkali metal ions. In addition, the capillary absorption of water and the outward diffusion of water in geopolymer materials provide a driving force for the leaching-out of the soluble ions.

Previous studies that sought to restrain efflorescence on fly ash–based geopolymer materials focused mainly on reducing the content of soluble ions in the matrix. One effective method is to form a more compact and fine microstructure with the use of different admixtures, such as aluminate cement [9] and slag [20]. Hydrothermal curing is also an effective method because it both promotes the extent of the reaction of raw materials and contributes to the formation of a denser structure [9,12,15]. The use of potassium hydroxide as an alternative alkali activator was also proven to be a useful technique [22] because of the strong complexation of potassium cations with an aluminosilicate framework. To the best of our knowledge, however, no study has examined the inhibition of efflorescence on fly ash–based geopolymer materials via isolation of the water supply. In addition, the above-mentioned countermeasures for inhibition of efflorescence are all applied during the manufacture or curing of the geopolymer materials rather than on the hardened materials.

It should be noted that most concrete deterioration phenomena involve the ingress of water. Surface treatment of hardened OPC concrete has proven to effectively prevent water ingress and the resulted deterioration and to thus improve the concrete durability [23–25]. Alkyl silane and/or silane derivatives have been widely used for surface treatment of OPC concrete to form a hydrophobic surface and to significantly reduce capillary water absorption [21]. However, it remains unknown whether such a surface treatment is applicable for fly ash–based geopolymer materials to cut off the water supply. It is obvious that OPC concrete and fly ash based geopolymer concrete have significantly different hydration/geopolymerization products and different chemical environments in the pore solutions [9,11,12].

The objective of this study was to examine the effects of silane surface treatment on the efflorescence on fly ash–based geopolymer. A typical alkyl silane monomer was used, and the efflorescence on the surface of treated and untreated geopolymer in contact with water was evaluated. The efflorescence process was observed and recorded with a digital camera. The mechanisms that affect efflorescence on the surface of the geopolymer were investigated by measuring the capillary water absorption and the soluble ion leaching rate. In addition, microstructure and chemical structure measurements such as X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy–energy dispersive spectrometry (SEM-EDS) and X-

Table 1
Composition and fineness of the class F fly ash.

Oxide (wt%)	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	K_2O	TiO_2	Na_2O	LOI	Fineness (cm^2/g)
Fly ash	58.3	24.3	8.3	2.1	3.6	0.7	1.1	0.5	1.7	2670

ray photoelectron spectroscopy (XPS) were also used to attain an in-depth understanding of the surface modification of silane on fly ash–based geopolymer.

2. Experimental program

2.1. Materials and sample preparation

The low-calcium fly ash (class F) used in this study was purchased from Changsha Fly Ash Factory (Hunan, China). The chemical composition and fineness of the fly ash used in this work are shown in Table 1.

The alkali activator used in this work was a mixture of sodium hydroxide and sodium silicate solution with an SiO_2/Na_2O ratio of 1.2 by mole ($Na_2O \cdot 1.2SiO_2$) and a solid concentration of 30 wt%. The raw soluble sodium silicate (34.2 wt% solid content, 8.2 wt% Na_2O, 26 wt% SiO_2, and an SiO_2/Na_2O ratio of 3.1–3.4 by mole) and sodium hydroxide (NaOH, 99% purity) were purchased from Beijing Sodium Silicate Factory. The sodium hydroxide and deionized water were added into the sodium silicate solution. The solution was continuously stirred until the sodium hydroxide solid was completely dissolved, then the mixture was cooled down to room temperature and a clear activator solution was obtained. The mix proportion of the fly ash-based geopolymer samples are listed in Table 2.

The pastes were mixed for 2 min and molded into specimens with three different dimensions: 40 mm × 40 mm × 160 mm for mortar flexural and compressive strength tests, 75 mm × 2.5 mm × 12.5 mm for the hydrophobicity test (JC/T 902-2002), and 20 mm × 20 mm × 20 mm for the leaching test. The molded specimens were then sealed with a plastic film to preserve moisture in the mixture and stored in the typical laboratory condition with a room temperature of 23 ± 2 °C and a relative humidity of 50 ± 5% for 24 h. After demolding, the specimens were cured in an air-conditioned fog room for 28 days at 20 °C and a relative humidity of greater than 95%.

Octyltriethoxysilane, purchased from Dow Corning Corp., was selected as the surface treatment agent. Its chemical formula is $H_3C \diagdown\diagup\diagdown\diagup Si(OEt)_3$. Before the silane treatment, the 28d cured 75 mm × 25 mm × 12.5-mm geopolymer samples were taken from the curing room and put in the typical laboratory condition for at least 24 h. The surface treatment was realized by immersion the samples in the silane monomer liquid for either 60 or 120 s. All sides of the prismatic samples were treated. Table 3 summarizes the types of specimens used in this study.

2.2. Testing methods and characterization

The compressive strength and flexural strength of geopolymer samples with and without surface treatment was tested with a universal testing machine (SANS 10t) according to the Chinese national standard GB/T 17671-1999.

Table 2
Mix proportion of the fly ash based geopolymer samples.

	Fly ash (g)	Water (g)	Activator solution (g)	Na_2O/powder (wt%)	Water/powder (wt%)
Sample	1000	36	720	10	55