Efflorescence: A Critical Challenge for Geopolymer Applications?

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Abstract: Efflorescence is the formation of white salt deposits on or near the surface of concrete. For ordinary Portland cement (OPC) concrete, efflorescence is generally harmless except for the discolouration, and is best described as being 'a skin trouble and not a deep-seated disease'. However, for geopolymers, as they contain much higher soluble alkali content than conventional cement, efflorescence can be a significant issue when the products are exposed to humid air or in contact with water. In this study, the efflorescence phenomenon of geopolymers that synthesised using different activators, solid materials and curing conditions is observed. The efflorescence product is mainly sodium carbonate heptahydrate ($Na_2CO_3 \cdot 7H_2O$). The efflorescence potential has been compared via measurements of cation concentrations by atomic absorption spectroscopy (AAS), and determination of pH and electrical conductivity of geopolymer leaching solutions. At the same alkali content (in terms of Na_2O), geopolymers synthesised at high temperature (80°C×28 d) exhibit less efflorescence rate than those synthesised at low temperature (20°C×28 d). NaOH activated geopolymers possess slower efflorescence than the sodium silicate solution activated specimens. Adding 20% slag can effectively reduce the initial efflorescence of a fly ash geopolymer. From a long term view, however, the efflorescence potential of such samples could be equivalent to the activated 100% fly ash when considering the alkali leaching results. Further investigations to prevent efflorescence, or at least to reduce its rate, are urgently required for wider applications of fly ash-based geopolymers.

Keywords: Geopolymer; Efflorescence; Fly ash; Leaching; Carbonation

1. Introduction

Geopolymer has emerged as a 'green' binder with high potential for manufacturing sustainable concretes. This innovative material can use industrial wastes, such as fly ash and metallurgical slags, as raw materials. Because the formation is usually completed at room temperature or slightly elevated temperature (40-80°C), and because it does not need the high temperature calcination and milling processes required in Portland cement clinker manufacturing, the emissions reduction compared to Portland cement can be up to 80%, greatly depending on the geopolymer mixture formula and materials supply [1, 2]. In the past decade, geopolymer concretes produced on laboratory scales have been widely reported to display similar engineering properties to OPC concretes, in many cases with superior mechanical properties when subjected to high temperature [3, 4] and highly corrosive media [5, 6]. However, using geopolymer to fabricate concretes is still rare in the real-world compared to normal Portland cement concretes. The slow commercialization of geopolymer relates to many technical issues, practical costs and durability considerations [7].
Efflorescence, the formation of white salt deposits on or near the surface of concrete, is one such issue [8]. For OPC concrete, efflorescence involves the reaction of $Ca(OH)_2$ with water and CO_2, and generally harmless except for the discolouration. However, for geopolymers, as they contain much higher soluble alkali metal concentrations than conventional cement, efflorescence could be a significant issue when the products are exposed to humid air or in contact with water [9]. In addition to the wet conditions, factors causing efflorescence include the reactivity of raw materials [10], alkali metal type [11, 12] and reaction condition [12]. Najafi Kani et al. [12] proposed two possible routines to reduce efflorescence (1) adding alumina-rich admixtures and (2) hydrothermal curing. The use of 8% calcium aluminate cement as an admixture greatly reduces the mobility of alkalis; curing at temperatures of ≥65°C also provides a significant effect in efflorescence reduction [12].
The utilization of slag in geopolymer synthesis can significantly shorten the setting time of fly ash–based geopolymer and increase the mechanical strength at early age [13, 14]. It is a highly promising method to avoid hydrothermal curing, ensuring that the industry is able to conveniently fabricate geopolymer concretes with existing equipment and procedures. The effect of slag addition on efflorescence has been reported [12], but not yet fully understood. In this paper, geopolymers

synthesised by sodium silicate activation of 100% fly ash, and a blend of 80% fly ash and 20% slag, are investigated to further understand the effect of slag addition on efflorescence. The effect of soluble silicate is studied by using a geopolymer synthesised by NaOH activation of 100% fly ash in comparison to the sodium silicate activated mix.

2. Experimental

2.1 Materials

The fly ash used in this work was obtained from Callide Power station in Queensland, Australia. The granulated blast furnace slag was a commercially available product supplied by a local concrete company. The chemical compositions of the fly ash and slag were determined by X-ray fluorescence (XRF), and are shown in Table 1.

Table 1. Oxide compositions of fly ash and slag as determined by XRF, loss on ignition at 1000°C (LOI), wt.%.

	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	Fe_2O_3	P_2O_5	SO_3	TiO_2	LOI
Fly ash	54.4	32.1	1.06	0.75	0.22	0.14	7.49	0.09	0.04	2.14	0.85
Slag	33.4	14.4	43.2	6.1	0.34	0.23	0.7	0	0.6	0.6	0.5

The mineral components of the fly ash and slag were examined by X-ray diffractometry (XRD). The XRD data were collected using an ARL 9900 Series X-ray workstation (Thermo Scientific) with Co Kα radiation, operated at 40 kV and 40 mA, with a step size of 0.02^o and count time of 1 s/step from 8 to 80° (2θ). The results are shown in Figure 1. The particle size distribution was determined by a laser particle size analyzer (Malvern Mastersizer 2000), and is presented in Figure 2. The surface area of the fly ash and slag as estimated by this method is 0.94 and 0.69 m^2/g, respectively.
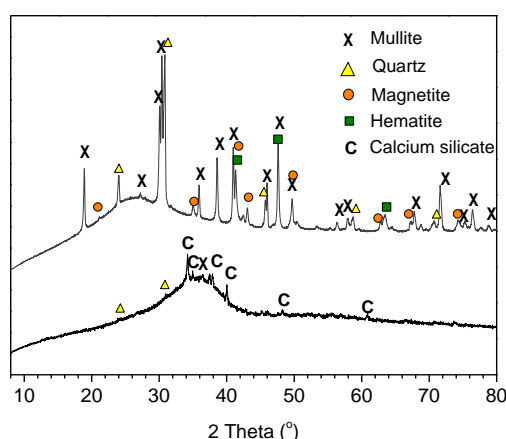

Figure 1. XRD pattern of fly ash and slag. Phases in fly ash: mullite - $Al_{1.83}Si_{1.08}O_{4.85}$ (ICSD# 43298), quartz - SiO_2 (89280), magnetite - Fe_3O_4 (ICSD# 43001), hematite - Fe_2O_3 (ICSD# 15840); in slag: tricalcium silicate - Ca_3SiO_5 (ICSD# 81100), quartz (s) - SiO_2 (ICSD# 71392 and 42498).

The activator solutions include a NaOH solution and a sodium silicate solution. The NaOH solution was prepared by dissolving NaOH pellets (purity of 99%) in water to a concentration of 12 mol/L, and cooled to room temperature. The sodium silicate solution was a mixture of D-Grade[TM] liquid sodium silicate (Na_2O=14.7 wt.%, SiO_2=29.4 wt.%, PQ Australia Pty. Ltd.) and the prepared NaOH solution in a proper ratio. It contains 24.1 wt.% of SiO_2, 16.6 wt.% of Na_2O. This activation solution was allowed to cool and equilibrate for ~3 h prior to use.
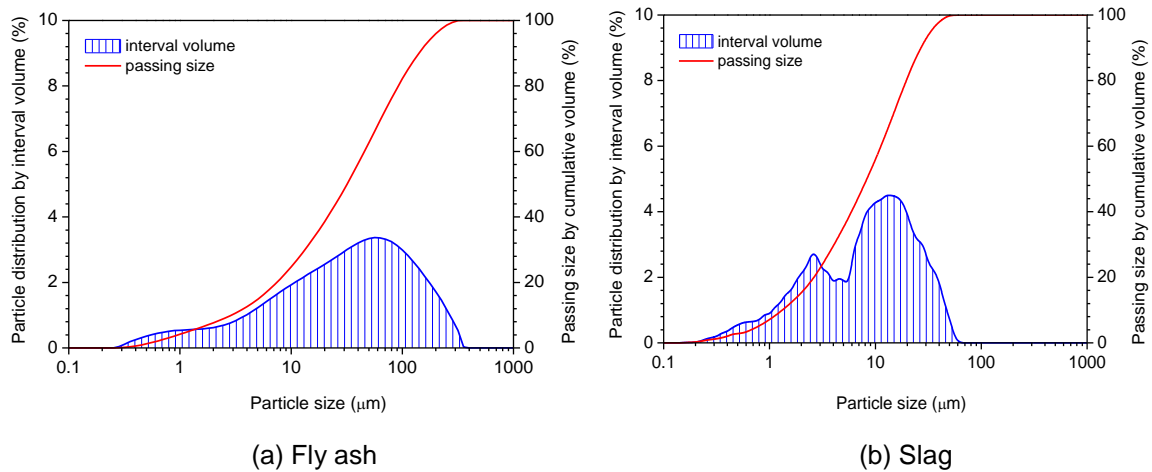
(a) Fly ash (b) Slag

Figure 2. Particle size distribution of solid materials

2.2 Geopolymer synthesis and strength testing

Geopolymer specimens were synthesized by adding the activator solutions to solid precursor (fly ash or a blend of fly ash and slag) at a constant Na_2O/precursor mass ratio of 5.8%. A small amount of additional water was used during mixing to achieve a suitable workability. The fresh pastes were poured into Ø23 mm × 24 mm cylindrical molds and subjected to humid curing with RH>90% at 25°C for 1 d. The demolded specimens were denoted as 'SN-FA100', 'NS-FA80SL20' and 'N-FA100', in which 'SN' means the activator is sodium silicate and 'N' means NaOH solution, 'FA100' means that the solid precursor is 100% fly ash and 'FA80SL20' means a blend of 80% fly ash and 20% slag. Specimens were further aged at 80±1°C or 25±2°C in sealed glass containers. To provide humid conditions, the containers contained water at the bottom but not in contact with specimens.

The compressive strength of geopolymers was tested at 1, 7, 14, 28, and 90 d using an MTS universal mechanical testing machine. The loading speed was 0.5 mm/min. Before testing, the top surfaces of the cylindrical specimens were carefully sanded flat, and the specimens reached a diameter to height ratio of 1:1.

2.3 Efflorescence evaluation and leachant analysis

To observe the severity of efflorescence, the 90 d-aged samples were put in contact with water at the bottom surface, and allowed to react under ambient conditions for 24 h. The white efflorescence product that scratched from the surface of geopolymer specimens was analyzed by XRD using conditions as described above.

To quantify the efflorescence potential, the leachability of alkali metals was investigated. The 90 d-aged samples were fractured and sieved. Particles between 1.25 and 1.50 mm were collected, mixed with deionized water in a solid/water mass ratio of 1:50 and stored at 25±2°C in laboratory conditions. 20 mL of statically leached supernatant solution was filtered and diluted with deionized water in a ratio of 1:25. This diluted solution gave suitable Na^+ and K^+ concentrations for atomic absorption spectroscopy (AA-7000, Shimadzu) analysis. The pH value and electrical conductivity of leaching solution were also measured using a MeterLab ION 450 pH and conductivity analyzer (Radiometer Analytical).

3. Results

3.1 Compressive strength

Figure 3 presents the strength development of geopolymers under two aging conditions. Geopolymers synthesized at 80°C exhibit much higher strength than those at 25°C at early age (<28 d). However, long-term high temperature curing has a negative effect on the strength retention, particularly for specimens synthesized with sodium silicate solution. The strength of geopolymers synthesized with NaOH solution is much lower than those activated with sodium silicate, but both increase with time at 80°C and 25°C at later age. This trend is contrary to the strength development of geopolymers synthesised with sodium silicate. As expected, slag addition significantly increases the early age strength.
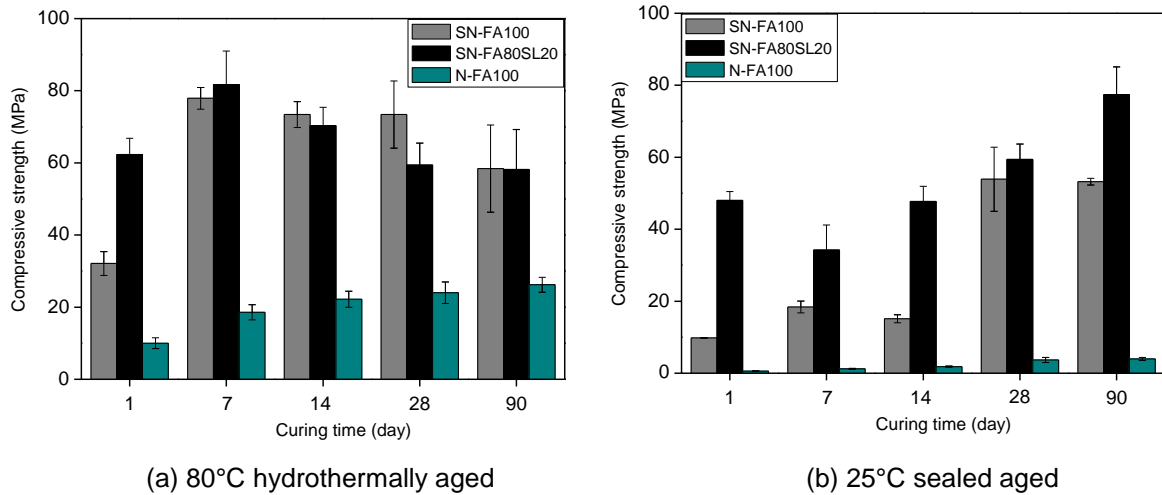
<table>
<tr><td>(a) 80°C hydrothermally aged</td><td>(b) 25°C sealed aged</td></tr>
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Figure 3. Strength development of geopolymers under different conditions

3.2 Efflorescence observation

Figure 4 and Figure 5 show visible formation of efflorescence on the surface of geopolymers. For the 80°C hydrothermal aged geopolymers, efflorescence is formed on specimens NS-FA100 and N-FA100 after 12 h in contact with water, but not naked-eye observable on NS-FA80SL20. In comparison, the 25°C sealed aged geopolymers exhibit more rapid efflorescence. NS-FA100 and N-FA100 both show efflorescence after 3 h and the white products become thicker after 6 h. NS-FA80SL20 specimens do not show efflorescence after 24 h in contact with water, similar as 80°C hydrothermal aged geopolymer. The trend that hydrothermal curing can reduce efflorescence is consistent with the results by Najafi Kani et al. [13].

To gain a better understanding of efflorescence mechanism, the white particulate product grown on the NS-FA100 specimen was collected and studied by XRD. In Figure 6 it shows that the efflorescence product is a hydrous alkali carbonate, $Na_2CO_3 \cdot 7H_2O$. Some minor diffraction peaks are not identifiable, which may be due to some particles of geopolymer gel and/or fly ash present in the sample. The carbonate should crystallize from inside pores and grow outside the specimens. The availability of sodium cations is the main reason for the efflorescence growth.

3.3 pH measurement of leaching solutions

Figure 7 presents the pH values of the leaching solutions. In general, geopolymeric gels formed by hydrothermal aging are more stable than those formed by room temperature aging in the early leaching period. After 24 h leaching, the pH values in the leaching solutions of hydrothermally cured samples are lower than in those which were room temperature cured, except for in N-FA100. The hydrothermally cured N-FA100 releases much more OH^- after 24 h leaching, unlike the hydrothermally cured NS-FA100 and NS-FA80SL20. Slag addition provides some benefits in decreasing the leaching rate of OH^- at early period, but does not change the leaching behavior from a long term point of view. The soluble silicate in the activator does not have any inhibition effect on OH^- leaching in the cases studied. The pH measurement result fits well with the efflorescence observation results.

3.4 Electrical conductivity of leaching solutions

Figure 8 presents the electrical conductivity of the leaching solution of geopolymer particles. The conductivity increases sharply with the leaching time from 3 to 12 h and increases slowly after 24 h. Comparing with the pH testing results, the electrical conductivity variation trend is consistent with the pH variation in the early stages of leaching (within 24 h). The electrical conductivity of NS-FA100, either by hydrothermal ageing or room temperature ageing, fits exactly the same trend as pH. However, the conductivity is nearly constant in all the 96 h-leaching solutions of sodium silicate activated samples, regardless of the curing conditions. This trend may be due to the effects of dissolved Si species. Si species start to form gels when their concentrations reach a certain level, and this will reduce the transport of cations in the solutions. In general, hydrothermal curing reduces the leaching rate in the period studied.
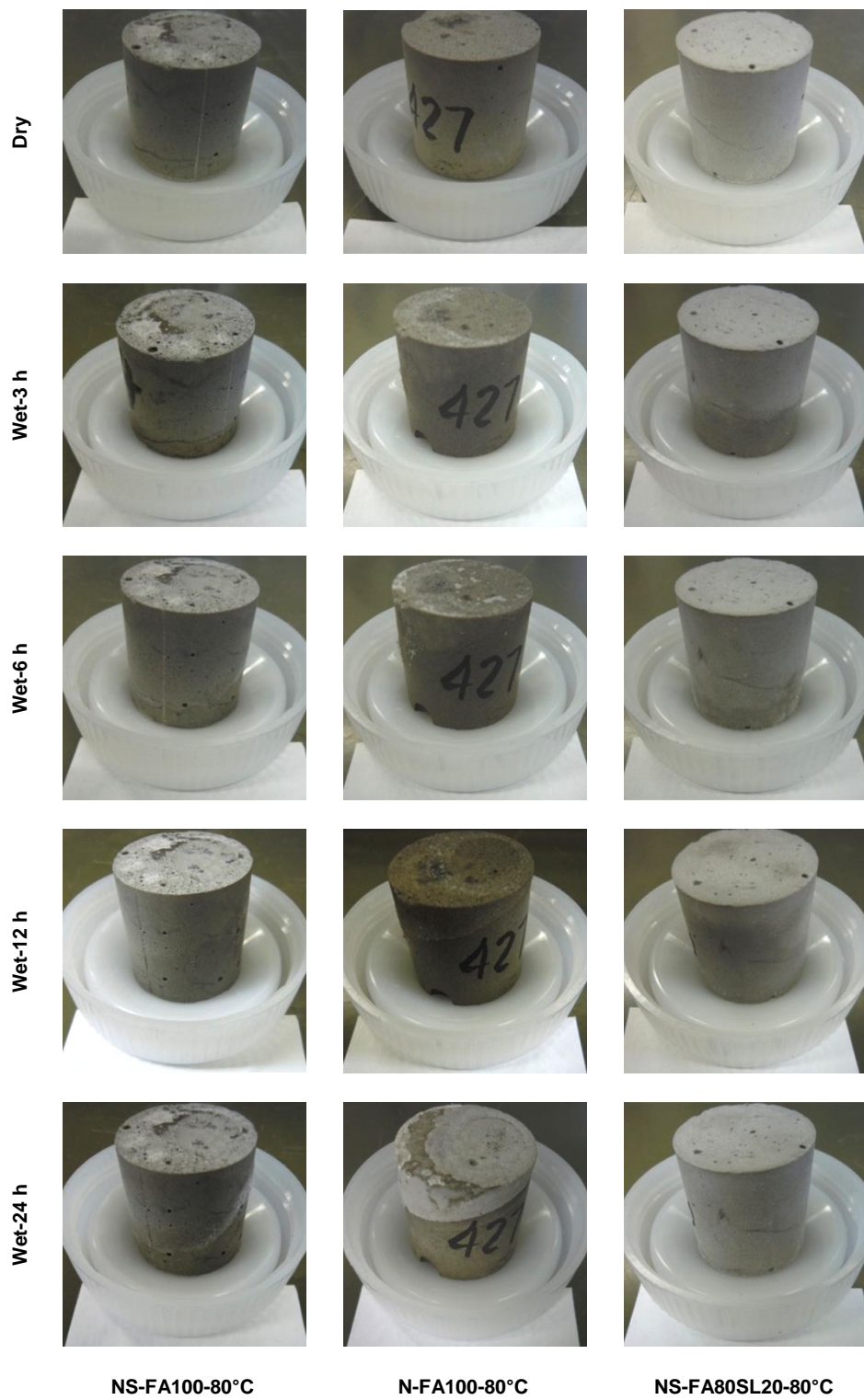
Figure 4. Efflorescence of 80°C hydrothermal 90 d-aged geopolymer specimens with the bottom in contact with water
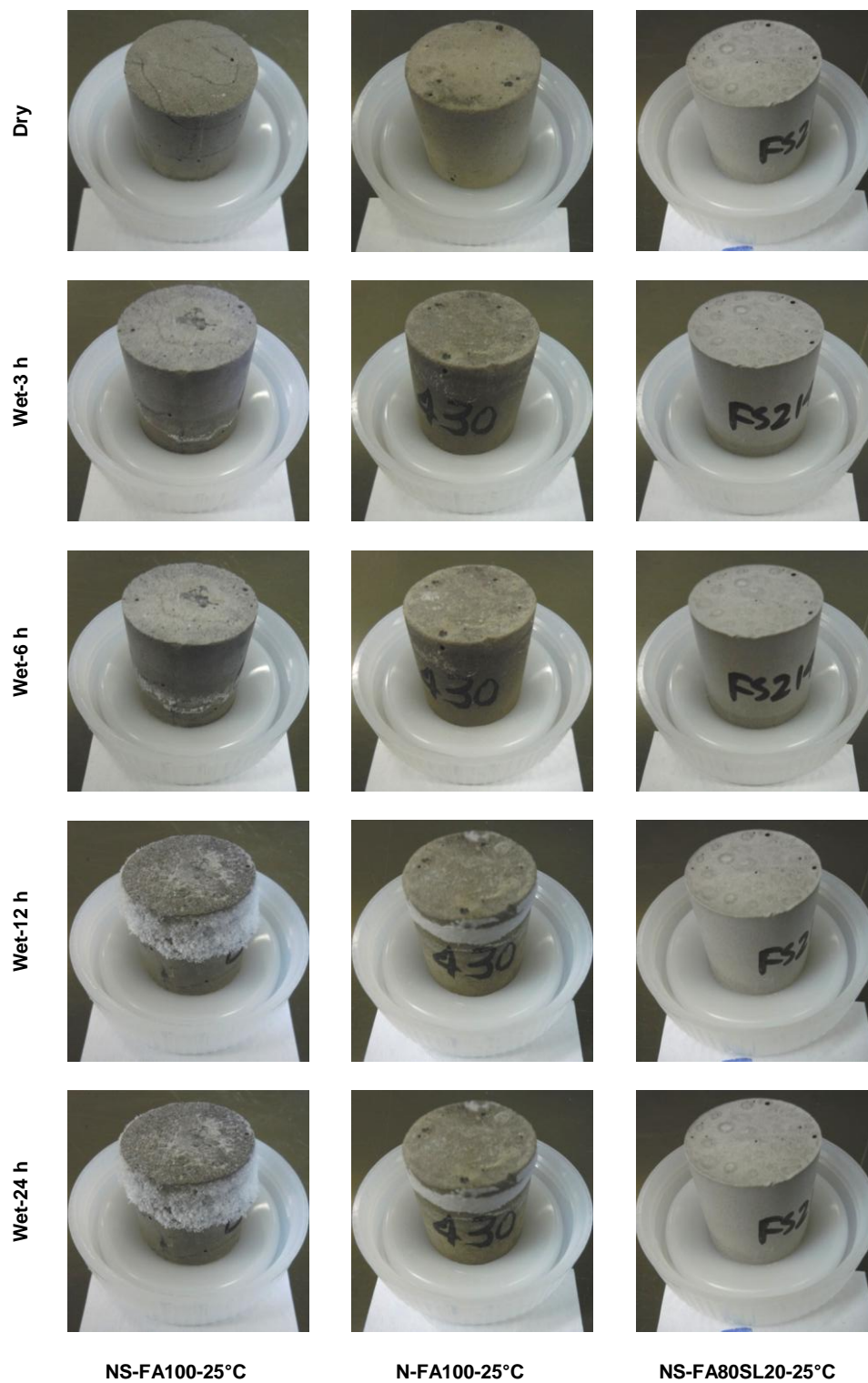
Figure 5. Efflorescence of 25°C sealed 90 d-aged geopolymer specimens with the bottom in contact with water
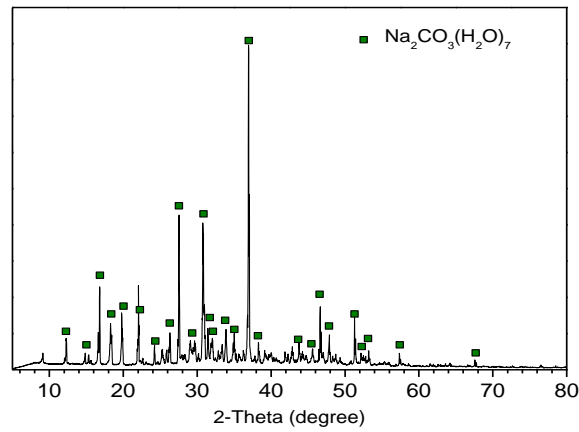
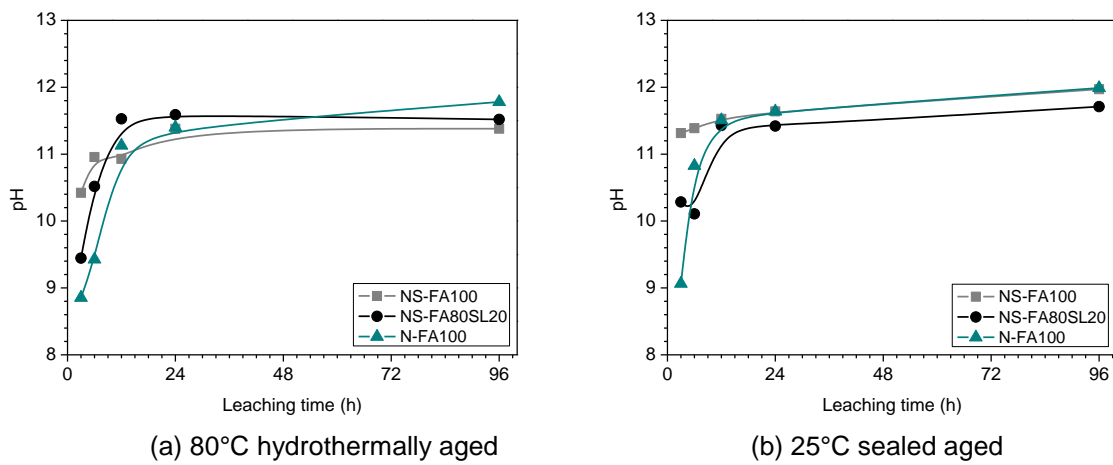**Fig.6. XRD pattern of the efflorescence product collected from geopolymer surface**

(a) 80°C hydrothermally aged

(b) 25°C sealed aged

Figure 7. The pH values of the leaching solution of 90 d-aged geopolymer particles

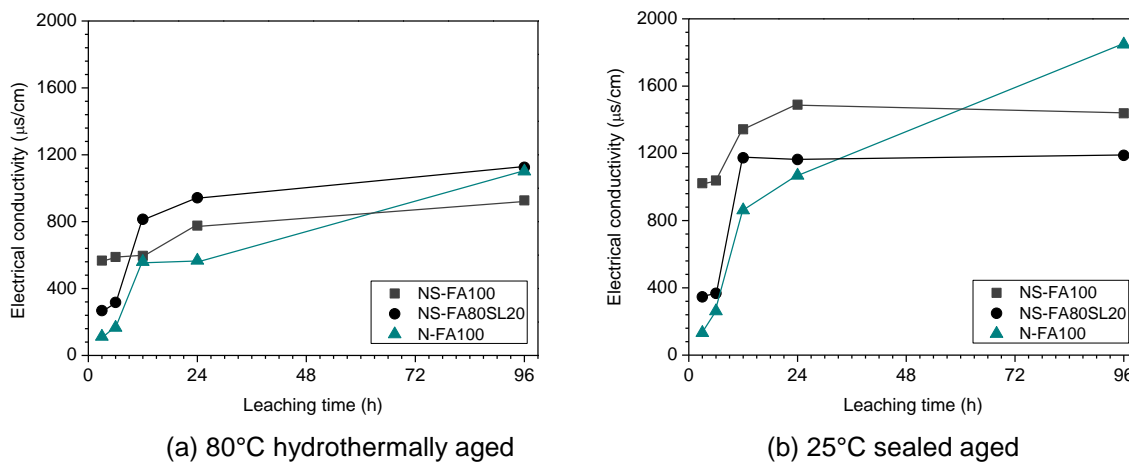(a) 80°C hydrothermally aged

(b) 25°C sealed aged

Figure 8. Electrical conductivity of the leaching solution of 90 d-aged geopolymer particles

3.5 Alkali metal concentration in leachant

Figure 9 shows the sodium and potassium concentrations in the leachant as determined by atomic absorption spectroscopy. The results indicate that sodium is the main leached alkali metal, as the activator is sodium based. For sodium silicate activated geopolymers, the addition of slag reduces the total alkali leaching rate and also the leaching amount. The hydrothermal aging environment is helpful in reducing the alkali leaching rate, but it has very limited influence on the total alkali leaching amount. This is consistent with the pH testing results. In combination with electrical conductivity

measurements, it is likely that Na$^+$, K$^+$ and OH$^-$ ions are key contributors to the conductivity of leaching solutions.
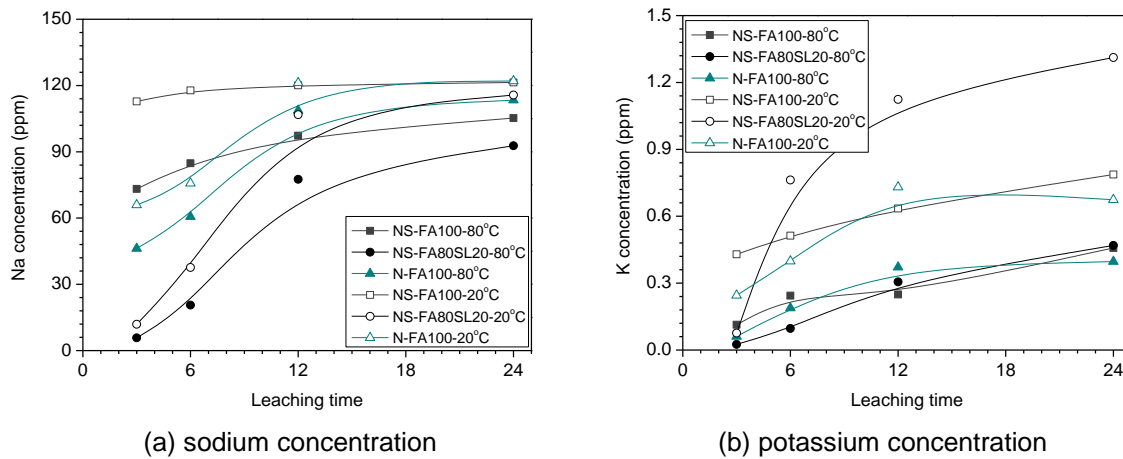

(a) sodium concentration   (b) potassium concentration

Figure 9. The concentration of alkali metals in leachant (not diluted) as determined by atomic absorption spectroscopy

4. Discussion

4.1 Effects of soluble silicate in activator on efflorescence

The use of a soluble silicate-containing activator is more favorable for achieving high strength geopolymers [16]. This is partially because of the more compact microstructure and higher volume of gels, either for metakaolin based geopolymers or for fly ash-based geopolymers [17, 18]. This is again shown in Figure 3. The pore solution analysis shows that an increased soluble silicate content in a geopolymer mixture tends to decrease the concentration of alkali metals [19]. This means that there will be less alkali metal cations to be leached from the pore solution. However, from the efflorescence appearance shown in Figure 4 and Figure 5, the soluble silicate present the in activator has a limited influence on the efflorescence reduction. Instead, the efflorescence becomes even heavier at early time (<12 h), and this is consistent with consideration of the leachability of OH$^-$ and the concentration of alkali metals as indexes of efflorescence potential.

The pH and the concentration of alkali metals in the first 12 h are higher in NS-FA100 leaching solution. After 12 h, these two indexes show that NS-FA100 and N-FA100 are similar in efflorescence potential. The sodium concentration seems to reach equilibrium leachability after 24 h. This trend is consistent with the results of Zheng et al. [20], who observed that their geopolymer cylinders released 40 to 60% of the total sodium after 45 h of immersion in acid solution, and kept constant at longer leaching time [20]. The faster approach to leaching equilibrium in the current study is mainly because the geopolymers are fractured to 1.25-1.50 mm size. The total leached alkali concentrations in NS-FA100 and N-FA100 are very close, particularly for the room temperature cured samples. This means that the efflorescence depends not only on the pore solution, but more significantly on the availability of alkali metal cations in geopolymeric gels. The soluble silica present in the activator can promote the early age efflorescence of geopolymers under wet conditions, and has limited influence on the long term efflorescence potential.

4.2 Effects of calcium on efflorescence

Using slag as a setting modifying and strengthen admixture introduces considerable calcium in the geopolymerization system. A recent study [15] shows that homogeneous and XRD amorphous sodium calcium aluminosilicate hydrates (N-C-A-S-H) are formed in sodium silicate activated fly ash-slag blends. The calcium containing gels help to form a more compact microstructure than when only fly ash is used. This is one of the reasons for the high strength achieved in slag containing geopolymers.

The slag containing specimens NS-FA80SL20, either with hydrothermal ageing (Figure 4) or room temperature ageing (Figure 5), show much less and slower efflorescence. The sodium leaching rate is significantly reduced in NS-FA80SL20 (Figure 9a). However, the pH and the electrical conductivity measurement show different effects under the two curing conditions. Slag addition results in higher pH and electrical conductivity in the leached solution of the hydrothermal cured samples, while for those cured at room temperature, slag addition reduces the pH and electrical conductivity. It means that the calcium plays different role under these two curing condition. It is reported that slag addition increases the alkali metal concentration in pore solution, and also increases the total leaching amount [19]. In

this work, this is true if only considering the concentration of leached potassium. However, the leached sodium at early age (which is much more dominant overall) is lower in the slag-containing geopolymer. This is believed due to the lower porosity in the geopolymeric gels of NS-FA80SL20. The final sodium leached amounts could be very close according to the leaching trend as shown in the curves. This implies that slag addition does not change the sodium binding property in the gels (potassium binding may be changed, but this is not yet clear). This suggests that slag addition reduces the alkali leaching rate, and thus reduces the efflorescence rate, but it will not change the efflorescence potential from a long term view.

4.3 Effects of hydrothermal aging on efflorescence

The use of hydrothermal curing or aging conditions has been suggested as an effective way to reduce efflorescence [13]. This study again demonstrates the positive effects of hydrothermal aging or curing on reduction of efflorescence. This is probably because of the higher reaction extent of raw materials at elevated temperature. The mechanism by which the utilization of reactive aluminates can reduce efflorescence may also lie in the increased extent of reaction [13]. More alumina is involved in geopolymer networks, leading to an increased extent of crosslinking in the geopolymer gels and reducing the mobility of alkalis. This is supported by the results of Temuujin and van Riessen [10], where it is found that heat-treated fly ash exhibits lower reactivity, and so the derived geopolymers show heavier efflorescence compared to original fly ash at the same alkali content. Moreover, as hydrothermal aging or curing also drives the geopolymerization systems to crystallize [21], the crystallization of geopolymeric gels may affect the alkali metal mobility and reduce efflorescence. This aspect needs further examination on the microstructure of geopolymer products.

5. Conclusions

This study shows the fast efflorescence of fly ash-derived geopolymers. The efflorescence occurred in 3 h after specimens were in contact with water at the bottom. The efflorescence could be a critical challenge for geopolymer applications, although its effects on mechanical and chemical stability have not yet been examined. In combination with the measurement of pH, electrical conductivity and alkali metal concentration, the efflorescence potential has been compared between several typical geopolymers. The soluble silica present in the activator can promote the early age efflorescence of geopolymers under wet conditions, but has limited influence on the long term efflorescence potential. Slag addition reduces the efflorescence rate, but does not change the efflorescence potential. Whether calcium present in geopolymers reduces the alkali metal mobility remains unclear, and this requires more investigations at a molecular level. The hydrothermal aging was confirmed to be an effective way to reduce efflorescence. The mechanisms that govern the mobility of alkali metal cations, mainly sodium, require further study on the phase property of geopolymers.

6. Acknowledgement

7. Reference

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