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Efflorescence control in geopolymer binders based on natural pozzolan

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ABSTRACT

This paper addresses methods to reduce efflorescence in a geopolymer binder based on a pumice-type natural pozzolanic material from Taftan, Iran. Geopolymer pastes samples are analyzed for compressive strength and efflorescence formation after curing at 95% humidity for 28 days. To reduce the extent of efflorescence, Al-rich mineral admixtures such as metakaolin, ground granulated blast-furnace slag, and three types of calcium aluminate cements are incorporated into the dry binder at a range of concentrations. Hydrothermal curing at elevated temperatures also shows a positive effect in efflorescence reduction. Calcium aluminate cements show the greatest effect in efflorescence reduction, which is attributed to their dissolution in alkaline media releasing high amounts of alumina into the aluminosilicate geopolymer gel. These results confirm that it is possible to develop a more reliable geopolymer binder with improved properties either by adding a suitable amount of active alumina to precursors such as natural pozzolan, or by manipulating the curing conditions to enhance alumina release from less-reactive precursor phases.

1. Introduction

Geopolymer cements are a group of alkali-activated materials produced by reactions between alkaline solutions (usually alkali metal silicates or hydroxides) and solid aluminosilicates [1]. The main role of alkalis in geopolymerization is initially to generate a sufficiently high pH to activate the aluminosilicate raw materials in geopolymerization reactions, and then to charge-balance the growing aluminosilicate gel framework [2]. The mechanism of geopolymerization is complex, but includes three main stages: (1) dissolution of raw materials in alkaline solution, (2) reorientation of the dissolved species, and (3) polycondensation to form networked gel structures [3,4]. Different parameters influence the formation mechanisms and properties of geopolymer binders, among which the sodium oxide concentration of the activator is one of the most important, as it essentially determines the extent of reaction and the densification of the microstructure [5].

Sodium aluminosilicate geopolymers, particularly those synthesized with a high Na_2O/Al_2O_3 ratio [6–10], can suffer from unsightly efflorescence caused by excess sodium oxide remaining unreacted in the material. Sodium cations are mobile within the pore network, particularly when there is movement of moisture within the sample. One example of such a situation is when a concrete column is in contact with damp soil at its base, so that water moves upwards through the concrete by capillary action and evaporates from its surface, leaving the surface enriched in the alkali cations which were present in the pore solution. The deposited alkalis can then react with atmospheric CO_2, resulting in the formation of the white carbonate surface deposits known as efflorescence. It should be noted that this is distinct from the process of atmospheric carbonation of the binder, which involves reaction between CO_2 and the calcium (and also sodium in alkali-activated materials including geopolymers) present in the solid binder phases [11,12]. Carbonation usually results in binder degradation, pH reduction and the deposition of carbonate reaction products in the bulk of the sample, which may or may not be visible to the naked eye, whereas efflorescence causes the formation of visible surface deposits, and may or may not be accompanied by further degradation of the binder.

The tendency towards efflorescence in geopolymers is due partly to the very open microstructure of some materials which have a lower extent of reaction, partly due to the high alkali concentration in the pore solution [13] and also partly due to the relatively weak binding (and exchangeability) of Na in the geopolymer structure [14–16]. Some attempts have been made to reduce efflorescence by using potassium hydroxide instead of sodium hydroxide in the activator [14,15], because potassium is more strongly bound to the aluminosilicate gel framework [17], and also because potassium carbonate crystals are usually less visually evident than their sodium counterparts.

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In recent years, researchers have investigated the possibility of utilizing a broad range of materials as raw materials in the production of geopolymer cements. The use of artificial pozzolans or aluminosilicate industrial waste materials such as metakaolin and fly ash has been reported by many authors [18–32]. Natural pozzolans are also aluminosilicate-type materials which can be activated with alkaline solutions [6,7,33–35]; particularly good results have been obtained by the alkaline activation of a pumice-type natural pozzolan from Taftan mountain, Iran, and this is the source material used in this investigation.

In this paper, two different procedures are used to reduce efflorescence in a sodium geopolymer binder based on a natural pozzolanic material: firstly, utilizing different Al-rich mineral admixtures (ground granulated blast furnace slag, metakaolin, and several different calcium aluminate cements) to enhance microstructural densification, and secondly, applying hydrothermal curing to increase the extent of reaction of the natural pozzolan.

2. Experimental

The natural pozzolan used in this work was a pumice-type pozzolan obtained from Taftan mountain in the south-east of Iran. The results of chemical analysis according to the standard procedures of ASTM C311 are shown in Table 1. Fig. 1 shows the X-ray diffraction pattern (Philips X'pert diffractometer, Cu Kα radiation, 2°/min, divergence and anti-scatter slits 1° each, receiving slit 0.01 mm) of the pozzolan. The crystalline mineral phases present in Taftan pozzolan include the minerals anorthite (a feldspar mineral), cordierite and tremolite (amphiboles), and biotite (mica), a small amount of quartz, and a small amount of zirconia introduced during the milling process.

The pozzolan was ground in a closed industrial mill to a Blaine specific surface area of 305 m^2/kg. The particle size distribution was determined by a laser particle size analyzer (Malvern Mastersizer 2000), and is presented in Fig. 2. Industrial sodium silicate solution (mass ratio $SiO_2/Na_2O = 0.92$ and SiO_2 content of 31.36 wt.%) and industrial-grade NaOH (99% purity) were used throughout all experiments.

Mixtures were prepared with molar ratios as given in Table 2. The chemical composition of the mixtures was varied by changing the SiO_2/Na_2O molar ratio of the activator and the overall Na/Al molar ratio. To prepare the activating solution, sodium hydroxide pellets were added to sodium silicate solution to reach the desired composition. The solution was then allowed to equilibrate and cool, and combined with the solid binder components to form geopolymers. It is noted that, due to the likely incomplete reaction of the natural pozzolan precursor (i.e. incomplete availability of Al), the Na/Al ratio of the geopolymer gel formed will be higher than the superficial Na/Al ratio calculated from the mix design. The mixtures were all prepared at a constant total H_2O/Al_2O_3 molar ratio of 8.5.

For compressive strength testing, the pastes were cast into 2 cm cubic molds, and cured at around 95% relative humidity (RH) and ambient temperature (25 °C) for 24 h before demolding. After demolding, the specimens were cured at 95% RH at 25 °C until testing of triplicate samples after 28 days using a Toni Technic instrument (Toni Technic, Germany) (Table 2).

To qualitatively investigate the severity of efflorescence, one 28-day cured 2 cm cube paste specimen from each mix was immersed in 40 mL of distilled water, and kept in an open-air atmosphere at ambient temperature (25 °C) until the water was completely evaporated. The results of the efflorescence test were obtained qualitatively by visual comparison of the specimens.

Selected mixes exhibiting relatively high 28-day compressive strengths (P2, P9, P14, P18, and P23) were selected to determine the leachability of alkali, as a quantitative measure of the tendency towards efflorescence. For this test, 1.0000 ± 0.0001 g of ground hardened paste was added to 20 mL of distilled water in a covered container. After 24 h, the solution was centrifuged to remove solids and placed in an oven to evaporate the water, leaving only the leached soluble salts, which were then weighed. This was used as a quantitative measure to describe the extent of efflorescence, based on the fact that alkali mobility is a primary cause of efflorescence.

Among the samples tested, those showing the lowest extent of efflorescence and high strength, primarily P2 and P9, were selected to be the basis of the next stages of the investigation; P14, P18 and P23 were also subjected to some additional analysis to provide information on high-strength alkali-rich samples which tend to be prone to efflorescence. Two different procedures, the use of admixtures and the application of hydrothermal curing, were considered and studied for possible effects in reducing the extent of efflorescence. Metakaolin (Zigma International, India), ground granulated blast-furnace slag (Isfahan Steel Complex, Iran), and three types of calcium aluminate cement (Secar 71 (Kerneos, France), Secar 80 (Kerneos, France), and Koracast (Iran Refractory Products, Iran); Table 1) were incorporated into the dry binder mixes at replacement levels of 2%, 4%, 6%, and 8% by weight. The chemical compositions of the admixtures are given in Table 1.

To investigate the effect of hydrothermal curing on efflorescence reduction, specimens of mixes P2 and P9 were cured hydrothermally in a steam saturated atmosphere at temperatures of 45, 65, 85, 105, and 125 °C for 20 h, after 7 days of precuring at ~95% relative humidity at 25 °C.

To better understand the effects of the admixtures, the dissolution properties of the dry binder (Taftan pozzolan), alone and mixed with the most effective admixture (Secar 71) were studied by mixing 1.0000 ± 0.0001 g of solids with 20 mL of either 1.0 or 10 M solutions of NaOH and KOH solution for periods of up to 72 h. After different leaching times, the liquor portion was collected by centrifuging at 5000 rpm for 10 min, and the leached concentrations of Al and Si were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES), using a Varian 720-ES instrument.

3. Results and discussion

3.1. Extent of efflorescence

Fig. 3 shows the extent of efflorescence at the end of the qualitative (water evaporation) test in a selection of mixes (P2, P9, P14,

Table 1
Chemical composition of raw materials (wt.% as oxides, as determined by X-ray fluorescence).

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O
Taftan pozzolan	61.57	18.00	4.93	6.69	2.63	0.10	1.95	1.65
Secar 71	0.55	70.2	0.2	28.3	0.2	0.1	0.1	0.25
Secar 80	0.3	79.0	0.2	20.0	0.1	0.1	–	0.15
Koracast	–	94.0	0.1	5.4	–	–	–	–
Blast furnace slag	36.06	9.16	0.70	36.91	10.21	1.15	0.70	0.48
Metakaolin	56.5	38.3	0.50	0.15	0.18	–	0.23	0.35

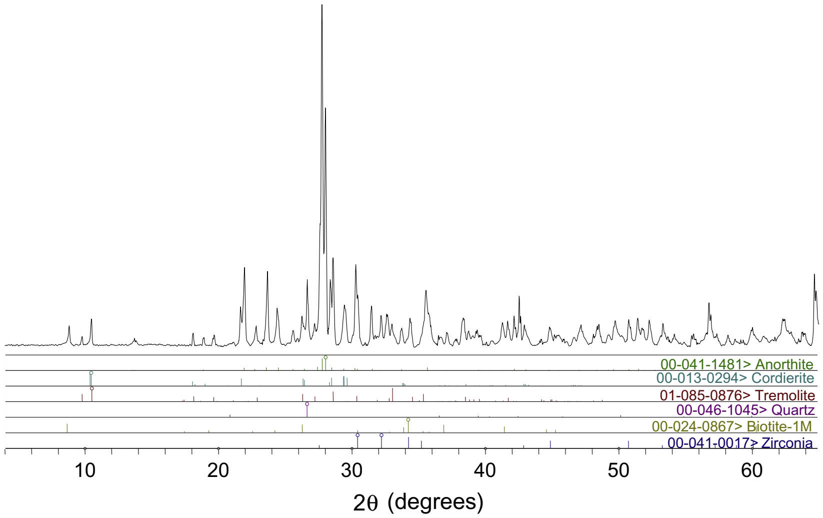

Fig. 1. X-ray diffraction data (Cu Kα radiation) for the Taftan natural pozzolan.

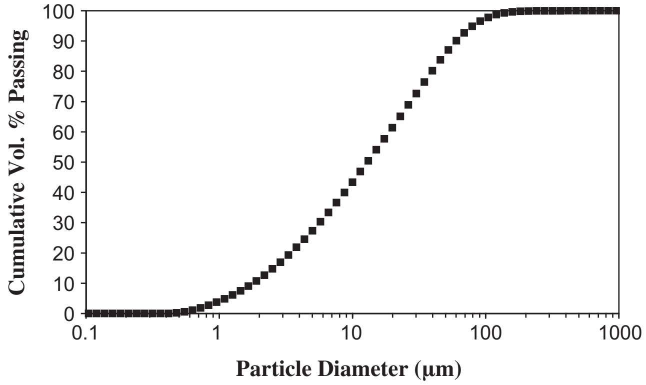

Fig. 2. Particle size distribution of the pozzolan.

Table 2
Chemical composition and compressive strength of geopolymer mixes prepared with no additives.

Mix name	Chemical composition		28-day compressive strength (MPa)
	Activator SiO_2/Na_2O molar ratio	Total Na/Al molar ratio	
P1	0.30	0.61	20.0 ± 2.0
P2	0.45	0.61	27.5 ± 2.0
P3	0.60	0.61	25.0 ± 2.0
P4	0.75	0.61	17.5 ± 2.0
P5	0.90	0.61	13.7 ± 2.0
P6	0.30	0.77	15.0 ± 1.0
P7	0.45	0.77	22.5 ± 1.0
P8	0.60	0.77	26.2 ± 1.0
P9	0.75	0.77	32.5 ± 1.0
P10	0.90	0.77	20.0 ± 1.0
P11	0.30	0.92	12.5 ± 1.0
P12	0.45	0.92	17.5 ± 1.0
P13	0.60	0.92	35.0 ± 1.0
P14	0.75	0.92	45.0 ± 1.0
P15	0.90	0.92	32.5 ± 1.0
P16	0.30	1.08	17.5 ± 1.0
P17	0.45	1.08	25.0 ± 1.0
P18	0.60	1.08	37.5 ± 1.0
P19	0.75	1.08	27.5 ± 1.0
P20	0.90	1.08	22.5 ± 1.0
P21	0.30	1.23	15.0 ± 1.0
P22	0.45	1.23	22.5 ± 1.0
P23	0.60	1.23	33.7 ± 1.0
P24	0.75	1.23	28.7 ± 1.0
P25	0.90	1.23	25.0 ± 1.0

P18, and P23), where these mixes were selected because they each displayed the highest 28-day compressive strength for a given Na/Al ratio. These photographs show that mixes P2 and P9 show a clearly lower extent of efflorescence compared to the other mixes, based on the presence of the deposits both on and around the samples.

Fig. 4 shows the extent of sodium leaching (as an indirect but quantitative measure of efflorescence) of the same samples, with comparison to their compressive strengths; the data are fundamentally consistent with the visible extents of efflorescence in Fig. 3. As seen from Fig. 4, geopolymer mixes with higher Na/Al molar ratios show a higher extent of alkali leaching, indicating a stronger tendency towards efflorescence. This follows the known trend in pore solution chemistry as a function of alkali content, where higher Na/Al ratios give more alkaline pore solutions [13]; the effect of permeability (which generally decreases with increasing extent of reaction, and thus would be lower at higher Na/Al ratios [37]) appears secondary when comparing different mix designs in this case. This may or may not be a general trend for geopolymers derived from other aluminosilicate precursors such as fly ash or metakaolin; this will depend on the specific extent of alkali binding in the gels formed in each instance, and has not yet been discussed in detail in the literature. Comparing 28-day compressive strengths and alkali leachability reveals that the highest achievable compressive strength (at an Na/Al molar ratio of 0.92, in mix P14) does not necessarily result in soundness and durability. In fact, mixes with lower Na/Al molar ratios, i.e. P2 and P9, show a lower extent of alkali leaching and consequent efflorescence. This shows that, in the absence of additives or heat curing, there appears to be a need to compromise between achieving the highest strength which is achieved with a denser microstructure (i.e., a higher extent of reaction [36,37]), and controlling the concentration of mobile alkalis in the pore solutions to prevent efflorescence.

3.2. Effect of admixtures

Figs. 5 and 6 show the variations in the extent of alkali leaching as a function of replacement percentage of natural pozzolan by different admixtures, for mixes P2 and P9 respectively. In the case of slag or metakaolin, a very minor decrease in the tendency towards

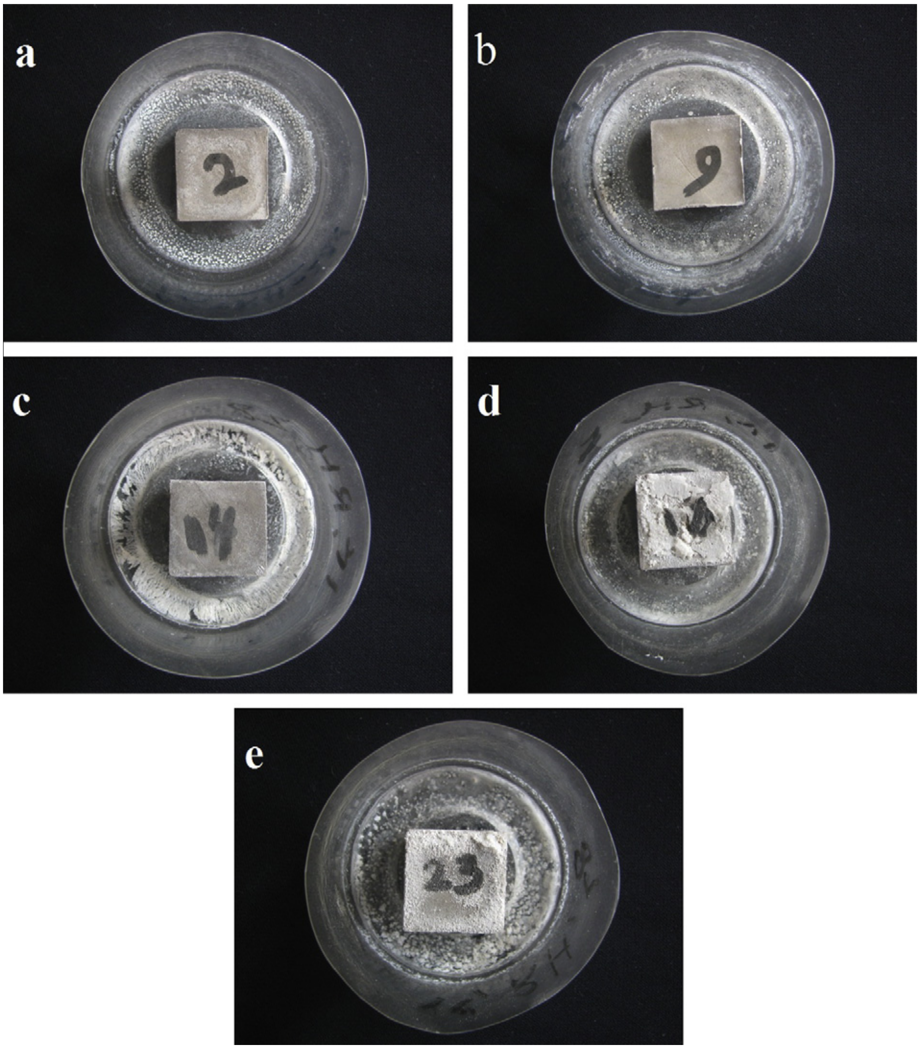

Fig. 3. Photographs of specimens tested qualitatively for their efflorescence extent, at the end of the test period: (a) P2, (b) P9, (c) P14, (d) P18, and (e) P23. Efflorescence crystal deposits on the tops of the specimens and white rings surrounding the specimens correspond to leached alkali metal salts.

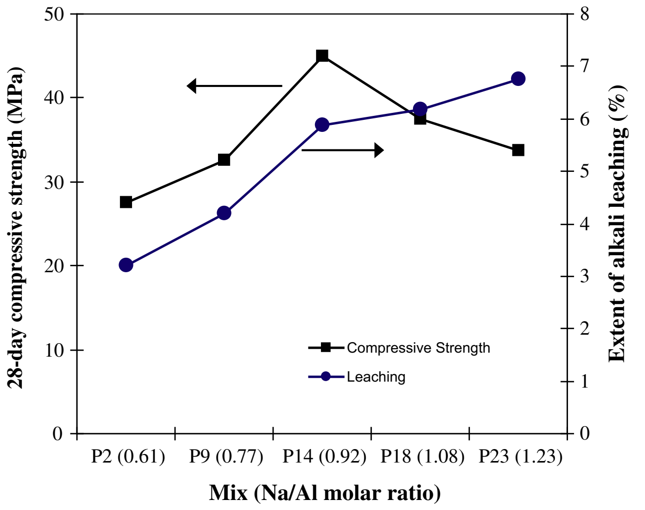

Fig. 4. Comparison of the extent of alkali leaching and 28-day compressive strength for mixes P2, P9, P14, P18 and P23.

efflorescence is observed, and only at the lowest replacement level of 2 wt.%. All three types of calcium aluminate cements, however, provide a considerable positive effect in efflorescence reduction for both mixes P2 and P9. The optimum replacement levels for calcium aluminate cements Secar 71, Secar 80, and Koracast are 6, 8, and 6 wt.% respectively.

The reasons for the limited effects of addition of slag and metakaolin may be attributed to the differences between the form and concentration of alumina in slag and metakaolin compared to high-alumina cements. In high-alumina cements, alumina is present in the form of calcium aluminates, whereas in the case of slag and metakaolin it is in the form of aluminosilicates. This important difference not only results in different behavior in geopolymerization reactions, but will also lead to the formation of different reaction products. Also, the alumina supplied in highly reactive form by the high-alumina cements – which is more readily available compared to that supplied by slag or metakaolin due to the fact that it is not associated with Si – means that more alumina enters into the geopolymerization reactions. This strengthens the tetrahedral geopolymer gel network which is generated by alkali activation of the pozzolan (which has reasonably low Al availability), and also leads to binding of the alkalis into a charge-balancing role in the gel, hence resulting in a lower extent of alkali leaching and efflorescence. It is interesting to note that the greatest influence on alkali leaching was shown by the Secar 71, with the lowest Al and highest Ca content of the three high-alumina cements tested; this again

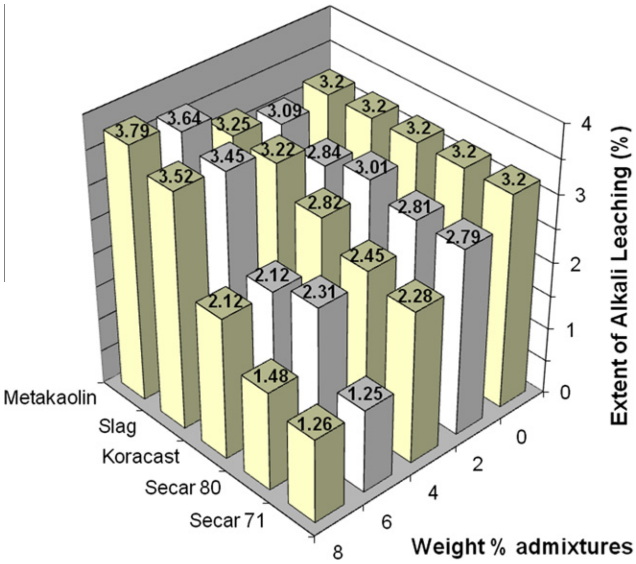

Fig. 5. Effect of admixtures on alkali leaching (as a proxy for efflorescence extent) in mix P2.

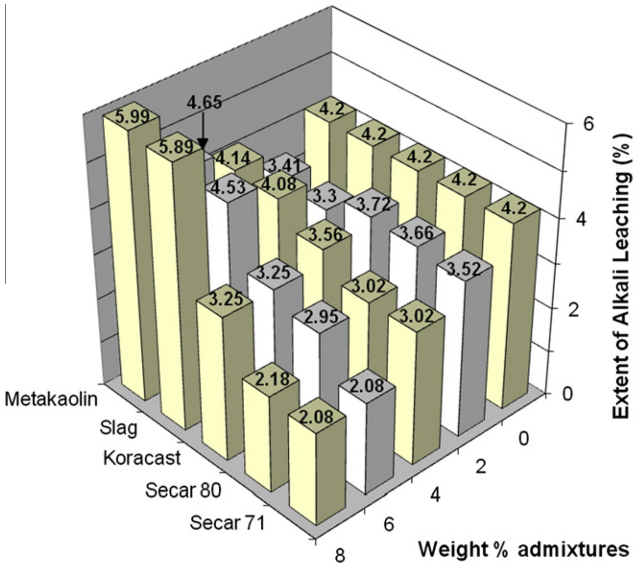

Fig. 6. Effect of admixtures on alkali leaching (as a proxy for efflorescence extent) in mix P9.

highlights that it is the availability of Al, not simply its presence, which is the most important point here. The Al is more readily available from the $CaAl_2O_4$ phase which dominates Secar 71 than from the $CaAl_4O_7$ and Al_2O_3 phases which are present in higher concentrations along with the $CaAl_2O_4$ in Secar 80.

Analysis of the alkali-activation of metakaolin–calcium aluminate cement blends has shown that even at 20% addition of a calcium aluminate cement (with 42% Al_2O_3, 39% CaO) to a metakaolin-based geopolymer, none of the hydrate phases characteristic of the hydration of calcium aluminate cement were observed. Instead, the extra aluminate participated in the growth of zeolites, even where the availability of Al from the metakaolin was already reasonably high [38]. Identification of crystalline reaction products by X-ray diffraction will be presented later in this paper, as part of the discussion of the causes of efflorescence reduction by the high-alumina cement.

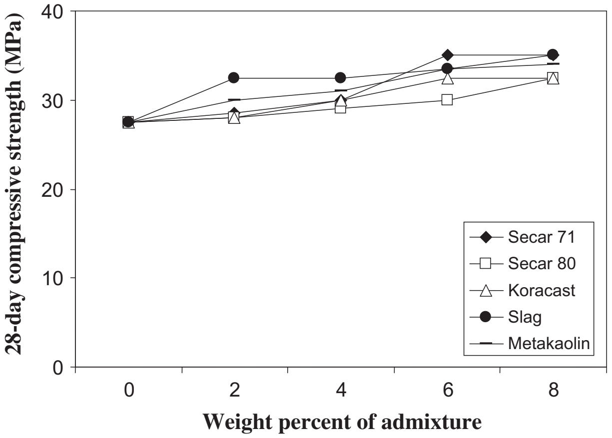

Fig. 7. Effect of admixtures on 28-day compressive strength of mix P2.

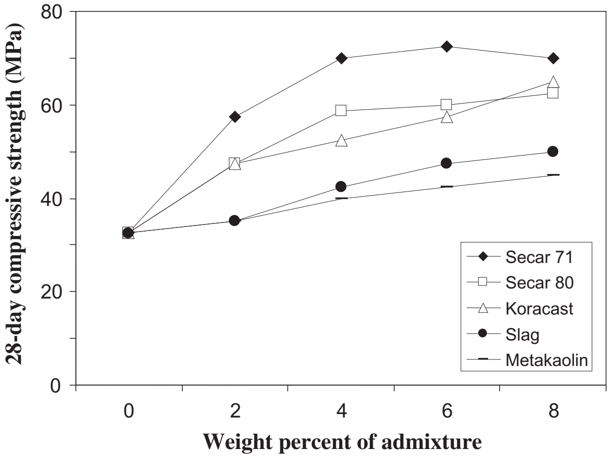

Fig. 8. Effect of admixtures on 28-day compressive strength of mix P9.

Figs. 7 and 8 show the variations in the 28-day compressive strength as a function of pozzolan replacement percentage by the different admixtures in mixes P2 and P9 respectively. All the admixtures show positive effects on compressive strength. For mix P2 (with a silica-poor activating solution), the increases in compressive strength are relatively minor, whereas for mix P9 (with a higher dissolved silica content) compressive strengths are significantly increased. Also, for mix P9, calcium aluminate cements are comparatively more effective, and can give more than a doubling in compressive strength performance compared to the reference samples. It is known that NaOH causes rapid setting of high-alumina cements, while the presence of silicate significantly retards their hydration [39], meaning that this difference in effects on strength development is likely to be related to a change in hydration rate between the low-silica and high-silica activating environments. The later release of aluminate into a geopolymerization process is known to be beneficial for microstructural and strength development [40], as the presence of excessive Al in solution early in the reaction process can impede the reaction of the aluminosilicate precursor. So, as the high-alumina cements are releasing Al more gradually in P9 compared to P2 due to the higher silicate concentration, this is beneficial for strength development. However, a comparison of the effects of the admixtures on both efflorescence extent and 28-day compressive strength shows that there is no strong general relationship between the admixtures which show a reduction in efflorescence extent and those which give an increase in compressive strength.

Fig. 9 shows the specimens of mixes P2 (Fig. 9a and b) and P9 (Fig. 9c and d) tested qualitatively for their efflorescence extent, without admixtures (Fig. 9a and c) and with optimum percentages of the Secar 71 calcium aluminate cement (Fig. 9b and d); the effectiveness of the admixture in reducing efflorescence is particularly visible for mix P2. Tests with the other calcium aluminate cements (Secar 80 and Koracast) also showed similar reductions in the formation of visible efflorescence deposits on the samples.

3.3. Effects of hydrothermal curing

Figs. 10 and 11 show the variations in the extent of alkali leachability and compressive strength as a function of hydrothermal curing temperature, for mixes P2 and P9 respectively. The baseline curing regime was a simple 28-day curing period in 95% relative humidity at room temperature (RT); hydrothermal (HT) curing was applied at temperatures of 45, 65, 85, 105, and 125 °C for 20 h, following 7 days of precuring at 25 °C and 95% relative humidity. For both mixes, hydrothermal curing at temperatures of 65 °C or higher results in reduced efflorescence extent and increased compressive strength. Hydrothermal treatment for 20 h at 45 °C is ineffective, increasing the tendency towards efflorescence and resulting in reduced compressive strength compared to a 28-day cure at 25 °C. The improvements brought about at temperatures higher than 65 °C may be attributed to the higher extent of geopolymerization reactions which can be achieved at these temperatures in these systems [33]. Hydrothermal curing at 125 °C gives both the highest strength and the greatest reduction in alkali leachability; however, this curing regime is still not as effective as the addition of Secar 71 in enhancing either of these two properties.

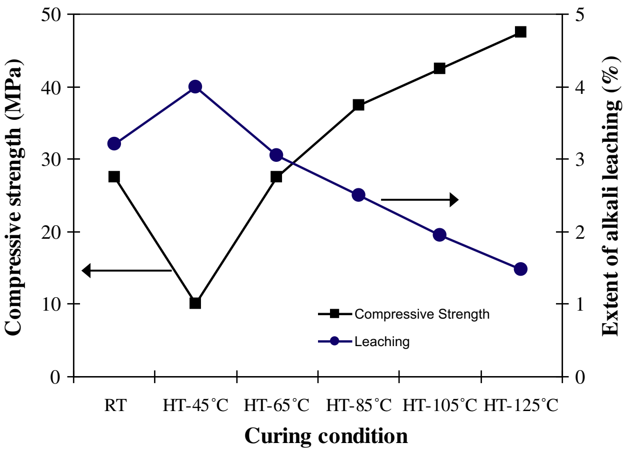

Fig. 10. Effect of hydrothermal curing on alkali leachability (as a proxy for efflorescence extent) and compressive strength of mix P2.

3.4. Characterization of the binders

The effects of curing time and temperature on the molecular structure of inorganic polymeric binders based on the Taftan natural pozzolan have been discussed in detail in a recent paper [33]. FTIR analysis of samples P2 and P9 with and without 6 wt.% Secar 71 (Table 3) shows that the addition of the high-alumina cement leads to an increase in the wavenumber of the Si–O–(Si,Al) asymmetric stretch peak, which is the strongest peak in the infrared spectrum of almost all geopolymeric materials, and is a key diagnostic region describing geopolymer gel network structures [41,42].

An increase in the wavenumber of this peak could be due to one of two factors: either an increase in network connectivity, or a decrease in the level of Al substitution [41]. Given that the addition of Secar 71 is supplying additional Al into the mixes, decreased Al substitution into the gels of the blended binders is unlikely, and thus the increase in FTIR peak positions is attributed to an increase in gel connectivity with the addition of the high-alumina cement. The higher compressive strengths observed with Secar 71 may also be attributed to the formation of a more crosslinked aluminosilicate gel, which in turn produces a dense, higher-strength molecular structure upon polycondensation. This is in accordance with previous work on systems

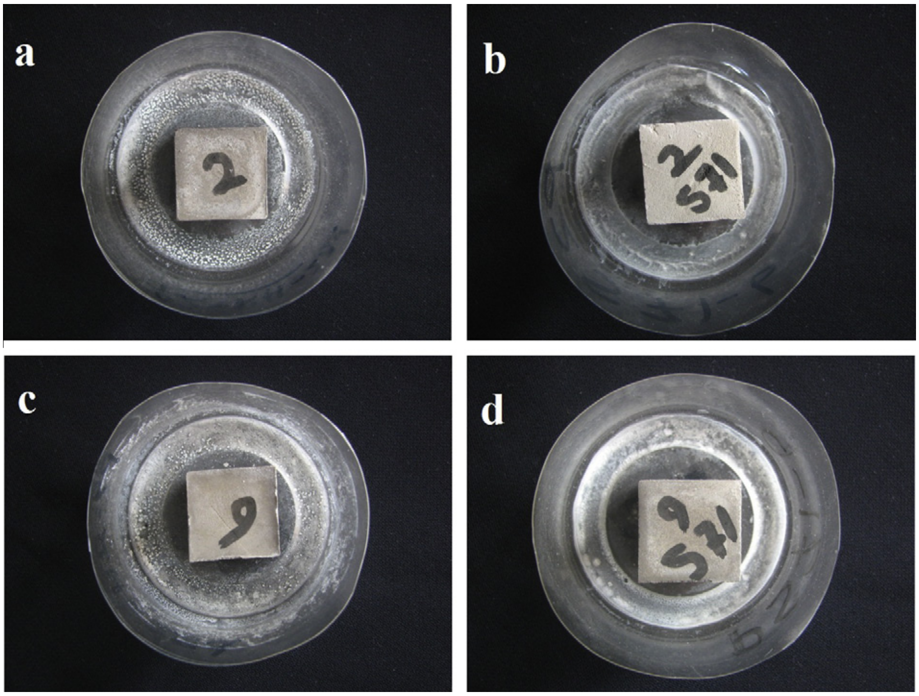

Fig. 9. Specimens of mixes P2 (a and b) and P9 (c and d) tested qualitatively for their efflorescence extent, without (a and c) and with (b and d) 6 wt.% Secar 71.

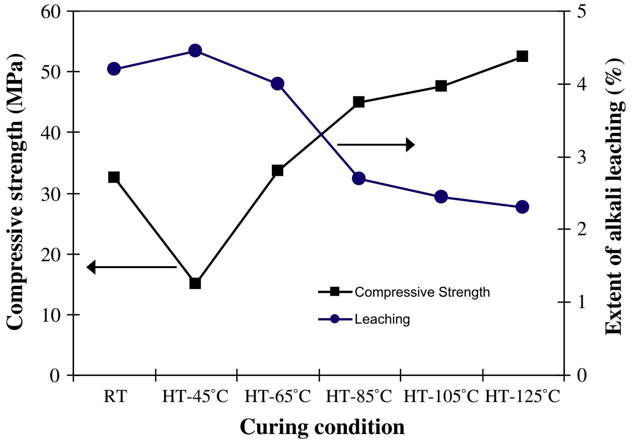

Fig. 11. Effect of hydrothermal curing on alkali leachability (as a proxy for efflorescence extent) and compressive strength of mix P9.

Table 3
Si–O–(Si,Al) asymmetric stretch peak positions in FTIR spectra of samples P2 and P9, with and without Secar 71.

Peak positions (cm^{-1})	Secar 71 content	
	0%	6%
Mix P2	998	1007
Mix P9	996	1004

based on Taftan pozzolan [33]; similar trends were also observed for the samples cured hydrothermally [33].

Figs. 12 and 13 display the X-ray diffraction patterns of hardened pastes of mix P2 with and without 6 wt.% Secar 71, after 20 and 40 days curing at 95% relative humidity and 25 °C. The mineral phases observed in mix P9 with and without 6 wt.% Secar 71 are similar to those in P2 (data not shown). The crystal phases shown in Fig. 1 to be present in the raw Taftan pozzolan are still present, but in lower quantities; biotite is almost entirely consumed in the first 20 days of reaction, and cordierite reacts significantly up to 40 days in the samples without Secar 71 (Fig. 12), but more rapidly in the presence of the high-alumina cement additive (Fig. 13). A small amount of residual calcium aluminate and Al_2O_3 due to the Secar 71 are also observable in Fig. 13; the Al_2O_3 observed in Fig. 12 is attributed to slight contamination during preparation of the sample for XRD analysis by grinding with corundum media.

The main identifiable crystallographically-ordered reaction products in the samples without Secar 71 (Fig. 12) are poorly crystalline zeolite-like phases (hydroxycancrinite, chabazite), carbonates (magnesite), and a layered double hydroxide phase similar to brucite. These are consistent with the zeolitic and other phases widely identified in geopolymer binders. The addition of Secar 71 (Fig. 13) gives slight changes in the nature of the zeolite-like phases, introduces aluminum hydroxide and oxyhydroxide phases, and also leads to the formation of a low-crystallinity sodium-calcium silicate hydrate phase. As was observed in the alkali-activation of high alumina cement–metakaolin mixtures [38], calcium aluminate hydrate phases as high-alumina cement hydration products are not observed here.

There are also changes in the carbonate phases formed in the samples; huntite, a mixed Ca,Mg-carbonate, is formed in addition to magnesite in the presence of the Ca supplied by the calcium aluminate cement, and some nahcolite (sodium bicarbonate) is formed within the binders. This is in contrast with the observed effect of the high-alumina cement in reducing the efflorescence effects in these samples, which are attributed to the formation of alkali carbonate and bicarbonate phases on the sample surface; it thus appears that the presence of alkali carbonates within the binder structure itself will not necessarily be a cause of efflorescence on the sample surfaces.

3.5. Dissolution properties of precursor blends

To understand the positive effects of the high-alumina cement admixtures, dissolution properties of precursor blends in concentrated alkaline solutions were considered. Figs. 14 and 15 display the extent of dissolution of the Taftan pozzolan with and without 6 wt.% Secar 71, in 1 and 10 M NaOH solutions for time periods of up to 72 h. As seen in these figures, and as expected, the extent of dissolution of Al at both concentrations of NaOH is increased considerably when the pozzolan is mixed with Secar 71. However, and less expectedly, it is seen that in 1 M NaOH, the extent of dissolution of Si from the pozzolan mixed with Secar 71 is higher than that which is observed for the pozzolan without any admixture. In 10 M NaOH solutions, the extent of dissolution of Si is quite similar in both dry binders without and with admixture. Dissolution

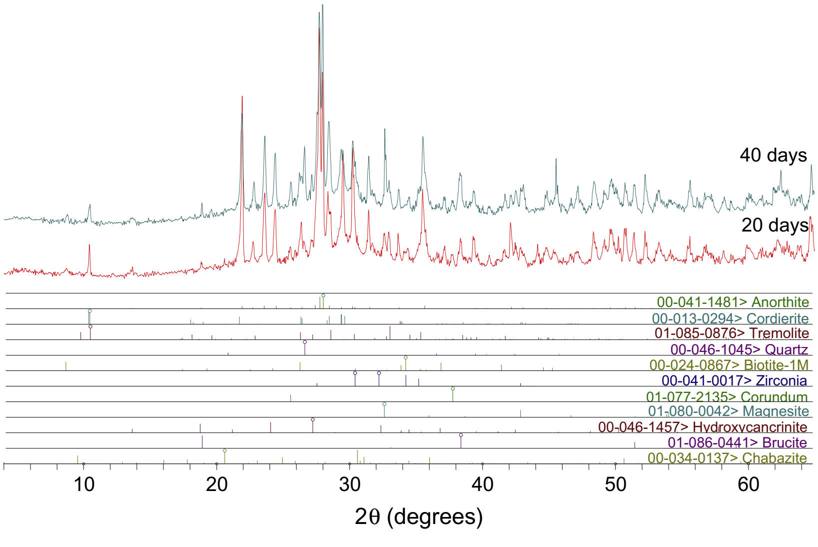

Fig. 12. X-ray diffractograms of hardened pastes of mix P2 after 20 and 40 days.

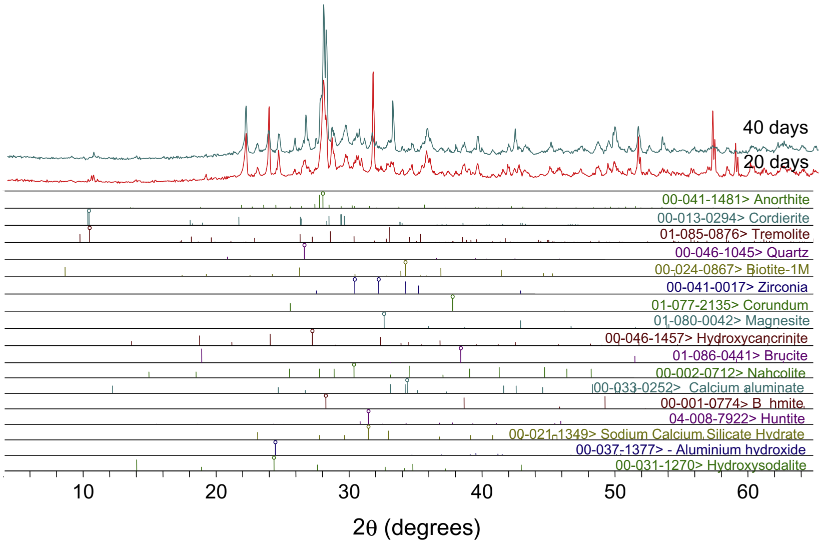

Fig. 13. X-ray diffractograms of hardened pastes of mix P2 with 6 wt.% Secar 71 after 20 and 40 days.

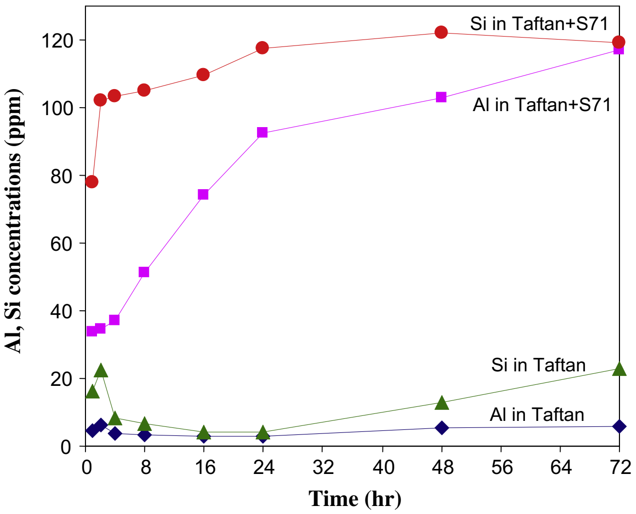

Fig. 14. Extent of Al and Si dissolution in 1 M NaOH solution for Taftan pozzolan, and for the pozzolan mixed with 6 wt.% Secar 71.

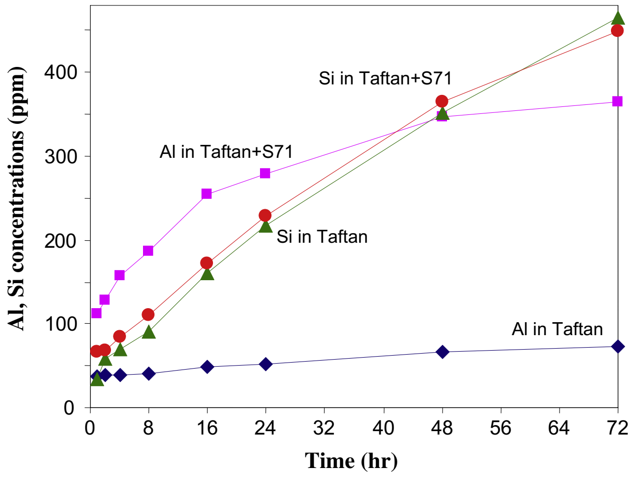

Fig. 15. Extent of Al and Si dissolution in 10 M NaOH solution for Taftan pozzolan and for the pozzolan mixed with 6 wt.% Secar 71.

testing in 1 M and 10 M KOH solutions also provided similar trends in both Al and Si dissolution rates and concentrations with time.

The most important reason for the positive effects of the high-alumina cement Secar 71 in efflorescence reduction and increasing mechanical strength is the production of higher amounts of aluminosilicate gel due to the higher availability of alumina for the geopolymerization reactions. This is the most likely reason for higher compressive strength in cementing mixes containing alumina cements compared to mixes containing slag and metakaolin, as discussed above. If the key effect was due to the calcium contained in the admixture, the slag would be expected to have a stronger effect than Secar 71 due to its higher Ca content. The additional effect of the high-alumina cement in enhancing Si release and solubility in 1 M NaOH can be attributed to the increased complexation of dissolved Si species by the higher levels of soluble Al, which shifts the solubility equilibrium of the pozzolanic material (which dissolves to release silicate monomers) to favor a higher extent of dissolution. Such an effect is not observed in the system with 10 M NaOH because the pH is so high that all of the dissolved silicate and aluminate species will be monomeric; no complexation or oligomer formation is possible under these conditions, and Si solubility is unchanged by the availability of extra Al.

4. Conclusions

Efflorescence is sometimes an issue in geopolymeric binders derived from natural pozzolanic precursors, but can be reduced either by the addition of alumina-rich admixtures or by hydrothermal curing. Each of these techniques provides benefits to the binder structure by enhancing the binder structure formation process. Hydrothermal curing at temperatures of 65 °C or higher also provides a significant effect in efflorescence reduction, as well as slight strength improvements. The addition of high-alumina cements is particularly beneficial; an optimum dosage of calcium aluminate cement, especially Secar 71, as an admixture is more effective than hydrothermal curing in reducing the extent of efflorescence in the natural pozzolan based geopolymer binders studied. The additional alumina supplied by the high alumina cement admixtures leads to an increased extent of crosslinking in the geopolymer binder, reduces the mobility of alkalis (which is the key cause of efflorescence in these materials), and also generates a hardened geopolymer binder product with markedly improved mechanical properties compared to the systems with no admixtures.

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