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The effect of ionic contaminants on the early-age properties of alkali-activated fly ash-based cements

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Abstract

Alkali-activated fly ash-based cements are concrete binders that utilise fly ash as their major solid raw material. The solid particles are activated using concentrated silicate and hydroxide solution to produce high-strength products. Due to the highly alkaline nature of the solution, precipitation of the reactive species, both from the solids and from the solution, proceeds at a very fast rate. This renders short setting times, which can be advantageous or disadvantageous depending on the practical situation. The present work examines the effects of inorganic salt addition towards the setting and rheological characteristics of the early pastes. Compressive strength, Fourier transform infrared spectroscopy (FTIR) and X-ray diffractograms were collected to examine the hardened products. It was found that calcium (Ca) and magnesium (Mg) salts shortened the setting time by providing heterogeneous nucleation centers in the initial paste solution. Potassium salts retarded setting only to the cements, which used less sodium silicate in the initial solution for activation. Managed ionic contamination can be used to increase the product early strength. However, its long-term effects still need to be identified. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Acceleration; Physical properties; Alkali-activated cement; Fly ash

1. Introduction

Alkali-activated fly ash-based cements are manufactured by mixing coal-fired power plant fly ash with strongly alkaline silicate solution. The resultant pastes are then cured under atmospheric pressure and room or elevated temperature. Such cements have already been shown to possess excellent physical and chemical properties, such as high compressive strength, high acid resistance and high heat resistance [1–4]. At the time when sustainable practices are demanded by the public and the industries, it is not surprising that researchers from cement industries have displayed strong interests in this technology, namely to convert industrial byproducts to useful and attractive building and construction materials.

One of the major chemical differences between the alkali-activated system and Portland cement system, apart from the apparent differences in the starting solid compositions, is the aqueous solution. The aqueous solution used for making Portland cement is water and the pH starts from neutral and gradually moves up to 12–13 with increasing solid dissolution [5]. The resultant product is a mixture of unhydrated cement particles as well as the various types of crystalline calcium silicate hydrates (CSH). On the other hand, alkali-activated system requires a strongly alkaline solution to ‘activate’ aluminosilicate solid dissolution [1–3]. To achieve the favourable solution composition for good physical and chemical properties of the hardened product, the soluble silicate is often added to the alkaline solution to a saturated or close-to-saturation level. This silicate is prevented from coagulation and polymerisation by the initial high solution pH [6]. As soon as the pH starts to decrease from its original value of close to 14 to a lower value due to solid dissolution, polycondensation will take place at a very fast rate. This may involve the solution silicate itself as well as the dissolved species from the solids. As a result, a series of polysialation, coagulation, colloidal formation, gelation and subsequent gel restructuring takes place and leads to the final product — a mixture consisting of undissolved aluminosilicate particles embedded in newly formed and mainly amorphous aluminosilicate matrix [1,2]. Because of the initial saturated silicate solution that is used

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for activation, alkali-activated cement often sets at a much faster rate than Portland cement. This can be an advantage or disadvantage, depending on the practical situation. The need to control the speed of setting of geopolymers therefore becomes obvious.

It is apparent from the literature of cement and concrete that the addition of small amounts of chemicals can affect setting and other material properties of the hardened products. For example, the addition of aqueous calcium chloride can accelerate the setting process of the cement paste. An addition of less than 2% of these chemicals could affect cement hydration throughout the setting period, and hence the mature concrete properties [7,8]. As alkali-activated systems are chemically different from Portland cement, the effect(s) of an inorganic salt solution, or even a suspension of water-insoluble inorganic salt addition, on alkali-activated cements cannot be predicted based on the existing data of Portland cement. In the present study, a conventional penetration test employing a Vicat needle was used to measure the effects of inorganic salts on the setting time of alkali-activated cements. Yield stress measurement was used to study the strength development of the early pastes before setting. Compressive strengths were obtained after 7 days while Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) techniques were used to examine the chemical and morphological changes induced by the inorganic salt addition on the hardened products.

2. Methods

2.1. Materials

Two sources of fly ash were used. One was from Port Augusta in South Australia and the other was from Gladstone in Queensland, Australia. Kaolinite of HR1 grade was obtained from Commercial Minerals (Sydney, Australia). Solids from different batches were bulk-mixed to ensure that the same solids were used for the entire investigation. The solid compositions, as determined by fusion analysis using a Siemens SRS3000 sequential X-ray fluorescence (XRF) spectrometer, are listed in Table 1. The chemicals used were inorganic salts of laboratory grade. These included KCl, K_2CO_3, KNO_3, KOH, $CaCl_2$, $Ca(OH)_2$, $CaCO_3$, $CaSO_3$, CaO, $MgCl_2{\cdot}6H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$ and MgO. Sodium silicate was obtained from PQ Australia (SiO_2:Na_2O = 3.22) with total silicon concentration of 6.63 M.

Table 1
The compositions of raw materials

Oxide	Port Augusta fly ash (mass percentage)	Gladstone fly ash (mass percentage)	Kaolinite (mass percentage)
SiO_2	48.5	50.0	54.5
Al_2O_3	29.6	28.0	29.4
Fe_2O_3	4.6	12.0	1.4
CaO	6.1	3.5	0.2
MgO	2.3	1.3	0.2
Na_2O	3.7	0.2	0.1
K_2O	0.9	0.7	0.2

Table 2
The compositions in terms of mass ratios of the various *Controls*

	Fly ash/kaolinite ratio	Sodium silicate solution/total solid ratio	15 M KOH solution/total solid ratio
System I[a]	2.02	0.05	0.31
System II[a]	9.00	0.18	0.28
System III[b]	9.00	0.22	0.28
System IV[b]	4.00	0.08	0.35
System V[b]	9.00	0.33	0.40

[a] Port Augusta fly ash was used.
[b] Gladstone fly ash was used.

2.2. Synthesis

Five alkali-activated cement systems were synthesised to study the effects of the inorganic salts. Samples were named according to whether chemical additives were used and what chemical additives were used. The *Control* sample did not contain any chemical additives and was used as the basis of comparison for examining the effects of the salts on a particular alkali-activated cement system. The compositions of the *Control* samples are listed in Table 2. The samples containing the various salts were named after the salts used and are expressed in *italics* in the main text of this paper.

Fly ash and kaolin of the appropriate ratio were mixed to homogeneity in a rotary mixer overnight before use. Potassium hydroxide solution of 15 M was prepared and allowed to cool to room temperature overnight. The alkaline silicate solution of KOH and sodium silicate was freshly prepared 2 min before mixing with the solids. Water was used as the transport medium for all the salt addition to cement pastes. The salts were dissolved or suspended in 20 g of water, 5 min before their addition. As the hydration time for the salts was relatively short, some of the less soluble salts were not allowed sufficient time to fully dissolve. Consequently, a classification of the salts is important, as will be discussed later (see Table 3).

Alkali-activated cements were synthesised as follows: After placing the solids in the mixing bowl, the alkaline silicate solutions prepared overnight were added. The contents of the mixing bowl were mixed in a mechanical mixer for 5 min to produce homogeneous pastes. Twenty grams of water was then added and mixed for a further 5 min to produce the *Control*. Alternatively, aqueous solution of water-soluble salts or suspension of water-insoluble salts was added to produce the contaminated cements. The

Table 3
The classification of the salts at 25 °C [9,10]

Water-soluble		Water-insoluble	
KCl	K_2CO_3	$Ca(OH)_2$	$CaCO_3$
KNO_3	$CaCl_2$	CaO	MgO
$Mg(NO_3)_2{\cdot}6H_2O$	$MgCl_2{\cdot}6H_2O$	$CaSO_3$	

Table 4
The effects of anions on the final setting time of the various alkali-activated cements at 40 °C

	Dosage (mol)	KCl (min)	K_2CO_3 (min)	KNO_3 (min)
System I	0	62	62	62
	0.02	84	70	69
	0.04	124	79	83
	0.08	153	88	95
System II	0	48	48	48
	0.02	47	46	45
	0.04	49	46	48
	0.08	44	47	48
System III	0	67	67	67
	0.02	67	67	67
	0.04	65	65	66
	0.08	67	69	67
System IV	0	34	34	34
	0.02	51	46	37
	0.04	65	52	49
	0.08	84	52	59

samples were named according to the salts used. The pastes were then transferred to plastic containers, which were basic-resistant, and cured under atmospheric pressure and 40 °C for 24 h. Subsequently, the hardened pastes were cured at room temperature of between 20 and 25 °C under atmospheric pressure until testing.

2.3. Characterisation/analysis

Setting time analysis was performed using a Vicat needle of 100 g and 1 mm diameter cross-section, as described in *ASTM C191 and 192*. Values of penetration distances were determined every 5 min after the paste had been made. Each final setting time reported was an average of three separate tests. The yield stress of the early pastes before setting was determined on a Haake vane rheometer using vane C. New pastes were prepared for each of the yield stress values collected. Only *System II* and *System III* cements were examined using FTIR and XRD. FTIR spectra were collected at the age of 1 day and 28 days using a Bio-Rad FTS 165 FTIR spectrometer in absorbance mode using KBr technique. X-ray diffractograms were obtained from samples that were 7 days old, using a PHILIPS instrument, model PW-1710, with a Cu anticathode. All the samples were pulverised and dried at 105 °C overnight before infrared and XRD analysis. Compressive strength tests were obtained, conforming to *ASTM C39* on an Amsler compression machine. All the values collected were the averages of three separate tests, with S.D. of less than 5%.

3. Results

Table 4 includes the results of the final setting time of the various cement systems with and without the presence of aqueous KCl, K_2CO_3 and KNO_3. It was found that the final setting time was not affected by the ionic contamination for *System II* and *System III*. Setting was, however, prolonged by the aqueous salts for *System I* and *System IV*. From Table 2, the initial solutions of both *System I* and *System IV* were relatively unsaturated with silicates as compared to *System II* and *System III*. It therefore appears that the effects of ionic contamination on setting time were silicate concentration-dependent. As the initial solution was already highly abundant in potassium cations and the added potassium from the salts was less than 10 mol% of the total potassium content in solution, the effects of the setting variation caused by the presence of the salts can be regarded as the result of the anions.

When salts of double charged cations were present, the trends observed above were complicated by the fact that double charged alkali cations were highly insoluble in the high pH environment, as mentioned in Table 3. When aqueous salts of calcium (Ca) and magnesium (Mg) were introduced to the alkaline silicate solution for alkali-activated cement production, alkali hydroxide precipitates formed almost immediately. This caused set acceleration

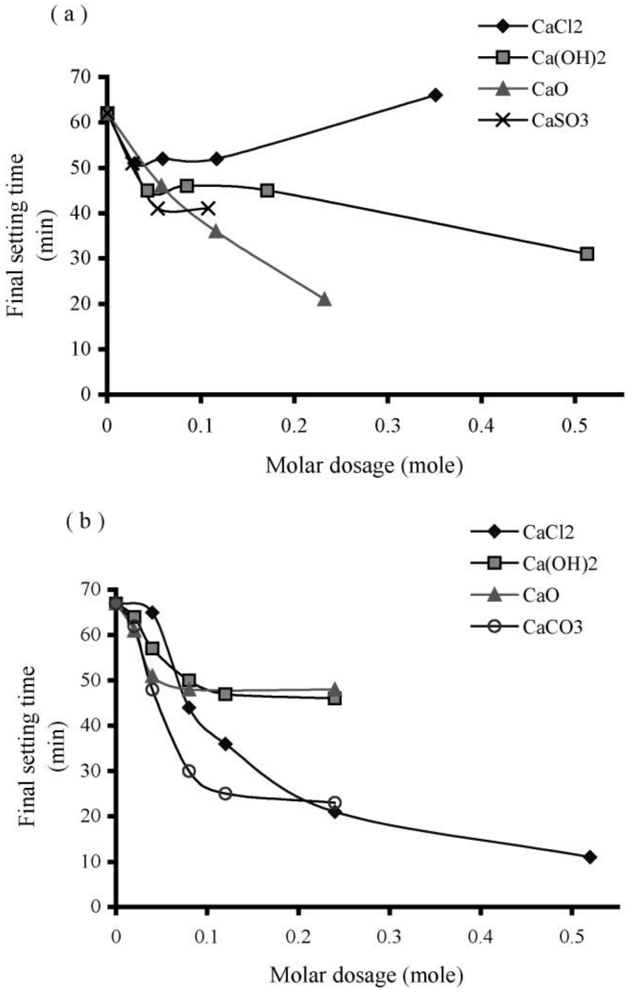

Fig. 1. The effect of molar dosage on the setting time of (a) *System I* and (b) *System III* cements.

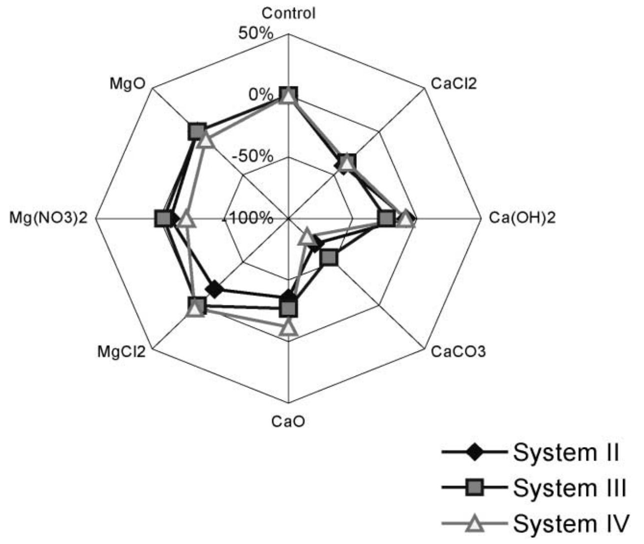

Fig. 2. The percentage change in setting time of alkali-activated cements caused by Ca and Mg salts at the molar dosage of 0.08764 mol.

when the contamination level was low (see Fig. 1). On the other hand, when the level was high, whether the effects were accelerating or retarding could be dependent on the initial solution composition of the alkali solution, the dissolved species from the solids and the nature of the contamination. Fig. 1 shows that when the initial soluble silicate concentration was low, setting was retarded by the $CaCl_2$ at high dosage. This trend was not observed from the samples containing water-insoluble salts. For *System III*, the effect of set acceleration by the insoluble salts reached its maximum at the dosage of around 0.15 mol. In *System I*, however, the maximum set acceleration appeared to be at a higher dosage. The latent region between 0.04 and 0.1 mol was interesting. Between these thresholds, the level of contamination did not affect the final setting time of the *System I* cements, except the ones containing CaO. The reason for this observation is still unknown, but it is unlikely to be fly ash- or kaolin-dependent. Very little time was allowed for solid dissolution for samples containing CaO of *System I* and $CaCl_2$ of *System II* at their shortest final setting times. Hence, the contribution from the solid dissolution to setting is not likely to be significant when compared to the initial alkaline silicate solution composition and the nature of the contamination.

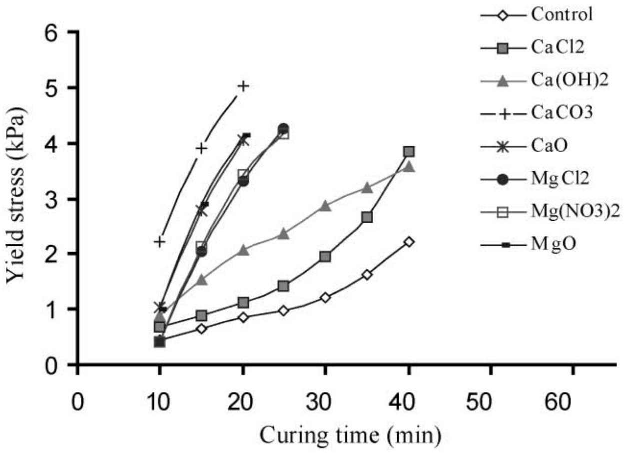

Fig. 3. The yield stress development of *System II* cements.

Fig. 2 is a radial plot that is not conventionally used for presenting scientific data. However, as demonstrated here, it can be a much easier tool than a tabulated form, as shown in Table 5, to study the trends of ionic contamination at the same contamination level. The 'percentage change in setting time' was defined as (Eq. (1)):

$$\text{percentage change in setting time } (\%) = [(a - b) \times 100]/b \tag{1}$$

where a is the setting time of the additive–inclusive system and b is the setting time of the *Control*. A more negative value of percentage change in setting time means that the setting time has been reduced to a greater extent through the use of a chemical additive, than a more positive value. A positive percentage change in setting time means that setting has been prolonged.

Fig. 2 describes the effects of various chemical additives on setting time, using the *Control* samples as the reference points. It is evident from the radial plot that all three systems possessed similar curves and the distribution of results was in a systematic manner. This result is important, as it allows the prediction of the effect of the chemical additives for a geopolymeric system that has never been tested. It also suggests that each of the chemical additives may affect geopolymerisation processes through a certain set of reaction mechanisms. Setting was generally accelerated by Ca salts for all the *Systems* examined at the molar dosage of 0.08764 mol. Mg salts, however, seemed to have little effect on acceleration.

Yield stress, common in chemical engineering practice for measuring attractive forces inside solid–liquid suspen-

Table 5
The final setting time of the various systems at 40 °C at the dosage of 0.08764 mol

Setting time (min)								
	Control	$CaCl_2$	$Ca(OH)_2$	$CaCO_3$	CaO	$MgCl_2$	$Mg(NO_3)_2$	MgO
System I	62	56	58	–	40	–	–	–
System II	48	29	44	14	31	39	44	48
System III	67	43	64	30	49	67	65	67
System IV	34	22	31	7	25	30	27	31

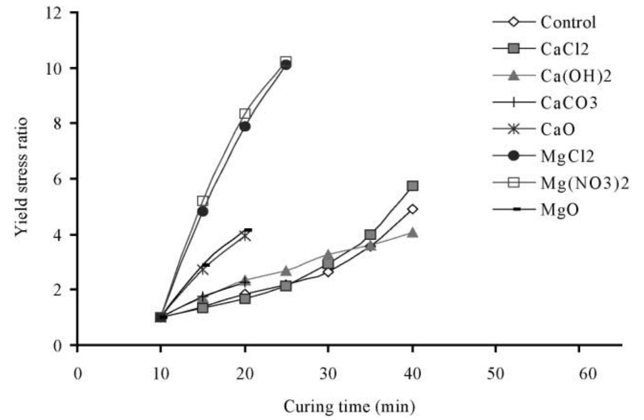

Fig. 4. The effect of Ca and Mg salts at the molar dosage of 0.08764 mol on the yield stress ratio of *System II* cements.

sions [11], was used to study the early strength of the alkali-activated cement pastes before setting. As shown in Fig. 3, the paste rheology of *System II* cements was clearly affected by the addition of the various salts. The results of yield stress measurement suggest that Mg salts did affect the setting processes. This was difficult to see using the conventional penetration test. A better insight can be established by comparing the results of Fig. 3 with yield stress ratio as shown in Fig. 4, which used the yield stress at 10 min as the reference for calculation. For example, the samples containing $Ca(OH)_2$ and $CaCO_3$ had the same rate of change of yield stress, but the sample containing $CaCO_3$ had higher yield stress at any given time. In other words, paste strength was initiated by $CaCO_3$ earlier than $Ca(OH)_2$. Once the paste strength was initiated, the subsequent strength development was the same for both the $Ca(OH)_2$- and $CaCO_3$-containing samples. Other classifications were also evident: water-soluble Mg salts, $MgCl_2$ and $Mg(NO_3)_2$ gave rise to the same yield strength at any given time; paste yield stresses for the samples containing oxides of Ca and Mg were the same. Calcium chloride seemed to affect the paste strength in a unique way, but it is anticipated that other water-soluble salts of Ca may give rise to the same yield stress curve as that of $CaCl_2$, probably due to the same reason as for $MgCl_2$ and $Mg(NO_3)_2$.

To better understand the nature of the setting processes of alkali-activated fly ash-based cements, Gladstone fly ash powders were ‘pretreated’ in a 15-M KOH solution for 1 h in a slurry of solid-to-liquid ratio equal to 1:5.333. A series of dilution, sedimentation, drying, comminution, mixing and finally sieving processes was then used to separate the solids from the liquid. Sieving was employed to make sure that the same particle size distribution was the same as that of the untreated system. As the result, physical differences caused by the pretreatment were minimised. The effects of surface pretreatment could therefore be regarded as only chemical-dependent. *System V* alkali-activated cements were then synthesised in the same way as producing the normal cements as described earlier. Fig. 5 shows that it took about 4.5 h for the normal cement to set, whereas setting was delayed almost four times if using the pretreated fly ash. Setting was generally accelerated by the addition of the various Ca and Mg salts, except $Ca(OH)_2$. Whether the chemical dosage used for $Ca(OH)_2$ was too small still needs to be investigated.

The 7-day compressive strengths of *System II* and *System III* cements are presented in Fig. 6. It can be seen that there were no short-term detrimental effects caused by the contamination of salts. It seems that careful salt addition may even be used for increasing the early strength of alkali-activated fly ash-based cements. The long-term impact of salt contamination needs to be further investigated.

FTIR and XRD techniques were used in an attempt to understand why inorganic salt contamination caused the

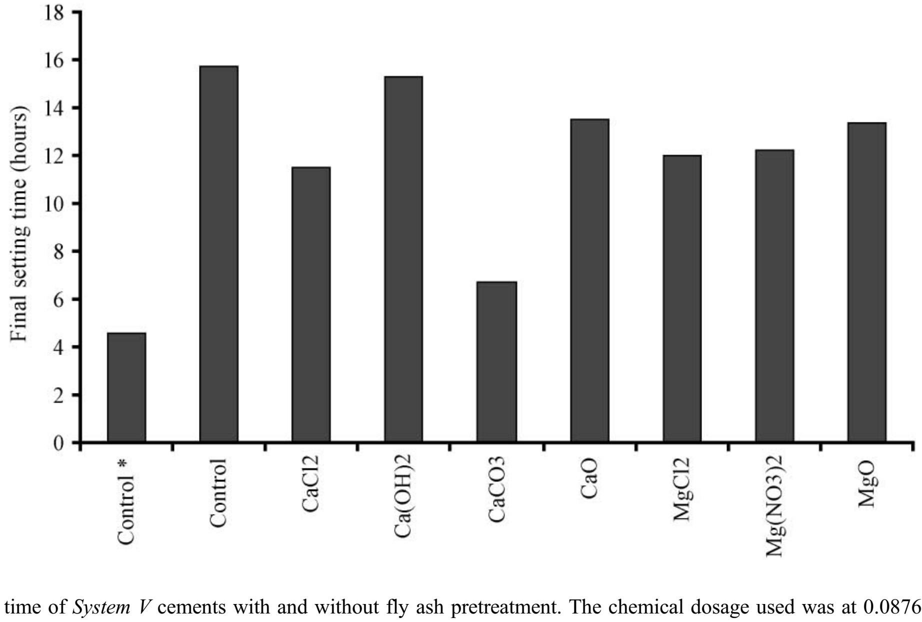

Fig. 5. The final setting time of *System V* cements with and without fly ash pretreatment. The chemical dosage used was at 0.08764 mol. * Denotes fly ash without surface pretreatment.

variations in product strength. It was found that no crystallinity change could be identified by the salt contamination in the first 7 days. More information was gathered from the infrared technique. Inorganic salt contamination did not cause noticeable changes to the spectra for the *Systems* examined except between 1350 and 1500 cm^{-1}. Consequently, Fig. 7 only shows spectra between these wavenumbers. The nitrate-containing samples showed peaks at 1385 cm^{-1}, which were also evident from pure KNO_3 and $Mg(NO_3)_2 \cdot 6H_2O$ at exactly the same wavenumber but were more diffuse. As infrared is a technique that identifies various kinds of molecular vibration modes, which are highly sensitive to the local chemical environments, nitrates in solution can be less diffuse than the solids due to less molecular interaction. Hence, it is likely that nitrates existed as anions in the pore solution of the alkali-activated cements. The peak at 1385 cm^{-1} of much less intensity was also evident from all other cement samples as well as the raw fly ash from Port Augusta and Gladstone. The peaks at 1463 cm^{-1} were identified as carbonates in solution, which might be in close association with Na^+ or K^+ cations [12]. Carbonation of all the cement samples appeared to be serious initially, but later disappeared upon aging as little or no carbonation could be observed on the samples at 28 days of curing in room temperature. *Control* was used as a representative for all the samples investigated. This suggests that CO_3^- from the atmosphere could be closely associated with Na^+ and/or K^+ cations. As more alkali ions were taken up by the negatively charged IV-coordinated aluminum due to continuous solid dissolution [1,2], less carbonation was possible. In other words, carbonation could be caused by the excess alkali in the pore solution. It is important to point out here that the addition of carbonates did not change the spectra significantly due to its small quantity as compared to the atmospheric carbonation. Other techniques are needed to fully understand the role of the salts in increasing the early strength of alkali-activated cements.

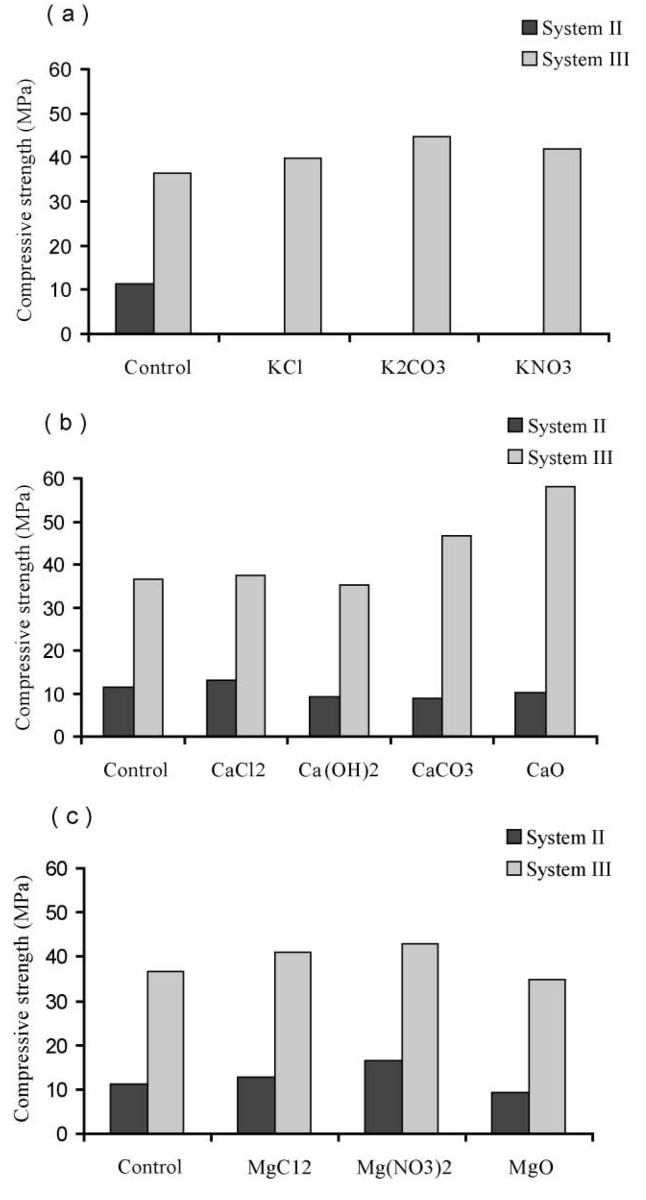

Fig. 6. The 7-day compressive strength of *System II* and *System III* cements containing (a) K salts, (b) Ca salts and (c) Mg salts.

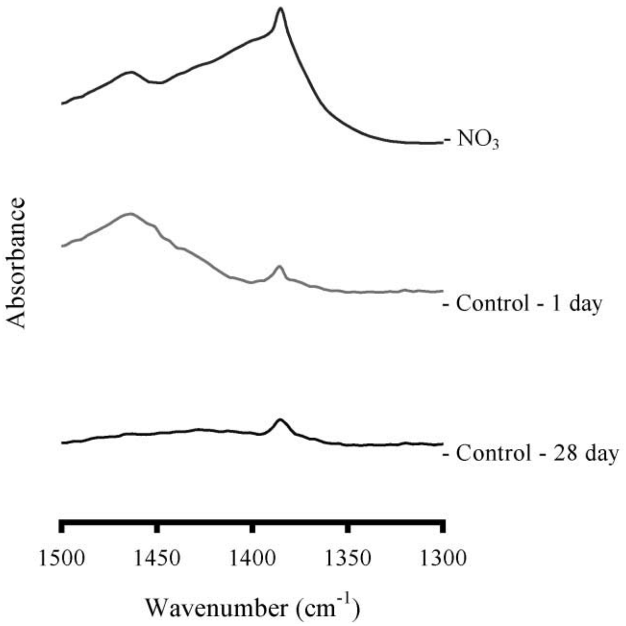

Fig. 7. The FTIR spectra of the *System III* cements plotted at the same intensity scale.

4. Discussion

Before solid dissolution started, the solution phase of an alkali-activated system can be regarded as consisting of alkali cations, soluble silicate anions and hydroxyl anions. When an aqueous solution of a salt of the metal other than the alkali *Group I* metals, such as Ca and Mg, is added to such a system, the immediate formation of the metal hydroxide precipitates removes much of the local hydroxyl ions. This induces a sudden pH drop around the newly formed metal hydroxide precipitates and triggers polymerisation and gelation of the silicate species nearby if the silicate concentration is close to the saturation level [6]. The resultant solid particles, the metal precipitates and the surrounding silicate gel have low surface energy due to the relatively large particle size as well as the relatively small surface curvatures. The end result is that the chance of coagulation upon collisions between the soluble silicates and the solid particles is enhanced [13–15]. Therefore, the introduction of aqueous Ca and Mg salt solutions to alkali-activated cement systems can produce many heterogeneous nucleation templates immediately upon the addition. Without the salt addition, the aqueous solution has to go through a series of solid dissolution processes before nucleation templates can be produced after supersaturation has been reached. Hence, the systems with Ca and Mg salts addition should be expected to demonstrate shorter setting times than the systems without. The growth of the solids using the species originally present in the solution via heterogeneous nucleation is now well recognised in the colloid, crystal and zeolite industries [16,17]. It should be noted that the speed of gel formation due to heterogeneous nucleation is highly dependent on the nature of the solids. If the solids are different, the rate of gel formation should be different.

The results obtained from this investigation can be used to prove the above postulate. From Table 5 and Figs. 1 and 2, it was found that setting of the alkali-activated fly ash-based cements was accelerated by the various Ca and Mg salt contaminations. Generally, the Mg salts had little effect on setting while the Ca salts shortened setting to varying degrees. This seemed to overturn the heterogeneous nucleation theory as suggested above. However, by examining the yield stress of the samples before setting, it is clear that Mg salts increased the early paste strength, thus initiating development of paste strengths earlier than the *System II Control*. The rates of strength development for the Mg-containing samples, however, dropped off at the later stages and this was why it appeared that Mg salts did not affect setting. The penetration test using a Vicat needle therefore is a less favourable technique to study the early paste strength as this technique can lead to incorrect conclusion regarding early paste strength development.

As $MgCl_2 \cdot 6H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ were soluble in water, the Mg dissociated from the parent salts upon their additions to water and existed as double charged cations. When these aqueous solutions were added to the fresh alkali-activated pastes, Mg cations from both salts immediately formed Mg hydroxides. These Mg hydroxides were chemically the same regardless of the origins. Because the same molar dosage was used, both samples gave rise to the same amount of Mg hydroxides and released the same amount of anions to the paste solutions. From Table 4, the anions did not affect the speed of setting if the solution used for activation was initially highly concentrated with soluble silicates and this was true for *System II* cements. Hence, the anions can be regarded as spectator ions for setting under the conditions of *System II*. The end result is that the same yield stress development was observed for both $MgCl_2$ and $Mg(NO_3)_2$ cements. A heterogeneous mechanism for the cause of the early paste strength initiation due to the addition of water-soluble Mg salts could therefore be suggested because the presence of the same precipitates gave rise to the same paste strength development.

Ca and Mg oxides were expected to hydrolyse in water and form the respective hydroxides. The fact, that the paste strength developments of the sample containing $Ca(OH)_2$ and the sample containing the hydrolysed CaO were different, meant that CaO was not completely hydrolysed in water due to the very short contact time used in this investigation. Furthermore, because the affinity of Ca for water molecules was higher than that of Mg [18], the extents of hydration for both salts should be different given the same hydrolysis time and the same chemical dosage used. If the heterogeneous nucleation mechanism suggested above were true, one should expect that the paste strength developments of both CaO-containing and MgO-containing samples should be different. However, the results in Figs. 3 and 4 showed that the samples *CaO* and *MgO* demonstrated exactly the same paste yield stress at any given time. This was unexpected because the hydrolysed products of the oxides were chemically different. The most probable explanation is that hydration spheres were formed in the alkaline solution surrounding the continually hydrolysing oxides. To form these hydration spheres, water molecules and hydroxyl ions were taken away from the bulk alkaline silicate solution and lowered the local solution pH, or increased the local silicate concentration beyond saturation level. As the result, silicate polymerisation outside the hydration spheres was triggered in the same way as that of heterogeneous nucleation. These hydration spheres masked the chemical differences between the Ca and Mg cations and thus gave rise to the same nucleation effects. When these hydration spheres were eventually broken down, differences towards paste strength were experienced, as is evident in Fig. 2.

The reason why yield stress developments of the $Ca(OH)_2$-containing sample and the $CaCl_2$-containing sample were different can once again be explained from the heterogeneous nucleation point of view. When aqueous solution of $CaCl_2$ was added to the alkaline paste solution, $Ca(OH)_2$ was produced by taking in hydroxyl ions from the surrounding solution. This caused gelation of the soluble silicates, as discussed above. For the $Ca(OH)_2$-containing sample, $Ca(OH)_2$ was already present and was insoluble in high pH environment. Hence, the mechanism for the heterogeneous nucleation of $Ca(OH)_2$-containing paste was different from that of $CaCl_2$-containing one. The increase of gelation rate thus should be of purely a collision type for the $Ca(OH)_2$-containing sample. The same can be expected for the highly insoluble $CaCO_3$ as well. The reason why $CaCO_3$ promoted gelation at a much earlier age than any of the salts is still unknown and deserves to be further investigated.

Fly ash pretreatment was designed to remove the surface reactive species before making alkali-activated cements. The consequence was clear from Fig. 5: The removal of the surface reactive species delayed setting significantly. Setting was delayed about four times for *System V* of solid-to-liquid ratio 0.73 when compared to *System III* of ratio 0.5. In both systems, the same solution composition was used. Thus, the reactive species from solid dissolution was important to build up the right gel composition before setting. Once the right gel composition had been achieved, *System V* paste started to set and the addition of the various Ca and Mg salts accelerated the setting in a similar fashion as all the other nontreated systems, as shown in Fig. 2. This means that inorganic salts of Ca and Mg were still active in promoting polymerisation even for a slowly reacting system and the theory of heterogeneous nucleation remains valid.

5. Conclusion

Ionic contamination during manufacturing of alkali-activated fly ash-based cements was found not to adversely affect the product early strength. However, the setting and rheological properties of the early pastes were changed significantly by the Ca and Mg salts through heterogeneous nucleation effects. Setting was accelerated by these salts once the right solution composition was achieved through solid dissolution. Potassium salts were found to delay setting only when the initial solution for solid activation was low in soluble silicate concentration. The anions of Cl^-, CO_3^{2-} and NO_3^- could affect the alkaline solution to achieve the right composition and thus retard setting. Careful addition of inorganic salts hence can be used to modify the setting and rheological characteristics of alkali-activated fly ash-based cements, which are vital for industrial applications. The long-term stability of the cements still needs to be determined.

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