Thermogravimetric investigation on the chloride binding behaviour of MK–lime paste

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Abstract

The hydration products of 2.5, 5 and 10% Cl^- containing metakaolin (MK)–lime pastes are compared with the same obtained from MK–lime paste to understand the chloride binding behaviour of MK during the hydration of cement. Results indicate that 2.5% Cl^- addition into the MK–lime paste initially enhances the formation of Friedel's salt ($Ca_2Al(OH)_6Cl\cdot2H_2O$), but Friedel's salt decomposes at later stages due to the formation of stratlingite (C_2ASH_8). In 5 and 10% chloride containing pastes, Friedel's salt is observed throughout the reaction periods along with the high amount of CSH. Small amount of stratlingite is also formed on or after 60 day hydration of 5% Cl^- containing MK–lime pastes. On the other hand, MK–lime-10% Cl^- containing pastes show the complete absence of stratlingite and C_4AH_{13} through out the hydration period, which are the major hydration products of MK–lime paste. Mesuarements of pH of the simulated pore fliuds help to understand the decomposition behaviour of Friedel's salt. From the experimental results, chloride binding mechanism of MK–lime paste is also discussed.
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Keywords: Hydration; Metakaolin–lime; Chloride; Friedel's salt; TG-DTA; XRD

Cement chemistry notations
C   CaO
S SiO_2
A Al_2O_3
H H_2O
C_2ASH_8 $2CaO\cdot Al_2O_3\cdot SiO_2\cdot8H_2O$
CSH $CaO–SiO_2–H_2O$
C_4AH_{13} $4CaO\cdot Al_2O_3\cdot13H_2O$
C_3AH_8 $3CaO\cdot Al_2O_3\cdot8H_2O$
CH $CaO\cdot H_2O$ or $[Ca(OH)_2]$

1. Introduction

Ingress of chloride ion into the reinforced concrete and corresponding corrosion behaviour is one of the major problems in cement and building material industry. It is found that the addition of pozzolanic materials like metakaolin (MK), FA can reduce the ingress of chloride by improving the microstructure and chloride binding behaviour [1–3]. In hardened cement,

chloride may be bonded in the CSH gel or as a formation of complex calcium oxychloride, Friedel's salt ($Ca_2Al(OH)_6Cl\cdot2H_2O$) [4,5]. It is reported earlier that the MK-Portland cement paste can bind considerable amount of dissolved chloride present in pore water with relatively low reduction in pH due to the formation of stable Friedel's salt. MK removes chloride and hydroxide ions from solution and also maintains a low $[Cl^-/OH^-]$ ratio, which is important from concrete corrosion point of view [6,7]. Again one major problem on the utilization of high chloride bearing wastes like municipal solid waste incineration (MSWI) ash as pozzolanic material or as a raw material for production of cement is the presence of high amounts of chloride salts [8]. However the amount of chloride can be reduced by mixing these materials or by blending produced waste based cement with other pozzolanic materials [9]. In this context, MK can be used to prepare this type of pozzolana or as a pozzolanic additive in waste derived cement, which can improve the chloride binding behaviour of cement.

The knowledge of chloride binding behaviour of cement based system containing MK or other similar types of pozzolana will therefore help to understand the chloride binding behaviour of these pozzolanic materials in concrete as well as help to develop some new class of pozzolanic materials for utilization

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and solidification of some high chloride containing waste materials like MSWI ash. In this communication we present the results, obtain from the experiments done to understand the hydration behaviour of MK–lime paste in presence of high amounts of chloride salts. TG/DTA and XRD analysis techniques are used to characterize the hydration products. To understand the mechanism of hydration, pH of the simulated pore fluids are also evaluated. The high amounts of chloride containing hydrating pastes are considered to understand the behaviour of Friedel's salt and stratlingite during the cement hydration, although the hydration reaction in presence of high amounts of chloride salts (>2.5%) has little importance from concrete corrosion point of view.

2. Experimental

All chemicals used in this investigation were reagent grade and collected from Kanto Chemical Company, Tokyo, Japan. Metakaolin was prepared by calcining kaolin (collected from SIGMA–ALDRICH Company, St. Louis, USA) for 1 h at 800 °C in a muffle furnace. Chemical compositions of kaolin were determined by using standard analytical methods. Kaolin and MK samples were also characterized by using X-ray diffraction (XRD) technique and using Cu Kα radiation (Miniflex, MJ14848B01, Rigaku, Japan). SiO$_2$ and Al$_2$O$_3$ content in the kaolin were 45.06 and 39.87%, respectively. The loss on ignition of kaolin (13.91%) was approximately same with pure kaolin (13.96%). XRD pattern of kaolin showed the characteristic peaks at $2\theta = 24.92°$, 12.39°, 37.74° and 62.25°. Formation of MK on calcination of kaolin was indicated by the disappearance of characteristic peaks due to kaolin [9].

MK–lime (1:1) and 2.5, 5 and 10% chloride (as NaCl and KCl) containing MK–lime (1:1) mixtures were prepared, homogenized and stored in airtight containers. The MK–lime pastes with and without containing chloride salts were prepared by mixing various cementitious compositions with distilled water for about 5 mins, maintaining water:solid ratio of 2.25:1 (ml/g) in a plastic container. The pastes were immediately tightened, kept in desiccator under vacuum and allowed to hydrate at ambient temperature for different time periods. Parts of the hydrated pastes were collected from the container after definite time intervals and dried in two steps to stop the hydration of the mixtures: the samples were vacuum dried for about 5 h in desiccator, powdered and again vacuum dried for further 6 h. The final powdered hydration products were stored in airtight containers and in desiccator under vacuum. The XRD and TG/DTA patterns of the hydration products were recorded as soon as possible to avoid the problems related to atmospheric carbonation and corresponding damage of the samples.

The thermal curves (DTA and TG) of the hydration products were taken in a thermo gravimetric apparatus (Shimadzo thermal analysis system, model TA-60WS). A total of 15–20 mg of the samples were taken in an alumina crucible and heated in nitrogen atmosphere up to 1000 °C, maintaining 10 °C/min heating rate and using α-Al$_2$O$_3$ as the reference material. The XRD patterns of the hydration products were recorded using Cu Kα radiation (Miniflex, MJ 14848 B01, Rigaku, Japan). The rate of hydra-

tion was determined from the TG curves of the hydrated pastes by measuring the CH contents. The weight loss in the temperature range of 420–550 °C was taken as the loss due to CH. The amounts of CSH and Friedel's salt, form during hydration were also determined from the TG curves. The weight losses in the temperature range of 100–150 and 310–385 °C were taken as the loss due to CSH and Friedel's salt, respectively.

It was not possible to extract the pore solution from the pastes due to the small amount of hydration product. Therefore, regeneration of pore solution was done by the method as described by Goni and Guerrero [10]. Accordingly, 0.5 g of the powdered hydration product was saturated with 2 ml of the distilled deionized water and kept at ambient conditions for 24 h. The pH of the filtered solution was then recorded by a combined electrode with a pH range of 0–14.

3. Results and discussion

3.1. Thermal analysis

The DTA patterns of the hydrated MK–lime and MK–lime–NaCl pastes are shown in Figs. 1–4. The behaviour of KCl during hydration is almost similar with NaCl (figure not shown). The dehydration of Friedel's salt (Ca$_2$Al(OH)$_6$Cl·2H$_2$O) takes place in a wide temperature range of 100–500 °C [11,12]. However DTA and TG curves of the chloride containing pastes show an endothermic minimum at about 335 °C and a weight loss region in the temperature range of 310–385 °C, which is absent in the thermal curves of MK–lime paste. The XRD patterns (discuss in the next section) of the chloride containing pastes also show the presence of Friedel's salt along with CH, CSH, stratlingite and chloride salts. The endothermic minimum observe in the temperature regions of 100–150, 150–220, 220–310, 400–520 °C along with the corresponding weight loss as observe from the TG curves correspond CSH gel, stratlingite (C$_2$ASH$_8$), C$_4$AH$_{13}$ as well as hydrogarnet, (C$_3$AH$_8$) and calcium hydroxide (CH), respectively [13–16]. Recent study shows that the formation of C$_3$AH$_8$, which shows an endothermic minimum at about 298 °C is only observed in the high temperature cured MK–lime paste [15]. Therefore, the endothermic minimum observed at about 230 °C can be considered as C$_4$AH$_{13}$ [15]. Again alkali salts in high chloride containing hydration products show an endothermic minimum at about 775 °C. Thus, the endothermic minimum at 335 °C along with the weight loss in the temperature region of 310–385 °C is due to the decomposition of Friedel's salt.

In MK–lime hydration, CSH gel, stratlingite and C$_4$AH$_{13}$ are the only hydration products, which amount increase with progress of hydration time. Formation of stratlingite and C$_4$AH$_{13}$ during the hydration of MK–lime paste at room temperature (20 °C) is a well known observation and our findings related to MK–lime hydration are almost similar with previously reported data [15,16].

The addition of 2.5% Cl$^-$ into the MK–lime paste enhances the formation of Friedel's salt along with CSH gel up to 3 day of hydration, which is indicated by the strong endotherms in the corresponding temperature regions of these compounds. The
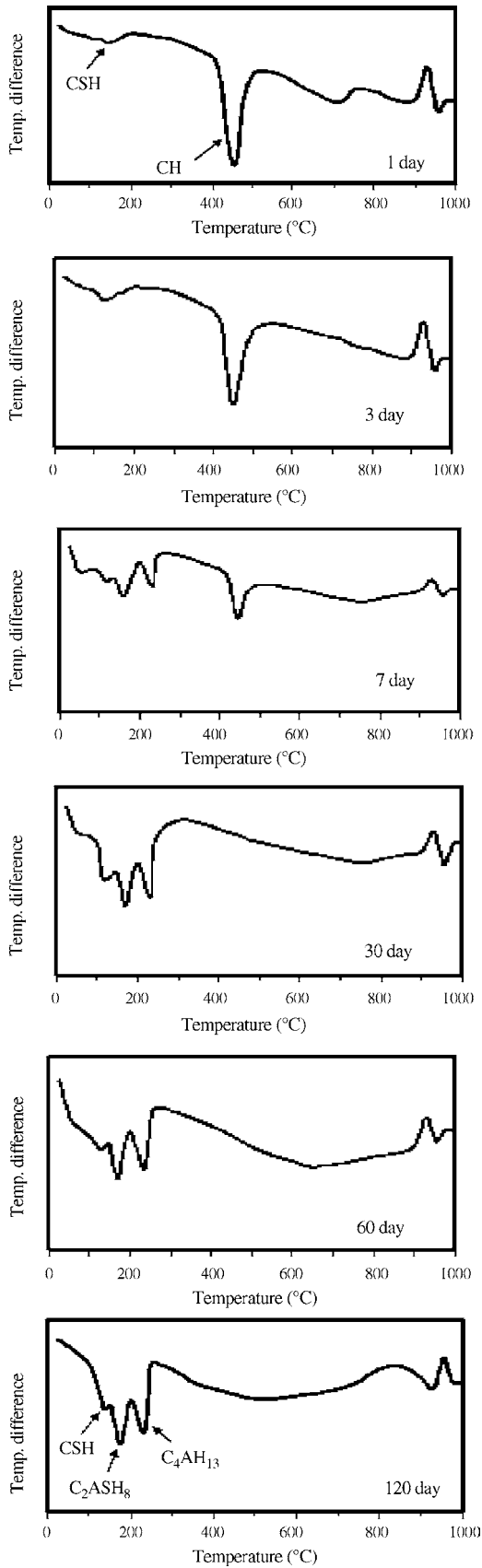
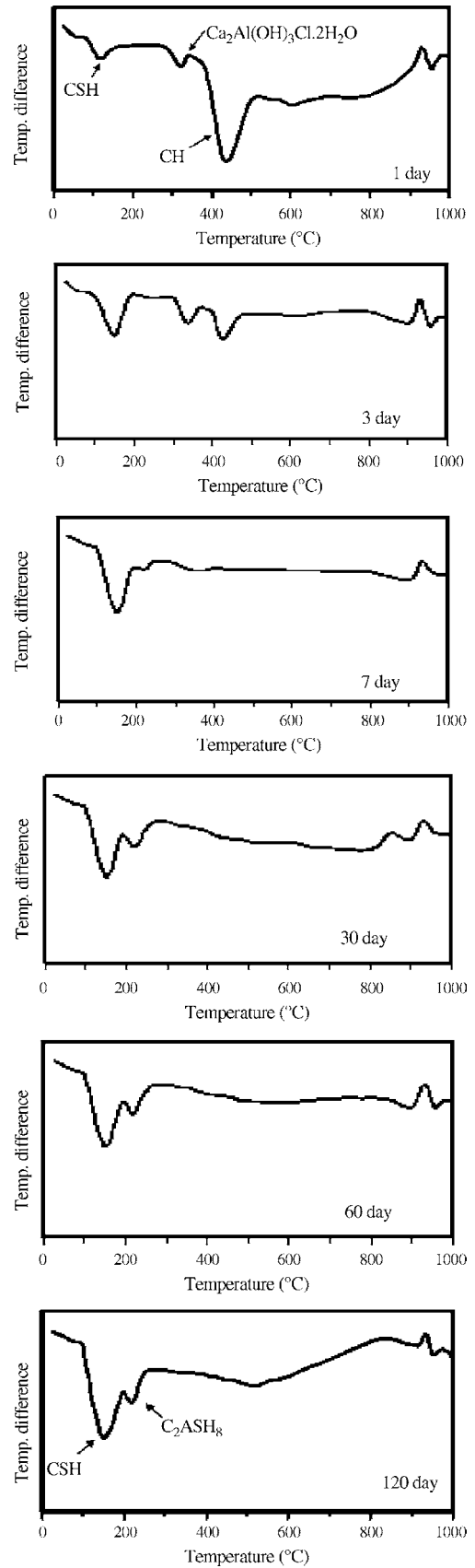Fig. 1. DTA patterns of MK–lime hydrated pastes (Endo down).

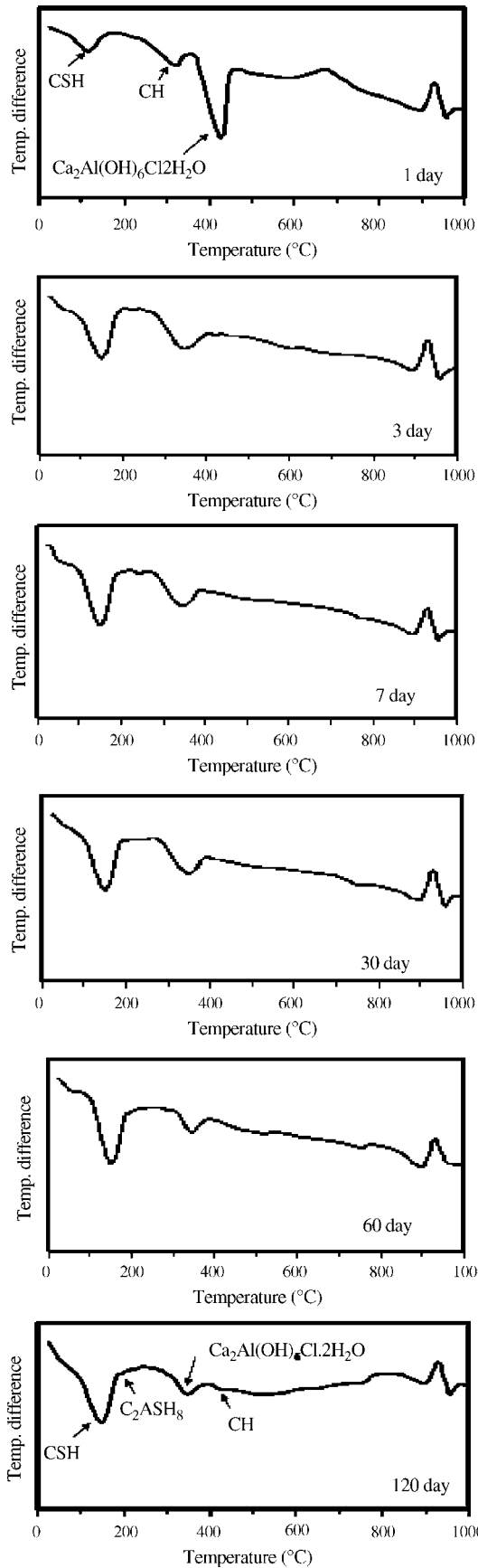Fig. 2. DTA patterns of 2.5% chloride (as NaCl) containing MK–lime hydrated pastes (Endo down).

Fig. 3. DTA patterns of 5% chloride (as NaCl) containing MK–lime hydrated pastes (Endo down).
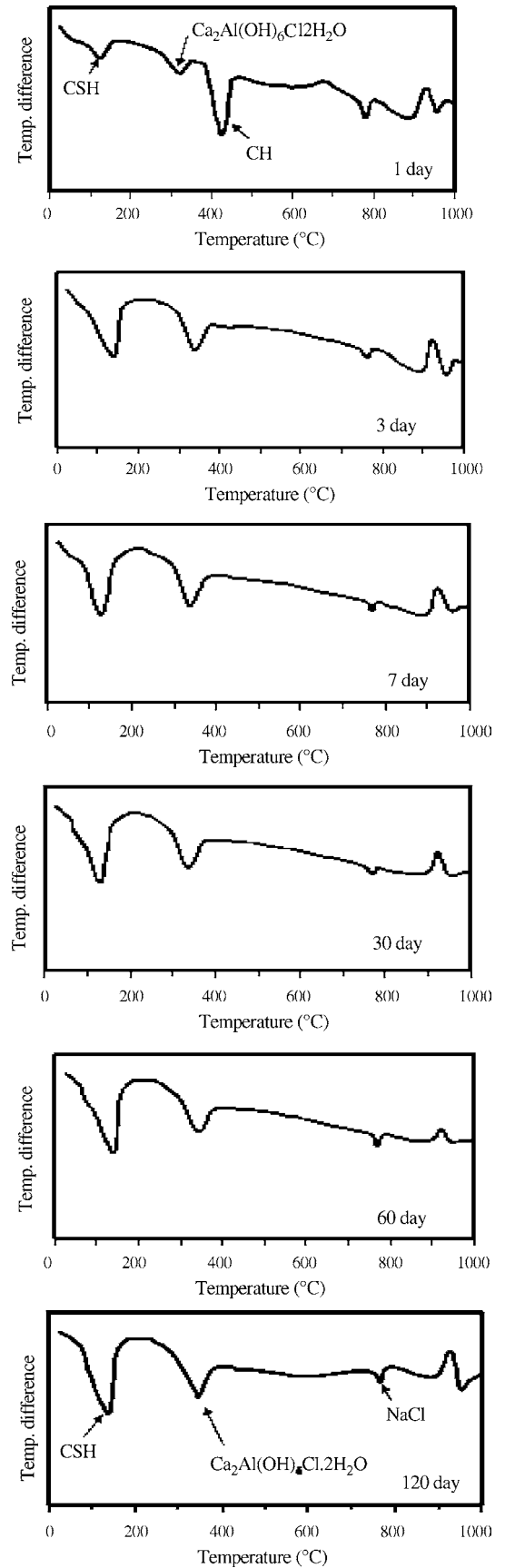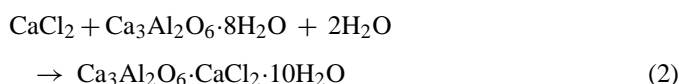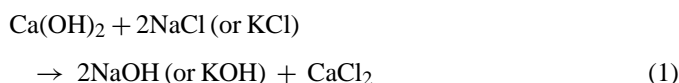

Fig. 4. DTA patterns of 10% chloride (as NaCl) containing MK–lime hydrated pastes (Endo down).

DTA pattern of 7 day hydrated paste show the presence of a weak endotherm due to Friedel's salt with a distinct endotherm at 150–220 °C region, due to the formation of stratlingite. Hydration at latter period shows the strong endotherms due to CSH and stratlingite with absence of corresponding endotherm for Friedel's salt. From the results, it is observed that the intensity of the endothermic minimum due to stratlingite is increasing as the endothermic minimum due to Friedel's salt reduces. Comparing the DTA patterns of MK–lime and 2.5% chloride containing MK–lime pastes, it is observed that the endothermic minimum corresponding to stratlingite in chloride containing paste is observed at higher temperature ($\sim$215 °C) than the same observed in the MK–lime paste ($\sim$175 °C). Possibly the presence of alkali chloride salts changes the composition of stratlingite and therefore increase the temperature of decomposition because stratlingite can incorporate relatively larger amounts of alkali metals, which displace Ca^{2+}, present in the crystal lattice [17]. Additions of 5 and 10% Cl^- into the MK–lime pastes show the presence of CSH gel and Friedel's salt through out the reaction period. However a weak endotherm in the 150–220 °C temperature region of 5% Cl^- containing MK–lime hydrated paste those collected after the hydration of 60 and 120 day indicates the formation of stratlingite at later stages of hydration. All chloride containing hydrated pastes also show the complete absence of C_4AH_{13} phase through out the reaction period, which is one of the major hydration products of MK–lime pastes. From the DTA patterns of hydrated pastes, it is also observed that the addition of chloride salts into the MK–lime paste enhances the formation of CSH along with the high reduction of CH during hydration. The disappearance of CH and the formation of Friedel's salt along with absence of C_4AH_{13} in the chloride containing pastes can be described by the following reactions:

$$Ca(OH)_2 + 2NaCl \,(or\, KCl)$$

$$\rightarrow 2NaOH \,(or\, KOH) + CaCl_2 \qquad (1)$$

$$CaCl_2 + Ca_3Al_2O_6 \cdot 8H_2O + 2H_2O$$

$$\rightarrow Ca_3Al_2O_6 \cdot CaCl_2 \cdot 10H_2O \qquad (2)$$

The CH, CSH and Friedel's salt contents in the hydrated MK–lime pastes with and without the presence of NaCl are shown in Fig. 5. The content of these constituents in KCl containing MK–lime pastes are almost similar with NaCl containing pastes. However the amount of CSH and Friedel's salt present in the KCl containing hydrated pastes are considerably lower than the same present in NaCl containing hydrated pastes. From Fig. 5, it is observed that the CH content in the chloride containing MK–lime hydrated pastes are always lower than the same present in MK–lime hydrated paste. This indicates that the addition of chloride into the MK–lime pastes enhances the rate of hydration reaction. The amounts of Friedel's salt present in the products those obtained after the 1 day hydrations of all chloride containing pastes are approximately same but the formed amount in 2.5% Cl^- containing paste is considerably lower than the same present in other two chloride containing pastes after 3 day of hydration. A decreasing trend on the content of Friedel's salt is also observed in 5 and 10% chloride contain-
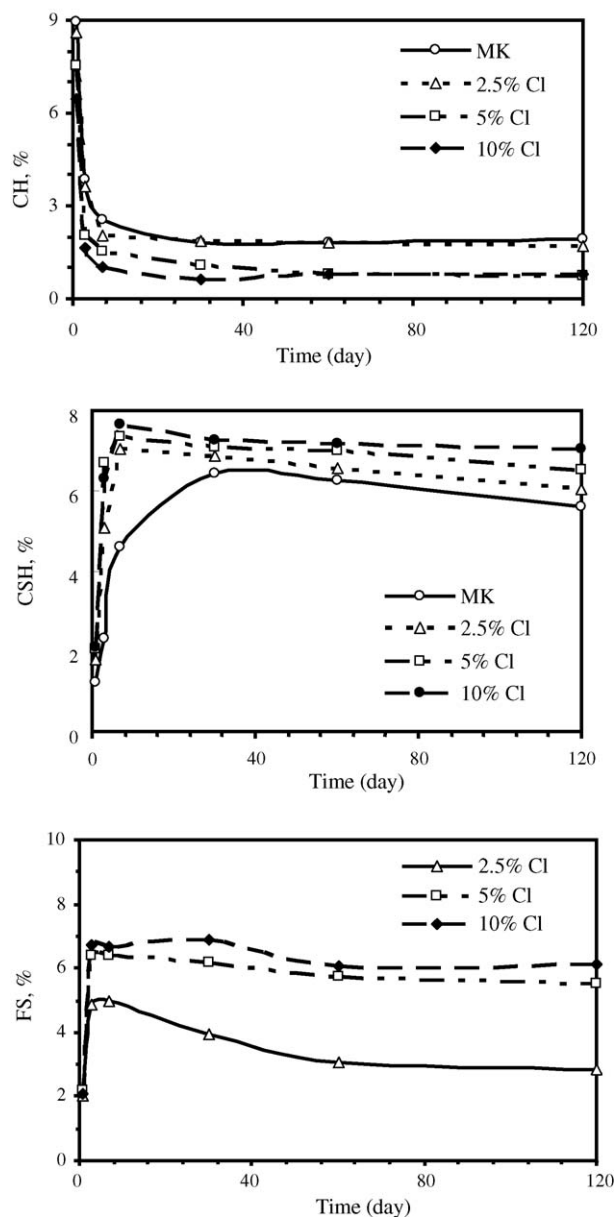

Fig. 5. CH, CSH and Friedel's salt (FS) contents in MK–lime and MK–lime–Cl⁻ (as NaCl) hydrated pastes.

ing hydrated pastes. From Fig. 5, it is also observed that the amounts of Friedel's salt form during the hydration of chloride containing pastes increase with increasing amount of chloride content in the pastes. Again from the measurements of CSH content in the hydrated pastes, it is observed that the addition of chloride salt into the MK–lime paste considerably increases the amount of CSH present in the hydrated pastes and the amount is also increased with increasing amount of chloride content in the paste.

3.2. XRD analysis

The XRD patterns of the products, obtain from the hydration of MK–lime with and without the presence of NaCl and KCl at different time intervals are shown in Fig. 6. Peak inten-
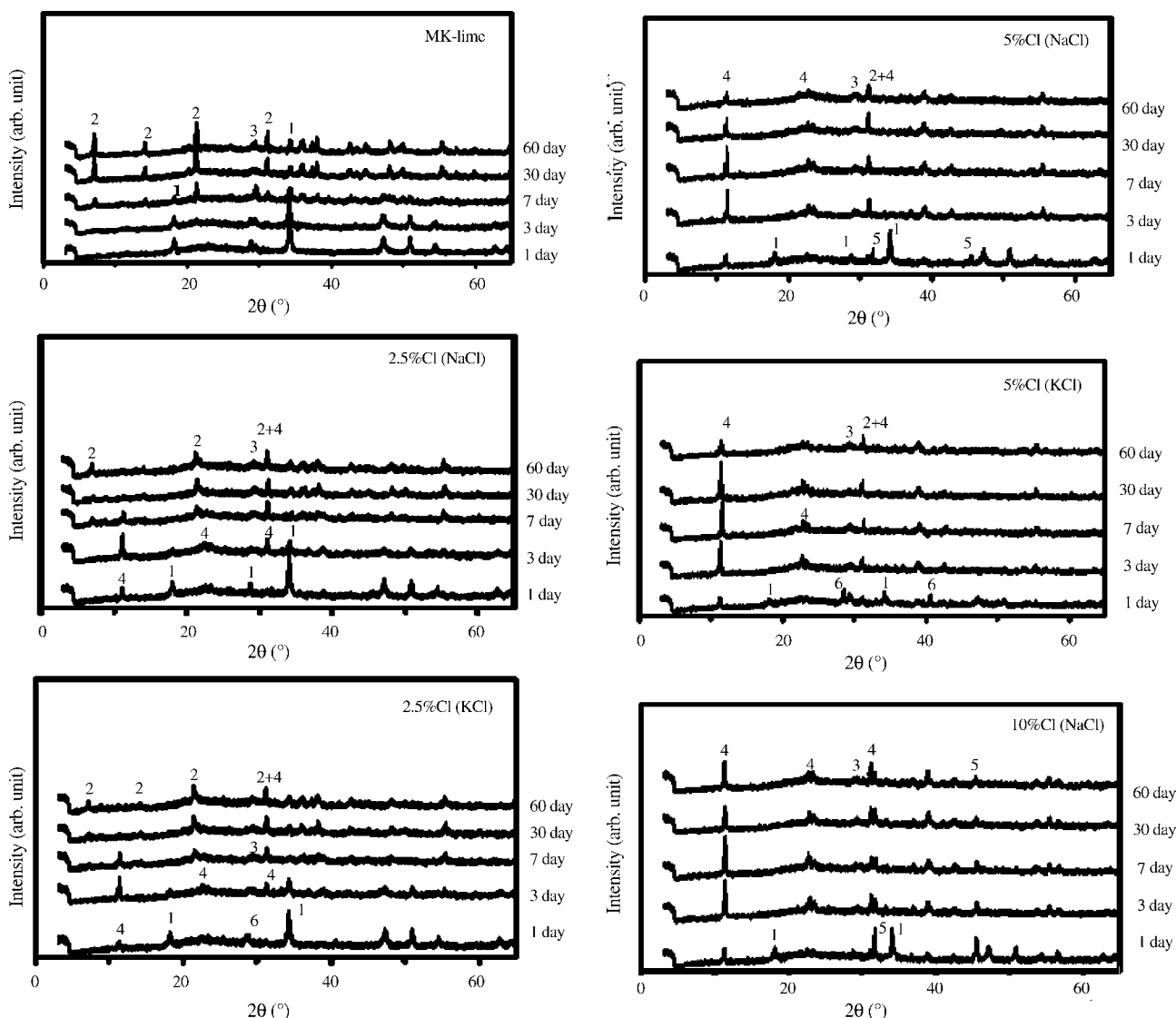
Fig. 6. XRD patterns of 10% KCl containing pates MK–lime and chloride containing MK–lime pastes (1: CH; 2: C_2ASH_8; 3: CSH gel; 4: $Ca_2Al(OH)_6Cl \cdot 2H_2O$; 5: NaCl; 6: KCl).

sities observe at $2\theta = 11.39°$, $22.78°$, $23.51°$, $38.99°$, $31.17°$, $42.66°$, $55.38°$, $35.70°$ correspond to Friedel's salt (PC-PDF No. 35-105), at $2\theta = 7.06°$, $21.28°$, $14.12°$, $31.09°$, $34.26°$, $38.01°$, $20.13°$ correspond to stratlingite (PC-PDF No. 29-285) and at $2\theta = 34.18°$, $18.18°$, $47.16°$, $50.83°$, $28.77°$ correspond to Ca(OH)$_2$, (CH).

From the XRD patterns of the products obtain from the MK–lime hydration, it is observed that the only hydration product form in MK–lime paste is crystalline stratlingite along with broad peak in the region of $2\theta = 29.28°$, due to the presence of amorphous CSH gel. The corresponding peaks of C_4AH_{13}, which is clearly observed from the DTA patterns of MK–lime paste, are not observed in the XRD patterns of the MK–lime hydrated pastes, probably due to its amorphous nature [15]. The XRD pattern of the 3 day hydration product of MK–lime paste shows the weak peaks due to the formation of stratlingite. On prolonging the hydration time, the intensities of the peaks due to stratlingite are increased along with the broad peak of CSH gel.

Addition of 2.5% chlorides into the MK–lime paste show the formation of Friedel's salt and CSH as the only hydration products up to the 3 day hydration. The peaks due to the formation of stratlingite are appeared in 7 day hydration products of 2.5% chloride containing pastes along with the decreasing intensities of the corresponding peaks of Friedel's salt. The intensities of the peaks due to stratlingite are increased at later stages of hydration, indicating formation of high amounts of stratlingite. The intensities of the peaks due to Friedel's salts are very weak in the XRD patterns of the hydrated products obtain after 7 day hydration. This indicates that almost all amount of Friedel's salts are decomposed at later stages of hydration. From the XRD patterns of the 2.5% chloride containing hydration products, it would appear that the intensities of the peaks due to Friedel's salt are decreasing as the intensities of the peaks due to stratlingite grow.

On the other hand, XRD patterns of the hydration products obtain from MK–lime pastes containing 5 and 10% chlorides show the presence of Friedel's salt and CSH as the major hydration products through out the reaction periods. However the

intensities of the peaks due to Friedel's salt's are decreased after 28 day hydration of the MK–lime pastes containing 5% chloride. Differential thermal analyses of the 5% chloride containing MK–lime pastes show the presence of small amount of stratlingite in the hydration products those obtain after 28 day. Although the XRD patterns of 5% chloride containing hydration products show the gradual decrease in the intensity of the peak at $2\theta = 11.39°$ due to the decomposition of Friedel's salt but another strong peak due to the presence of Friedel's salts as well as stratlingite at $2\theta = 31.10°$ is almost same through out the reaction periods. This indirectly suggests the formation of stratlingite at later stages of hydration, which destabilize the Friedel's salt present in the hydrated pastes.

From the XRD patterns, it is also observed that the peak due to chloride salts are completely absent in the 7 day hydration products of 2.5 and 5% chloride containing pastes. Therefore MK–lime paste with 1:1 ratio can take up to 5% chloride within the 7 day of hydration. Large amounts of chloride salts are also consumed during the hydration of 10% chloride containing MK–lime pastes. Again the decreasing intensities of Friedel's salt as observed in 2.5 and 5% chloride containing hydrated pastes at later stages of hydration do not regenerate the corresponding peaks of chloride salts. This indicates that chloride and alkali metals present in pastes combine with some hydration products like stratlingite, CSH and CASH gel [17,18].

3.3. pH of the pore fluid

The pH values of the simulated pore fluids of the hydrated pastes collected at different time intervals are shown in Fig. 7. The pH values of the fluid obtain from the MK–lime paste are approximately constant up to 3 day, decreased up to 30 days and increased at later stages of hydration. Initial constant pH is probably due to same dissolution and consumption rate of lime. After 3 days of hydration, pH of the pore fluid is decreased due to the consumption of high amounts of CH. DTA and XRD patterns of the hydrated MK–lime paste also show the formations of different hydration products after 3 day of hydration. An increase in pH at later stages of hydration is probably due to the dissolution of some hydrated phases. The pH values of the pore fluid of 2.5% chloride containing both pastes show approximately same behaviour through out the hydration period. The pH values of the pore fluids initially decrease up to 7 day, become approximately constant up to 30 day and slightly decrease at later stages of hydration. The initial pH decrease is due to consumption of high amounts of CH due to the formations of Friedel's salt and CSH. From figure, it is observed that the pH of the pore fluid of these pastes drops to a value slightly less than 12.0 after 3 day of hydration. The lowering of pH probably destabilize the already formed Friedel's salt and therefore started to decompose, which generates a constant pH during the hydration period of 7–30 day [10]. The decrease in pH at later stages of hydration of these pore fluids is probably due to the formation of stratlingite, which consumes considerable amounts of CH and alkali metals from the pore fluid [17]. The pH behaviour of the pore fluids obtain from 5 to 10% chloride as NaCl containing hydrated pastes show the similar trend like 2.5% chloride containing pastes. On the

other hand, the initial pH values of the pore fluids obtain from 5 and 10% chloride as KCl containing pastes increase up to 3 day and approximately constant up to 7 day in 5% Cl and decrease slightly in 10% Cl containing pastes. The pH values of the pore fluids of both KCl containing pastes are approximately constant at later stages of hydration. From the comparison of the pH data of both chloride (NaCl and KCl) containing pore fluids it is observed that the pH values of the pore fluid obtained from KCl containing MK–lime pastes are always lower than the pH values of the pore fluid obtained from NaCl containing pastes. Again the pH values of the pore fluids obtain from 5 and 10% chloride (NaCl and KCl) containing hydrated pastes cannot be related with the behaviour of Friedel's salts during the hydration of these pastes. From the results, it is also observed that the pH values of the pore fluids increase with the increasing content of chloride in the pastes. This can be explained by considering Eq. (1), where alkali chlorides react with CH and form alkali hydroxides and increase the pH of the pore fluid.

3.4. Discussions of the results

The structures of Friedel's salt and stratlingite are similar and both have the layer structure with same basic building unit $[Ca_4Al_2(OH)_{12}]^{2+}$ [19]. The net positive charge of this layer, which is arisen due to the substitution of Ca^{2+} by Al^{3+}, is balanced by the anions like OH^-, SO_4^{2-}, CO_3^{2-}. In case of Friedel's salt and stratlingite, this site is occupied by Cl^- and $(SiAl)O_4^-$ tetrahedral layer, respectively. The different numbers of anions required for charge balance as well as their different sizes and polarisabilities, control the interlayer water contents and control the exact layer stacking sequence. The formations of Friedel's salt in cement containing high amounts of tri calcium aluminate was explained by two mechanisms: adsorption mechanism and an anion exchange mechanism [20,21]. According to adsorption mechanism, Friedel's salt forms due to adsorption of bulk Cl^- ions present in pore solution into the interlayers of principle layers, $[Ca_2Al(OH)_6^- \cdot 2H_2O]^+$ of AFm (alumino ferrate mono) structure to balance the charge. As a result of this formation process, an amount of the Na^+ ions equivalent to the adsorbed Cl^- ions are removed from the pore solution to maintain the ionic charge neutrality and these Na^+ ions bind with C–S–H gel to balance the charge arising due to the replacement of Si^{4+} ions by Al^{3+} and Fe^{3+} ions. In the anion exchange mechanism, a fraction of the free chloride ions bind with the AFm hydrates (C_4AH_{13} and its derivative) exchanged with the OH^- ions present in the interlayers of the principal layer, $[Ca_2Al(OH)_6^- \cdot 2H_2O]^+$. The release of OH^- ions from the AFm hydrate into the pore solution maintain the charge imbalance, due to the presence of large amount of Na^+ ions and thereby increasing the pH of the pore fluid.

From our results, it can be assumed that two main components namely amorphous CSH gel and a layer structured product having same basic building unit, $[Ca_4Al_2(OH)_{12}]^{2+}$ are actually produced during the hydration of MK–lime paste with and without the presence of Cl^-. Formation of layer structured compound is probably depended on the presence of anions and the degree of competition among different anions present in pore
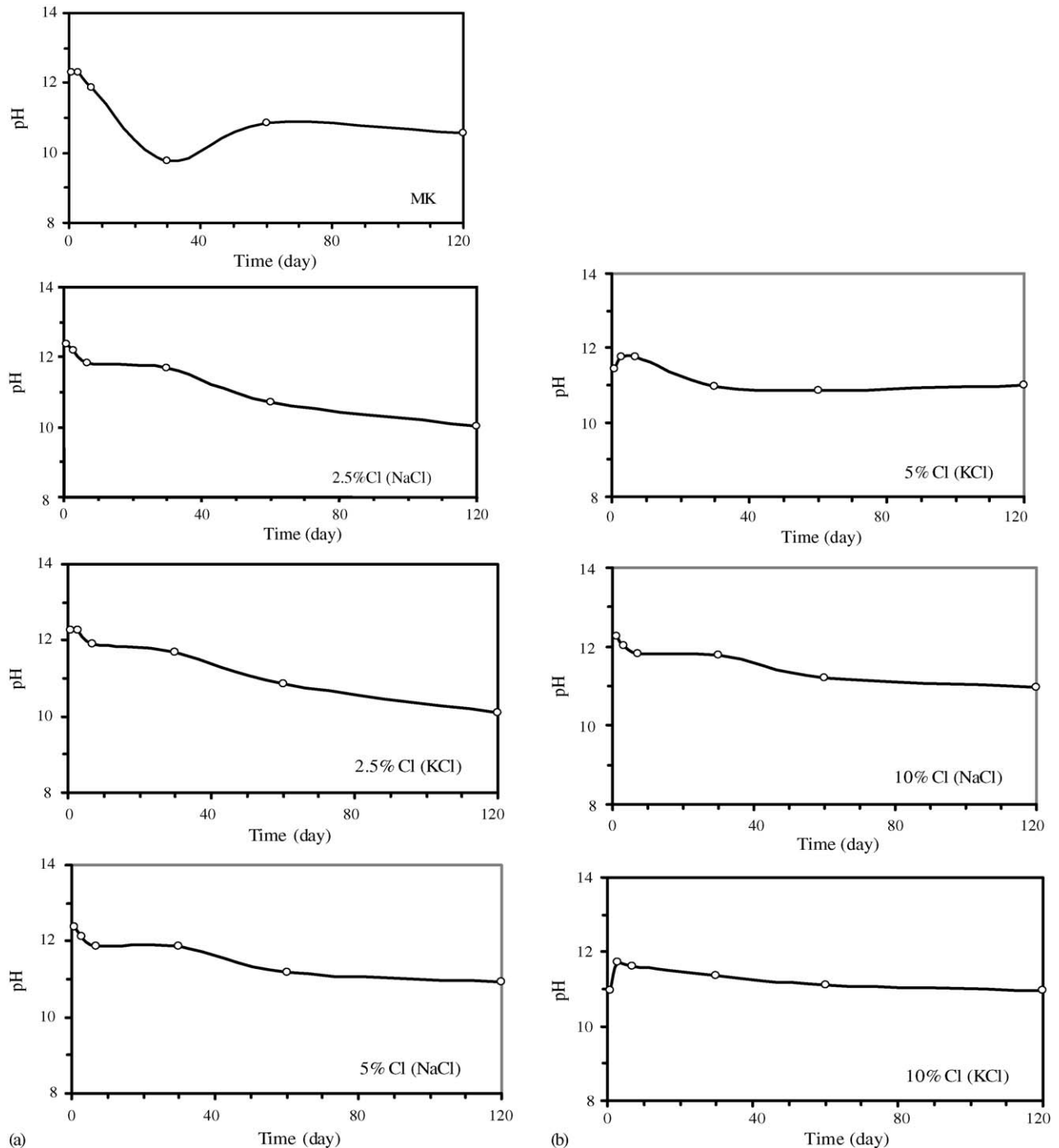
Fig. 7. pH values of the pore fluids, extracted from different hydrated pastes.

fluid for intercalation. In MK–lime–Cl⁻ pastes, this competition is mainly occurred between Cl⁻ and $(SiAl)O_4^-$ ions. Since Cl⁻ is readily available in the pore fluid of the hydrating pastes and therefore formation of Friedel's salt quickly started because formation of $(SiAl)O_4^-$ and stratlingite requires the dissolution of Si and Al from the MK. Probably initial deficiency of Al in the pore fluid, which is due to the formation of positively charged main building unit also favours the formation of Friedel's salt [22]. The remaining Si, present in pore fluid combines with Ca and form more amount of CSH gel. In the

initial stages of lime–MK-2.5% Cl⁻ and in the later stages of lime–MK-5% Cl⁻ containing pastes hydrations, formation of $(SiAl)O_4^-$ and also stratlingite are started due to the consumption of all available Cl⁻ ions present in the pore fluid. From the result of 2.5% chloride containing pastes, the instability of Friedel's salt at later stages of hydration can be correlated with the general view on the destabilization behaviour of Friedel's salt but it cannot be related in high chloride containing pastes. Generally it is assumed that the destabilization mechanism of Friedel's salt is pH dependent. Friedel's salt dissolves at 20 °C generating

a pH value of 12.0, due to carbonation and pozzolanic mineral additions [10,23,24]. In 2.5% chloride containing pastes, the solubilization of Friedel's salt is observed after 7 day of hydration due to the decrease in pH of the pore fluid to a value lower than 12.0. However one possible mechanism, which is probably occurred simultaneously during the conversion of Friedel's salt into stratlingite in MK–lime-2.5 and 5% Cl$^-$ pastes as observed from the thermal and XRD analyses is the anion exchange intercalation reaction of Cl$^-$ with tetrahedral (SiAl)O$_4$$^-$ ion. Recent studies also indicate that layered double hydroxides with similar structure of Friedel's salt like [Ca$_2$Al(OH)$_6$]NO$_3$·2H$_2$O, [LiAl$_2$(OH)$_6$]OH·H$_2$O, [LiAl$_2$(OH)$_6$]Cl·H$_2$O and particularly Cl$^-$ containing layered double hydroxide (Cl$^-$-LDH) show the high anion exchange intercalation reactions with different anions [25,26]. Since Friedel's salt is a one kind of Cl$^-$-LDH, therefore high anion exchangeability may enhance the formation of stratlingite from Friedel's salt, due to the intercalation of Cl$^-$ by (SiAl)O$_4$$^-$ in low chloride containing pastes. In 10% chloride containing pastes, Cl$^-$ is available throughout the reaction period, which inhibit the formation of stratlingite by forming [Ca$_4$Al$_2$(OH)$_{12}$]$^{2+}$ as well as Friedel's salt and therefore by blocking the Al^{3+}, which is necessary to form (SiAl)O$_4$$^-$. Due to this, excess amounts of Si, present in the pore fluid combine with Ca and form more amount of CSH, which is also observed from TG and XRD analyses. The XRD pattern of 10% chloride containing pastes also show the presence of chloride salts throughout the reaction period, which may be the constant source of chloride during the hydration reaction.

4. Conclusions

The results obtained from the hydration behaviour of MK–lime paste with and without the presence of chloride can be summarized as follows:

(1) In MK–lime hydration, CSH gel, stratlingite and C$_4$AH$_{13}$ are the major hydration products, which amounts increase with increasing hydration time.

(2) In 2.5% chloride containing pastes, although the initial hydration products are Friedel's salt and CSH gel up to 3 days of hydration, but at later stages, Friedel's salt gradually transfers to more stable stratlingite, without changing pH of the pore fluid. Again decomposition of Friedel's salt during hydration can be related with the formation of stratlingite. In 5 and 10% chloride containing pastes, Friedel's salt is observed throughout the reaction periods with formation of high amounts of CSH. In case of 5% chloride containing pastes, small amounts of stratlingite is also observed after 60 day hydration.

(3) MK–lime paste with a ratio of 1:1 can take ∼5% of chloride from both NaCl and KCl containing pastes. Addition of chloride salts into the MK–lime paste enhances the hydration reaction due to the formation of Friedel's salt. Again decomposition of Friedel's salt at later stages of hydration does not regenerate chloride salts and therefore alkali metals are combined with some hydration products.

(4) The initial formation of Friedel's salt in all the chloride containing pastes can be explained by assuming high reactivity of chloride than the (SiAl)O$_4$$^-$ towards the formation of layered structured hydration products having same basic building unit, [Ca$_4$Al$_2$(OH)$_{12}$]$^{2+}$ and also low availability of Al^{3+} to form (SiAl)O$_4$$^-$, which is necessary to form stratlingite. The decomposition of Friedel's salt at later stages of hydration in 2.5% chloride containing pastes is probably due to the decrease in pH of the pore fluid to a value <12.0 and also due to the formation of more stable stratlingite. Again the high stability of Friedel's salt in 10% chloride containing pastes is due to the availability of chloride ions through out the reaction period.

References

[1] R.K. Dhir, M.R. Jones, Development of chloride-resisting concrete using fly ash, Fuel 78 (1999) 137–142.

[2] P.C. Hewlett, G. Hunter, M.R. Jones, Bridging the gaps, Chem. Br. 35 (1) (1999) 40–43.

[3] G. Batis, P. Pantazopoulou, S. Tsivilis, E. Badogiannis, The effect of metakaolin on the corrosion behavior of cement mortars, Cem. Concr. Compos. 27 (2005) 125–130.

[4] E.P. Nielsen, D. Herfort, M.R. Geiker, Binding of chloride and alkalis in Portland cement systems, Cem. Concr. Res. 35 (2005) 117–123.

[5] A.K. Suryavanshi, J.D. Scantlebury, S.B. Lyon, The binding of chloride ions by sulphate resistant Portland cement, Cem. Concr. Res. 25 (3) (1995) 581–592.

[6] N.J. Coleman, C.L. Page, Aspects of the pore solution chemistry of hydrated cement pastes containing metakaolin, Cem. Concr. Res. 27 (1) (1997) 147–154.

[7] O.M. Jensen, P.F. Hansen, A.M. Coats, F.P. Glasser, Chloride ingress in cement paste and mortar, Cem. Concr. Res. 29 (1999) 1497–1504.

[8] A. Polettini, R. Pomi, P. Sirini, F. Testa, Properties of Portland cement stabilized MSWI fly ashes, J. Hazard. Mater. 88 (2001) 123–138.

[9] N. Saikia, A. Usami, S. Kato, T. Kojima, Hydration behaviour of eco-cement in presence of metakaolin, Resour. Process. 51 (2004) 35–41.

[10] S. Goni, A. Guerrero, Accelerated carbonation of Friedel's salt in calcium aluminate cement paste, Cem. Concr. Res. 33 (2003) 21–26.

[11] J. Csizmadia, G. Balazs, F.D. Tamas, Chloride ion binding capacity of aluminoferrites, Cem. Concr. Res. 31 (2001) 577–588.

[12] C. Abate, B.C. Scheetz, Aqueous phase equilibria in the system CaO–Al$_2$O$_3$–CaCl$_2$–H$_2$O: the significance and stability of Friedel's salt, J. Am. Ceram. Soc. 78 (1995) 939–944.

[13] M.A. Serry, A.S. Taha, S.A.S. El-Jemaly, H. El-Didamony, Metakaolin–lime hydration products, Thermochim. Acta 79 (1984) 103–110.

[14] N.J. Saikia, P. Sengupta, P.K. Gogoi, P.C. Borthakur, Hydration behaviour of lime–co-calcined kaolin–petroleum effluent treatment plant sludge, Cem. Concr. Res. 32 (2002) 297–302.

[15] M. Frias, J. Cabrera, Influence of MK on the reaction kinetics in MK/lime and MK-blended cement systems at 20 °C, Cem. Concr. Res. 31 (2001) 519–527.

[16] P.S. de Silva, F.P. Glasser, Phase relations in the system CaO–Al$_2$O$_3$–SiO$_2$–H$_2$O relevant to MK–lime hydration, Cem. Concr. Res. 23 (1993) 627–639.

[17] T.R. Jones, Metakaolin as a pozzalanic addition to concrete, in: J. Bensted, P. Barnes (Eds.), Structure and Performance of Concrete, second ed., Spon Press, New York, 2002, pp. 372–391.

[18] S.-Y. Hong, F.P. Glasser, Alkali sorption by C–S–H and C–A–S–H gels, Part II. Role of alumina, Cem. Concr. Res. 32 (2002) 1101–1111.

[19] M. Uehara, T. Sasaki, Hydration of Ca A-type zeolite and $Ca(OH)_2$, Chem. Lett. 30 (2001) 1040–1041.

[20] A.K. Suryavanshi, J.D. Scantlebury, S.B. Lyon, Mechanism of Friedel's salt formation in cements rich in tricalcium aluminate, Cem. Concr. Res. 26 (5) (1996) 717–727.

[21] M.R. Jones, D.E. Macphee, J.A. Chudek, G. Hunter, R. Lannegrand, R. Talero, S.N. Scrimgeour, Studies using ^{27}Al MAS NMR of AF_m and AF_t and the formation of Friedel's salt, Cem. Concr. Res. 33 (2003) 177–182.

[22] N.J. Coleman, W.R. Mchinnie, The solid state chemistry of metakaolin-blended ordinary Portland cement, J. Mater. Sci. 35 (11) (2000) 2701–2710.

[23] C.L. Page, O. Venneland, Pore solution composition and chloride binding capacity of silica fume-cement pastes, Mater. Construction 16 (91) (1983) 19–25.

[24] A.K. Suryavanshi, R.N. Swamy, Stability of Friedel's salt in carbonated concrete structural elements, Cem. Concr. Res. 26 (5) (1996) 729–741.

[25] L. Lei, F. Millange, R.I. Walton, D. O'Hare, Efficient separation of pyridinedicarboxylates by preferential anion exchange intercalation in $[LiAl_2(OH)_6]Cl·H_2O$, J. Mater. Chem. 10 (2000) 1881–1886.

[26] N. Iyi, K. Okamoto, Y. Kaneko, T. Matsumoto, Effects of anion species on deintercalation of carbonate ions from hydrotalcite-like compounds, Chem. Lett. 34 (7) (2005) 932–933.