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# 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.

*Keywords:* Hydration; Metakaolin–lime; Chloride; Friedel's salt; TG-DTA; XRD

*Cement chemistry notations*

| | |
|---|---|
| C | CaO |
| S | $SiO_2$ |
| A | $Al_2O_3$ |
| H | $H_2O$ |
| $C_2ASH_8$ | $2CaO\cdot Al_2O_3\cdot SiO_2\cdot 8H_2O$ |
| CSH | $CaO–SiO_2–H_2O$ |
| $C_4AH_{13}$ | $4CaO\cdot Al_2O_3\cdot 13H_2O$ |
| $C_3AH_8$ | $3CaO\cdot Al_2O_3\cdot 8H_2O$ |
| 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 $Al_2O_3$ 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-$Al_2O_3$ 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 hydration 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 ($Ca_2Al(OH)_6Cl{\cdot}2H_2O$) 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 ($C_2ASH_8$), $C_4AH_{13}$ as well as hydrogarnet, ($C_3AH_8$) and calcium hydroxide (CH), respectively [13–16]. Recent study shows that the formation of $C_3AH_8$, 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 $C_4AH_{13}$ [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 $C_4AH_{13}$ are the only hydration products, which amount increase with progress of hydration time. Formation of stratlingite and $C_4AH_{13}$ 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