The Formation of Stratlingite in Calcium Aluminate Containing Castable Systems

T. Shinmey, M. Ohkawa, A. Borovsky, M. Iiyama, Chr. Parr

The hydration mechanism of low cement castables has been long investigated but only a limited number of studies focused on specific hydrates are available. This paper will investigate a formation of stratlingite (C\textsubscript{2}ASH\textsubscript{8}), which is believed to prevent a conversion of metastable hydrates to the stable C\textsubscript{3}AH\textsubscript{6} in high alumina cement-silica fume systems. The stratlingite formation at 21 °C and 35 °C was confirmed by XRD. Its early formation at higher curing temperature is accelerated by the addition of sodium tripolyphosphate as evidenced by XRD.

1 Introduction
A bonding matrix of low-cement castables (LCC) typically consists of high alumina cement (HAC) and silica fume (SF) [1–3]. Hardened LCC contain a range of calcium aluminate hydrates including CAH\textsubscript{10}, C\textsubscript{2}AH\textsubscript{6}, C\textsubscript{2}AH\textsubscript{12}, C\textsubscript{2}AcH\textsubscript{11}, C\textsubscript{2}AH\textsubscript{6}, and C\textsubscript{2}ASH\textsubscript{8} (stratlingite) [4–6]. C\textsubscript{2}ASH\textsubscript{8} (stratlingite) is known as a hydrate stable over a long period of time [7–8]. The study aims to obtain a better understanding of the internal structure of the cement paste, its development over time and composition and the formation of stratlingite in simplified LCC systems.

The use of a siliceous material in combination with a sodium salt in CAC was recently reported to be more effective than the siliceous material alone in promoting formation of stratlingite [9] instead of hydrogarnet (C\textsubscript{3}AH\textsubscript{6}) [5, 7, 9, 10]. Siliceous materials, including natural zeolites, fly ash, slag and silica fume (SF) were effective in inhibiting hydrogenation and preventing strength reduction of CAC products when added in combination with a sodium salt. In particular, silica fume has been reported to favour the formation of stratlingite (C\textsubscript{2}ASH\textsubscript{8}) [11]. Silica fume reacts to form silicates in a high pH environment. This reaction is accelerated in the presence of an increased amount of alkali ions acting as a catalyst activating silica fume surfaces. Silicate anions then react with hydrated calcium aluminates to produce stratlingite [5].

Although the chemical analyses of stratlingites in castables had been reported by many researchers, the reported chemical data of stratlingite show a composition of non-uniformity [12–14]. This study investigates the formation and alteration of stratlingite in cement paste samples with or without deflocculant at two different curing temperatures, 21 °C and 35 °C. The nature, sequence, composition and microstructure of hydrated phases present in cement pastes consisting of CAC and SF with and without deflocculant were analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM) and electron probe microanalyzer (EPMA). Evolution of the cement paste hydration and a cause of changes in the hydrates in sealed glass bottles were determined by field emission scanning electron microscopy (FE-SEM) and energy dispersing X-ray analysis (EDX). Since stratlingite formation also occurs in LCC after a long curing time, and is considered to inhibit a hydrogarnet formation, it is also the aim of the present work to shed more light on the mechanism of LCC hardening [15].

2 Experimental
Materials used in this study included Secar 71, a 70 % alumina cement (CAC), produced by Kerneos; commercially available silica fume (SF) El kem 971-U produced by Elkem Materials; and reagent grade sodium tripolyphosphate (TPP). Chemical composition of raw materials as provided by the

<table>
<thead>
<tr>
<th>L.o.I.</th>
<th>SiO\textsubscript{2}</th>
<th>Al\textsubscript{2}O\textsubscript{3}</th>
<th>Fe\textsubscript{2}O\textsubscript{3}</th>
<th>TiO\textsubscript{2}</th>
<th>CaO</th>
<th>MgO</th>
<th>Na\textsubscript{2}O</th>
<th>K\textsubscript{2}O</th>
<th>C</th>
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<tr>
<td>CAC</td>
<td>0,14</td>
<td>0,21</td>
<td>69,49</td>
<td>0,17</td>
<td>0,02</td>
<td>29,79</td>
<td>0,27</td>
<td>0,21</td>
<td></td>
</tr>
<tr>
<td>SF</td>
<td>0,50</td>
<td>98,4</td>
<td>0,20</td>
<td>0,01</td>
<td>0,20</td>
<td>0,10</td>
<td>0,15</td>
<td>0,20</td>
<td>0,50</td>
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</table>
Manufacturers of cement paste samples with 60 mass-% of CAC and 40 mass-% of SF were prepared by mixing the required amounts of solids and deionized water at a water/solid ratio of 0.864 for 3 min, 0.41 mass-% of TPP was dissolved in a required amount of water in advance, and then the water was mixed into the solid sample. The freshly mixed cement paste was placed into small glass bottles (φ 20 x h 40 mm), and then sealed with a plastic lid. These bottle samples were divided into two groups; one group was placed in a 21 ± 2 °C water-bath while the other in a thermostatic oven at the temperature of 35 ± 1 °C.

After 2 days of curing, each bottle sample was split into several fragments of about 0.5–1.5 cm². These fragments were then reinserted into a new glass bottle with a water-soaked cotton ball placed inside and sealed with a plastic lid. In this way the atmosphere above the paste was approximately saturated with water vapour, and the heat of reaction was quickly conducted away from the sample. The repackaged samples were cured for a predetermined period of time under the same conditions as before, i.e. at 21 ± 2 °C or at 35 ± 1 °C. Subsequently, a designated quantity was cut daily from the surface of a sample stored in a bottle, washed in acetone to stop the hydration [6] and air-dried before being analyzed.

In this paper, the prepared cement paste samples were labeled hf and hft (h for high alumina cement = CAC, f for SF and t for TPP), numbers 21 and 35 are a reference of the curing temperature.

2.1 XRD (X-ray Diffraction) analyses

RIGAKU MultiFlex X-ray diffractometer was used, Copper Kα radiation with λ = 0.15418 nm at 40 kV and 40 mA was employed. The fragment samples (the total amount of 0.300 g) were taken with a spatula from the bottles, and then the samples were ground to a fine powder (<63 μm) in acetone. A special reagent grade of corundum (Al₂O₃) was used as the reference material for intensity and d-spacing, 10 mass-% of the reagent was mixed into the powdered sample, X-ray analyses were done at the predetermined periods as follows: 8 h later, every day in the first week, weekly during the following six weeks, and 94 days later.

2.2 EPMA (Electron Probe Microanalysis) analyses

Samples of about 5–8 mm in size, hydration of which was stopped by acetone, were prepared after 27 days and embedded in a resin, then polished half way through to expose a cross-section of the material. In order to prevent further hydration a liquid lubricant DP-Lubricant Blue (Stuers Corp.) was used. EPMA was carried out for analyses of the following 9 components: SiO₂, CaO, Fe₂O₃, Al₂O₃, P₂O₅, Na₂O, K₂O, MgO, and TiO₂, using a JEOL JXA-8200 EPMA with an accelerating voltage of 15 kV, a beam current of 5 nA, and a spot size of 3 µm. Back-scattered electron (BSE) imaging was also conducted. Note that the measurement was performed 9 days after the acetone treatment.

2.3 SEM (Scanning Electron Microscopy) analyses

The polished samples used for the EPMA measurement were trimmed to 9 mm x 5 mm fractions for FE-SEM (Hitachi S-5200) analyses. Chemical analyses were carried out by the EDX (EDAX Genesis XM2) X-ray analyzer. The measurement was performed 114 days after the acetone treatment.

3 Results and discussion

3.1 XRD analyses

Samples cured at 21 °C with TPP (hf) and without TPP (hf) were left to harden for about 8 h while those samples at 35 °C for about 6 h before they were analyzed. (1) CAH₁₀; CAH₁₀ hydrate was detected only in the samples cured at 21 °C as shown in Figs. 1 and 3. In the samples cured at 35 °C this hydrate was converted as evidenced from Fig. 2 and 4. CAH₁₀ has been detected along with C₂AH₈ in hf-21 without TPP since the beginning of curing (Fig. 3) but in the samples...
with TPP, both hydrates crystallized only after 1 day (Fig. 1). From curves depicted in Fig. 1 and 3 it is evident that there is an increase in the CAH_{10} peak intensity over time in the samples without TPP until an abrupt drop is observed, followed by a plateau. Samples with TPP give more gradual curves, the XRD intensity in the figures was a quotient of the higher peak of the component for that of the reference material (corundum).

(2) C_2AH_8
The C_2AH_8 hydrate has crystallized in large quantities in the samples cured at 35 °C with or without TPP since the beginning of curing (Fig. 2 and 4). Other trend was observed in the samples cured at 21 °C (Fig. 1 and 3). In general, in samples with TPP the C_2AH_8 peak lasts longer and is also slightly stronger but as one observes, especially at higher curing temperature, the peak disappears more quickly. The descending curve of C_2AH_8 is crossing an ascending curve of stratlingite as formation of stratlingite is preceded by the formation of meta-stable C_2AH_8 [13].

(3) C_3AH_6
C_3AH_6 hydrate was not observable in samples cured at 35 °C of Hft-21, and then completely disappeared after 1 day. Although C_3AH_6 is described as a transient hydrate for C_4AH_11 and C_2AH_8 hydrates [11], such end products were not detected in this study.

(4) C_4AH_{13}
As evident from Fig. 1–4, stratlingite crystallized precociously in the samples cured at higher temperature and with TPP. TPP is available because its sodium ions have a significant influence on stratlingite formation [10]. Mineralogical phases CA and CA_2 (Fig. 1–4) disappeared more rapidly at higher curing temperature while their dissolution is slightly delayed at lower curing temperature. This delay in dissolution of CAC, through addition of TPP, seemed to slightly speed up the stratlingite formation.

(5) Al(OH)_3
Gibbsite [Al(OH)_3] was detected in Hft-35 already after 6 h. At 35 °C its peak intensity increases rapidly before a plateau is reached.

(6) C_3AH_6
C_3AH_6 did not crystallize in samples cured at 21 °C. In Hft-35 without TPP C_3AH_6 was detected after 9 days. In Hft-35 with addition of TPP its crystallization was delayed and occurred only after 5 weeks.

<table>
<thead>
<tr>
<th>Tab. 2 Results of EPMA analyses</th>
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<td>Molar Ratio</td>
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Hft-21 represented by sample P1–P12 in Tab. 2
A number of features can be identified from the BSE images (not shown). The space between the masses is filled with plate crystals and an amorphous material. Furthermore, big crystals of different hydrates are often surrounded by SF masses. The samples appear to have heterogeneous texture. Analyses of the grey part (P1) reveals that it is CAH_{10} and an irregularly shaped white area (P2) is an unhydrated CAC. EPMA analyses of a smooth part (P3) of bulky white-gray crystals show that its composition is close to the stratlingite composition.
3.3 SEM

The composition of crystalline hydrate indicates $C_2\text{ASH}_8$ with a high SiO$_2$ molar ratio mainly probably because (1) fine crystals of $C_2\text{ASH}_8$ are surrounded by unreacted SF [11], or (2) $C_2\text{ASH}_8$ crystals are contaminated with silicates [11], or (3) amorphous silica is attached to the surface of $C_2\text{ASH}_8$ crystals. A previous study [14], does not provide an evidence for statements (1) and (2).

In this study the surface of $C_2\text{ASH}_8$ crystals with a high SiO$_2$ molar ratio was observed by FE-SEM and is shown in Fig. 5a–c. The SEM image of the area near P36 shows (Fig. 5b) irregularly shaped grains of about 0.5 µm clearly attached to the surface. They were found to be composed of SF. These grains of SF can increase the SiO$_2$ molar ratio of surface (Fig. 5d), and as such a possibility of these structures cannot be denied. Outside of the crystals there is a chunk of SF. SEM image (Fig. 5c) shows irregularly shaped particles of less than 0.5 µm covered in a gelatinous substance. EDX elemental analyses of P37 detected mostly Si and some Al with some residual quantity of Ca. In the center of well-developed plate-like crystals, a smooth matrix is visible (Fig. 6a). Its surface was magnified up to 300 000 but any adhesion/attachment of SF particles was not recognized (Fig. 6b). The EDX elemental analyses of P38 (Fig. 6c) indicate molar ratios of main components are close to $C_2\text{ASH}_8$. However, a flat side of the polished surface is very small for any detailed observation.

4 Conclusions

CAC pastes with SF some containing TPP were mixed. The paste was then cast into a bottle and cured at 21 °C and 35 °C. Development of different hydrates over time was analyzed by XRD and during the final stages, by EPMA, some selected samples were observed by EPMA and FE-SEM.
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C2 AH8 has crystallized in all samples since the beginning of hydration. The higher the curing temperature, the higher is its X-ray peak intensity. It soon started to disappear and crystallization of stratlingite was observed as the C2 AH8 hydrate was found to convert to stratlingite.

After three months of curing at 21 °C, regardless of the TPP presence, in addition to CAH10, gibbsite and stratlingite were detected, C3 AH6 and calcite were not detected. In samples without TPP cured at 35 °C, C3 AH6 crystallized along with gibbsite and stratlingite, calcite was also de-

The hardening of samples with TPP, regardless on the curing temperature, was delayed but the early crystallization of stratlingite was observed because of the presence of sodium ions. The stratlingite formation was further accelerated at higher curing temperature.

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tected. When TPP was added, in addition to stratlingite and gibbsite, C₃AH₆ and calcite were detected at later stages.

- EPMA analyses showed that SF developed in and around large plate-like crystals with a smooth surface that match with the composition of stratlingite. The analyses of what appears to be a rough surface show variations in a molar ratio of SiO₂, mainly higher molar ratio.

- FE-SEM images show that a rough surface of big plate-like crystals is covered with small grains of SF. These plate crystals were identified by EDX analyses as stratlingite containing a higher SiO₂ molar ratio. This higher molar ratio of SiO₂ can be explained by the presence of these SF grains.

This study aimed to gain a better understanding of the internal structure of the cement paste, its development over time and composition. However, the surface area of cement paste is subjected to different chemical alterations than its interior. Generally, efflorescence occurs on a surface of the cement paste. Further studies will aim at investigating the effect of atmosphere and CO₂ on stratlingite.

Acknowledgements

The authors thank Prof. H. Hidaka of the Hiroshima University for his advice and guidance. Thanks also to Prof. K. Terada and Dr. J. Ando of the same university for their valuable comments, and to Y. Shibata of the same university for his help with the EPMA analysis. This study was supported by research grants from Kerneos.

References

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