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Early Hydration of Alite with and without Polycarboxylate Ether Based Superplasticizer

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Abstract

Monoclinic and triclinic alite, the main components of Portland cement are synthesized to study the single phase hydration chemistry. The hydration of the two forms of alite with and without additives are monitored by calorimeter and in-situ FTIR.

The calorimetry results show that the hydration of the two forms of alite are almost unaffected of the different water to solid ratio when additives are absent. The hydration of monoclinic alite is accelerated with respect to the hydration of triclinic alite; this may be due to the presence of the minor amount of MgO and Al_2O_3 in monoclinic alite. This maybe also due to the monoclinic alite has a larger surface area compared with triclinic alite.

The calorimetry hydration curves of the two forms of alite are shifted to right when M.G. SKY 558, M.G. ACE 410 and Sikament H-D 10 are used, though the effect is stronger on triclinic alite. The induction period is more prolonged when increasing the dosage of the additives (the curves are shifted more to right).

The time derivative of peak area at 1100-920 cm^{-1} and 3660-3600 cm^{-1} of IR-results show the delayed formation of C-S-H and $Ca(OH)_2$ when M.G. SKY 558 is used in case of monoclinic alite, which are in agreement with the calorimetry results.

In contrast, in the case of triclinic alite, the time derivative peak of peak area at 1100-920 cm^{-1} and 3660-3600 cm^{-1} of IR-results cannot show the delayed formation of C-S-H and $Ca(OH)_2$ when M.G. ACE 410 is used.

According to the IR-result the addition of M.G. SKY 558 in hydration of monoclinic alite and M.G. ACE 410 in hydration of triclinic alite seems to increase the total formation of C-S-H and to decrease the total formation of $Ca(OH)_2$ within the first 25 hours.

Even the influence of adipic acid (pure) on the hydration of triclinic alite is investigated. The addition of adipic acid seems to decease both the formation of C-S-H and the formation of $Ca(OH)_2$ within the first 25 hours, in contrast to when pure water is used.

Contents

1 Introduction

Cement functions as a binder in concrete and in mortar that binds together stones or bricks. The constructional cement can be either hydraulic or non-hydraulic. Hydraulic cement can be used in wet conditions or underwater. This is due to the replacement of some of the cement components by activated aluminum silicates, pozzolanas. The non-hydraulic cement will not set in wet conditions or underwater. The hardening of non-hydraulic cement is a carbonation process, a reaction with the carbon dioxides that present in air. Non-hydraulic lime and gypsum are examples of non-hydraulic binders. Hydraulic cement is hardened by hydration, a reaction with water. Hydraulic lime and Portland cements are hydraulic binders. [1]

Production of cement is very energy consuming and the emission of carbon dioxide is high. According to Ylmén [2] the production of one ton cement consumes 3 GJ of energy and emits 0.8 tons carbon dioxide. World production of cement in 2014 is about 4 billion tons and of which about 60% is produced in China [3].

2 Purpose

The purpose of this project is to try to understand the early alite hydration chemistry of cement and how different additives, such as polycarboxylate (ethers) based superplasticizers,

impact the hydration process. The techniques are employed in this study are high-temperature synthesis, isothermal calorimetry, XRD, BET-model and *in-situ* FTIR.

3 Theory

3.1 Portland cement

Portland cement is made by heating a crushed mixture of limestone and clay or other materials of similar composition in a rotary kiln to about 1450°C; during heating fusion happens and nodules of clinkers are formed, according to equation (1). The main component of clinkers are alite, Ca_3SiO_5(tricalciun silicate), belite, Ca_2SiO_5(dicacium silicate), aluminate, $Ca_3Al_2O_6$(tricalcium aluminate) and ferrite, $Ca_4Al_2Fe_2O_{10}$ (tetracalcium aluminoferrite); minor amounts of lime and other oxides can also be found in clinkers. In cement chemistry, an abbreviation of the formula of alite, belite, aluminate and ferrite are C_3S, C_2S, C_3A and C_4AF, respectively. Normal Portland cement clinker consists of 50-70% alite, 15-30% belite, 5-10% aluminate and 5-15% ferrite. The clinkers are grinded with a few percent addition of gypsum $(CaSO_4 \cdot 2H_2O)$. Gypsum has an ability to control the rate of set and can be replaces by other materials that contain sulfates. Other admixtures can be designed and added to meet different requirements. [4, 5]

$$CaCO_3 + clay + heat \rightarrow clinkers + CO_2 \qquad (1)$$

3.2 Hydration

Hydration of a cementitious material is the process of changing that occurs when water is added to the anhydrous cement. The typical water to cement ratio (w/c) is 0.3-0.6. When the main cement components, alite and belite, react with water a compressive strength is developing through hydration according to equations (2) and (3). [4]

The hydration of alite, equation (2), is concerned in this project.

The products formed are calcium-silicate-hydrate, $C_3S_2H_3$, also called the C-S-H gel and crystalline calcium hydroxide, $Ca(OH)_2$, [CH]. Calcium-silicate-hydrate is an amorphous phase of variable composition of the C-S-H, which depends on the hydration conditions e.g. hydration temperature and the amount of hydration water available. The formation of C-S-H gel is thought to slow down the hydration reaction rate to a minimum in the earlier period, an induction period. Calcium hydroxide, also known as portlandite, is formed when Ca^{2+} ions released from the cement component react with water. The presence of calcium hydroxide gives the cement slurry its basicity of pH about 13. [12, 15]

Alite hydrates quicker than belite. About 70% alite is reacted in 28 days and all in 1 year; in contrast, about 30% belite is reacted in 28 days and 90% in 1 year. The earlier hydration is controlled by alite. Belite affects the final strength of the hardened cement. [4]

$$C_3S + H \rightarrow \text{C-S-H-} + CH + heat \qquad (2)$$

$$C_2S + H \rightarrow \text{C-S-H} + CH + heat \qquad (3)$$
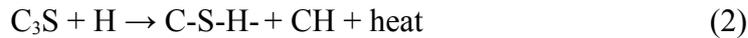
The aluminate and ferrite react with water and form calcium-aluminate-hydrate, C_3AH_6. This reaction is strong at the beginning of hydration and therefore affects the rheology of the cement slurry. Unlike the C-S-H gel calcium-aluminate-hydrates do not form a hindered layer that may prevent the further hydration of aluminate. [4]

Gypsum, which is added to cement to control the rate of earlier setting, reacts with water and releases calcium and sulfate ions. These ions then react with aluminate and hydroxyl ions forming ettringite, $C_3A3CS \cdot 32H$ (trisulfoaluminate hydrate). [4, 2]

3.3 Superplasticizer
Superplasticizers are added to cement to reduce water to cement ratio, without affecting the flow of cement suspension in concrete or mortar system [6, 10]. A lowered w/c ratio can decrease the porosity of the hardened concrete and thereby increase the density and strength of the concrete [11].

Superplasticizers can be classified into three groups, sulphonated polymers, carboxylated polymers and synthetic polymers. The synthetic polymers can be either sulphonated or carboxylated that incorporate supplementary functional groups [13]. The superplasticizers are used in this project are all carboxylated polymers: MasterGlenium SKY 558, MasterGlenium ACE 410 and Sikament H-D 10, which

Figure 2 structure of adipic acid

were provided of CBI in Borås. The solid content for M.G. SKY 558, M.G. ACE 410 and Sikament H-D 10 are 28.5%, 23% and 40% respectively (see figure 1).
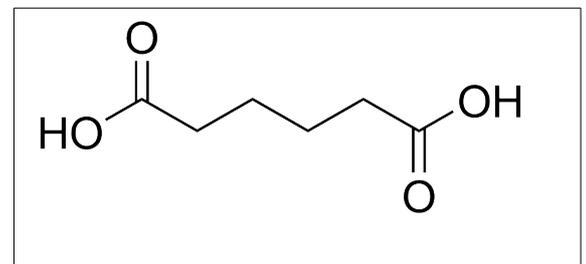Even the influence of adipic acid (pure form) on hydration triclinic alite is investigated and the results are presented, compared and discussed in a separate part of the report. The structure of adipic acid is shown in figure 2.

3.4 High temperature synthesis
A high temperature furnace is used in the synthesis of monoclinic and triclinic alite in this project.

3

3.5 XRD

X-ray diffraction is an analytical method used to identify atomic or molecular structure of a crystal. When the X-ray radiation hit the molecule or atom in the sample the X-ray is diffracted by the electrons it hits. A detector collects the diffracted X-ray and sends it to a computer that processes the collected data.

Because the molecules and atoms are structured the diffracted radiation intensity will be in maxima or minima. This is governed by the Bragg´s law, $n\lambda=2d\sin\theta$; n is an integer, λ is the X-ray wavelength, d is distance between the crystal plan and θ is the diffraction angle. The distance d, which provides information about the crystal structure, can be calculated when the other parameters are known.

A diffraction pattern is often obtained as the diffraction intensity versus the angle. The depth of the XRD measurement is from a few micrometers to a few hundred micrometers. It depends on the density of the sample. [7, 13] In this project, XRD technique is used to see if the intended monoclinic and triclinic alite are formed.

3.6 BET-model

The specific surface area of the two forms of alite are determined by using a Micromeritics ASAP2020 Gas Adsorption Instrument. This is an instrument that uses the BET (Brunauer-Emmett-Teller) theory to accurately measure the surface area of small solid particles and the gas is used in the measurement is nitrogen gas. The surface area determinations are not the main scope of this study, thus, the working principle of this technique and the setup of the instrument can be found elsewhere.

3.7 Isothermal calorimeter

Chemical reactions, physical changes and phase transitions can be exothermic or endothermic. A calorimeter is a devise that measures the heat flux during reactions over time. The hydration characteristic of the two forms of alite is studied by this technique in this project.

3.8 FTIR

Fourier Transform Infrared Radiation (FTIR) is a technique that uses infrared radiation to record movements of molecules by using a computer based program. The sample molecules absorb some certain amount of light at a certain wavelength in the infrared range and reflect the rest; this is due to the different types of bonds that present within the sample. The FTIR technique utilizes this behavior to obtain a spectrum of the analyzed sample. On the spectrum an intensity of absorbance or transmittance versus wavenumbers can be shown. A disappearing peak at a given wavenumber may indicate the disappearing compound/bound

vibration and an increasing peak at another wavenumber at the same time may present the formation of another compound/bound vibration. The hydration process of the two forms of alite within the first 25 hours is monitored of in-situ FTIR.

4 Experimental

4.1 Synthesis of alite

The monoclinic and triclinic alite used in this project are synthesized in the lab. The respective chemicals (given in table 1 and 2) are blended with water to make the mixture more uniform. Later water is removed by drying the slurry in an oven at 150°C for 24 hours.

Table 1. The substances and the amount used to synthesize monoclinic alite.

Substance	Weight (g)
$CaCO_3$	127.619
SiO_2	25.844
Al_2O_3	0.703
MgO	1.177
Ca/Si	2.9642 mole ratio

- Triclinic alite

Table 2. The substances and the amount used to synthesize triclinic alite.

Substance	Weight (g)
$CaCO_3$	131.509
SiO_2	26.314
Ca/Si	3.0000 mole ratio

In order to form the monoclinic alite the raw material mixture contains also small amount of Al_2O_3 and MgO. The presence of Al_2O_3 and MgO will stabilize the monoclinic crystalline structure which is similar to alite that is found in Portland cement [8, 9].

Two platinum crucibles are used to contain the dried mixture for the high temperature synthesis of alite. The high temperature furnace is run in three segments: first heat the samples to 1000°C at a rate of about 1000°C/h and stay at 1000°C for about 0.3 hour so the CO_2 can slowly go away from the samples (to prevent the samples to seep out of the platinum containers); second heat the samples to 1400°C at a rate of 300°C/h and stay at 1400°C for about 12 hours; third cool the samples to room temperature.

The FTIR-spectrum shows only that there is alite but it hard to tell which form is which. So XRD is used to distinguish the two forms of alite.

The finely ground sample is analyzed with XRD to see if the intended monoclinic and triclinic alite have been formed.

4.2 Isothermal calorimetry monitored hydration of monoclinic and triclinic alite

In this section the hydration of monoclinic and triclinic alite with and without additives are investigated. The solid phase and the liquid phase are weighed separately and then hand-mixed for about 30 seconds. In some of the procedures the diluted solution is used in order to investigate the influence of additives on the hydration process. The dilution of superplasticizer is based on the dry mass of the superplasticizer. M.G. SKY 558 is diluted to 0.1%, 0.25% and 0.5%. M.G. ACE 410 is diluted to 0.125% and 0.25%. Sikament H-D 10 is diluted to 0.125% and 0.25%.

4.2.1 Hydration of monoclinic and triclinic alite without additives

Table 3 displays the calorimetry hydration of monoclinic alite with different water to solid ratio and table 4 is the calorimetry hydration of triclinic alite with different water to solid ratio.

Table 3. Hydration of monoclinic alite with different water to solid ratio.

Hydration nr	Water (g)	Monoclinic alite (g)	w/s ratio
1	0.895	2.235	0.4
2	1.038	2.075	0.5
3	1.26	2.102	0.6
4	0.8	1.0	0.8

Table 4. Hydration of triclinic alite with different water to solid ratio.

Hydration nr	Water (g)	Triclinic alite (g)	w/s ratio
1	0.896	2.241	0.4
2	1.036	2.071	0.5
3	1.255	2.093	0.6
4	1.647	2.058	0.8

4.2.2 Hydration of monoclinic and triclinic alite with MasterGlenium SKY 558

Table 5 presents the calorimetry hydration of monoclinic alite with MasterGlenium SKY 558 and table 6 is the calorimetry hydration of triclinic alite with MasterGlenium SKY 558.

Table 5. Hydration of monoclinic alite with MasterGlenium SKY 558

Hydration nr	Diluted M.G. SKY 558 (%)	Diluted M.G. SKY 558 (g)	Monoclinic alite (g)	w/s	Superplasticizer to solid weight (%)
1	0.1	0.4	1.0	0.4	0.04
2	0.25	0.4	1.0	0.4	0.1
3	0.5	0.4	1.0	0.4	0.2
	Water (g)	Monoclinic alite (g)	Undiluted M.G. SKY 558 (g)	w/s	Superplasticizer to solid weight (%)
4	0.365	1.0	0.035	0.4	1.0
5	0.312	1.0	0.088	0.4	2.5

Table 6. Hydration of triclinic alite with MasterGlenium SKY 558

Hydration nr	Diluted M.G. SKY 558 (%)	Diluted M.G. SKY 558 (g)	Triclinic alite (g)	w/s	Superplasticizer to solid weight (%)
1	0.1	0.4	1.0	0.4	0.04
2	0.25	0.4	1.0	0.4	0.1

4.2.3 Hydration of monoclinic and triclinic alite in the presence of MasterGlenium ACE 410

Table 7 presents the calorimetry hydration of monoclinic alite with MasterGlenium ACE 410 and table 8 is the calorimetry hydration of triclinic alite with MasterGlenium ACE 410.

Table 7. Hydration of monoclinic alite with MasterGlenium ACE 410

Hydration nr	Diluted M.G. ACE 410 (%)	Diluted M.G. ACE 410 (g)	Monoclinic alite (g)	w/s	Superplasticizer to solid weight (%)
1	0.125	0.4	1.0	0.4	0.05
2	0.25	0.4	1.0	0.4	0.1

Table 8. Hydration of triclinic alite with MasterGlenium ACE 410

Hydration nr	Diluted M.G. ACE 410 (%)	Diluted M.G. ACE 410 (g)	Triclinic alite (g)	w/s	Superplasticizer to solid weight (%)
1	0.125	0.4	1.0	0.4	0.05
2	0.25	0.4	1.0	0.4	0.1

4.2.4 Hydration of monoclinic and triclinic alite in the presence of Sikament H-D 10

Table 9 shows the calorimetry hydration of monoclinic alite with Sikament H-D 10 and table 10 is the calorimetry hydration of triclinic alite with Sikament H-D 10.

Table 9. Hydration of monoclinic alite in the presence of Sikament H-D 10

Hydration nr	Diluted Sikament HD 10 (%)	Diluted Sikament HD 10 (g)	Monoclinic alite (g)	w/s	Superplasticizer to solid weight (%)
1	0.125	0.4	1.0	0.4	0.05
2	0.25	0.4	1.0	0.4	0.1

Table 10. Hydration of triclinic alite in the presence of Sikament H-D 10

Hydration nr	Diluted Sikament HD 10 (%)	Diluted Sikament HD 10 (g)	Triclinic alite (g)	w/s	Superplasticizer to solid weight (%)
1	0.125	0.4	1.0	0.4	0.05
2	0.25	0.4	1.0	0.4	0.1

4.2.5 Hydration of triclinic alite with adipic acid

Table 11 displays the calorimetry hydration of triclinic alite with adipic acid.

Table 11. Hydration of triclinic alite with adipic acid

Hydration nr	Diluted adipic acid (%)	Diluted adipic acid (g)	Triclinic alite (g)	w/s	Superplasticizer to solid weight (%)
1	0.25	1.6	4	0.4	0.1

4.3 In-situ ATR- FTIR monitored hydration of monoclinic and triclinic alite

To save time not all the additives are investigated with in-situ FTIR method. M.G. SKY 558 is selected to obtain the in-situ FTIR spectra for monoclinic alite; and M.G. ACE 410 is chosen to obtain the in-situ FTIR spectra for triclinic alite. Triclinic alite is chosen for investigating the influence of adipic acid (pure) on the alite system.

Table 12 is the in-situ FTIR hydration of monoclinic alite with pure water; table 13 is the in-situ FTIR hydration of monoclinic alite with MasterGlenium SKY 558; table 14 is the in-situ FTIR hydration of triclinic alite with pure water; table 15 is the in-situ FTIR hydration of triclinic alite with MasterGlenium ACE 410; table 16 is the in-situ FTIR hydration of triclinic alite with adipic acid.

Table 12. IR/ *Hydration of monoclinic alite without additives*

Hydration nr	Water (g)	monoclinic alite (g)	w/s
1	0.1	0.244	0.41

Table 13. IR/*Hydration of monoclinic alite with MasterGlenium SKY 558*

Hydration nr	Diluted M.G. SKY 558 (%)	Diluted M.G. SKY 558 (g)	Monoclinic alite (g)	w/s	Superplasticizer to solid weight (%)

| 1 | 0.25% | 0.114 | 0.252 | 0.45 | 0.11 |

*Table 14.*IR/*Hydration of triclinic alite without additives*

Hydration nr	Water (g)	Triclinic alite (g)	w/s
1	0.1	0.241	0.415

Table 15. IR/*Hydration of triclinic alite with M.G. ACE 410*

Hydration nr	Diluted M.G. ACE 410 (%)	Diluted ACE 410 (g)	Triclinic alite (g)	w/s	Superplasticizer to solid weight (%)
1	0.25	0.204	0.508	0.402	0.10

Table 16. IR/Hydration of triclinic alite with adipic acid

Hydration nr	Diluted adipic acid (%)	Diluted adipic acid (g)	Triclinic alite (g)	w/s	Superplasticizer to solid weight (%)
1	0.25	0.22	0.502	0.44	0.11

The hydrating paste is placed on the diamond crystal of the ATR. A clamper is used to keep the sample close to the diamond. To prevent water from evaporating a plastic film is used to cover the sample and the gap between the plastic film and the sample holder is sealed with tape. A piece of a wet tissue is placed beside the hydrating sample to create 100% humidity (see figure 3).

Figure 3 in-situ FTIR

5 Result

In this section the results from synthesis of monoclinic and triclinic alite, the measurement of the surface area and hydration of the two forms of alite with and without additives are described and discussed.

5.1 The XRD result of the synthesized monoclinic and triclinic alite

Figure 4 shows the XRD result of the synthesized monoclinic alite. The red bars represent monoclinic alite; the blue bars represent belite and the green bars are for CaO.
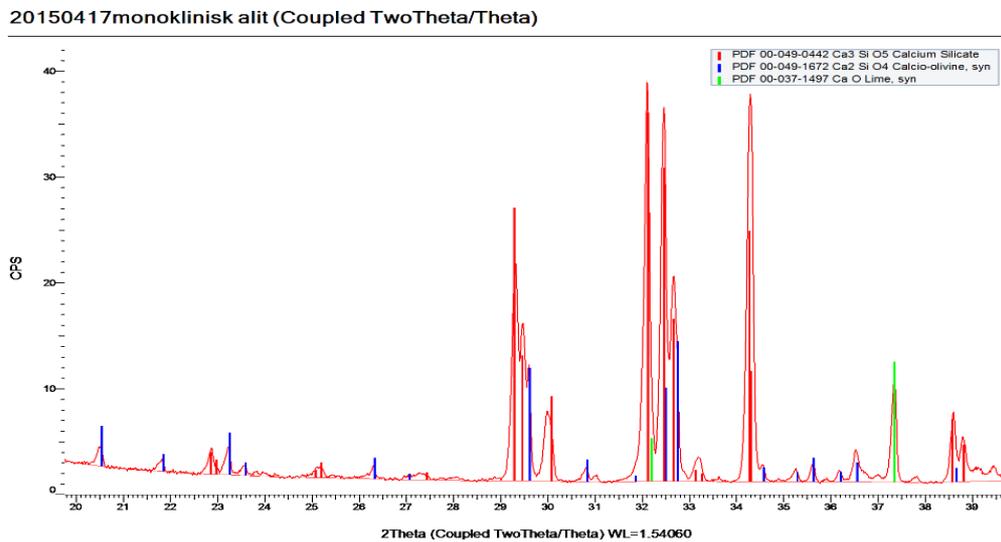

Figure 4 XRD monoclinic alite

Figure 5 shows the XRD result of the synthesized triclinic alite. The pink bars represent triclinic alite; the green bars represent belite and the blue bars are for CaO.
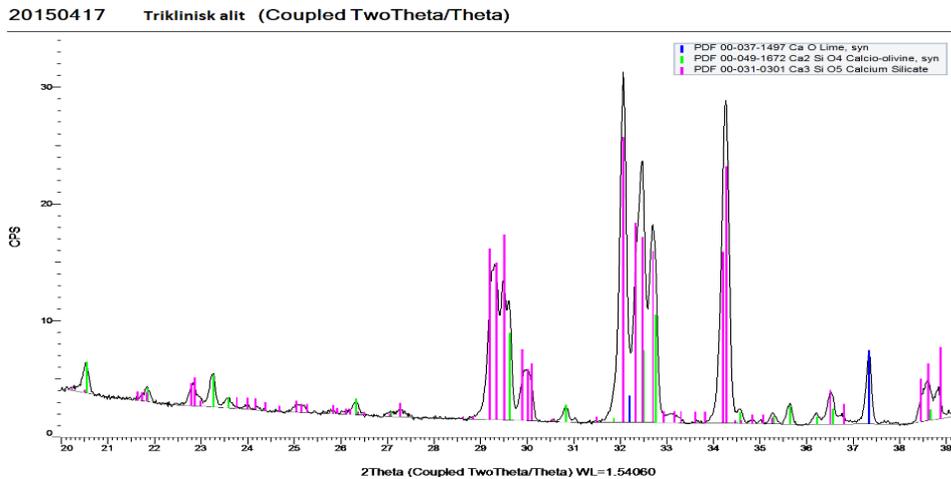
Figure 5 XRD triclinic alite

The intended monoclinic and triclinic alite are formed, though there are small amount of unreacted CaO. After a comparison with earlier result the percentage of the unreacted CaO is considered to be less than 5% [18].

5.2 The surface area of monoclinic and triclinic alite

Table 17 shows the measured surface area of monoclinic and triclinic alite. The surface area of monoclinic alite is somewhat larger than that of triclinic alite.

Table 17. The BET surface area of monoclinic and triclinic alite

Alite	BET surface area (m^2/g)
Monoclinic alite	0.7465
Triclinic alite	0.6510

5.3 Hydration of monoclinic and triclinic alite with and without superplasticizer

In this section the calorimetry and in-situ FTIR results of hydration of monoclinic and triclinic alite with and without superplasticizers are described, compared and discussed.

5.3.1 Calorimetry: Hydration of monoclinic and triclinic alite with different amount of water available

The results for hydration of monoclinic alite with different w/s ratio are shown in figure 6. As can be seen the shape of the curves and the total amount of heat released within the first 24 hours are almost the same with little deviation at the induction period (the local minimum) between about 0.5-3 h and the second deceleration period between 15-25 h. The local maximum is at 12-15 h.
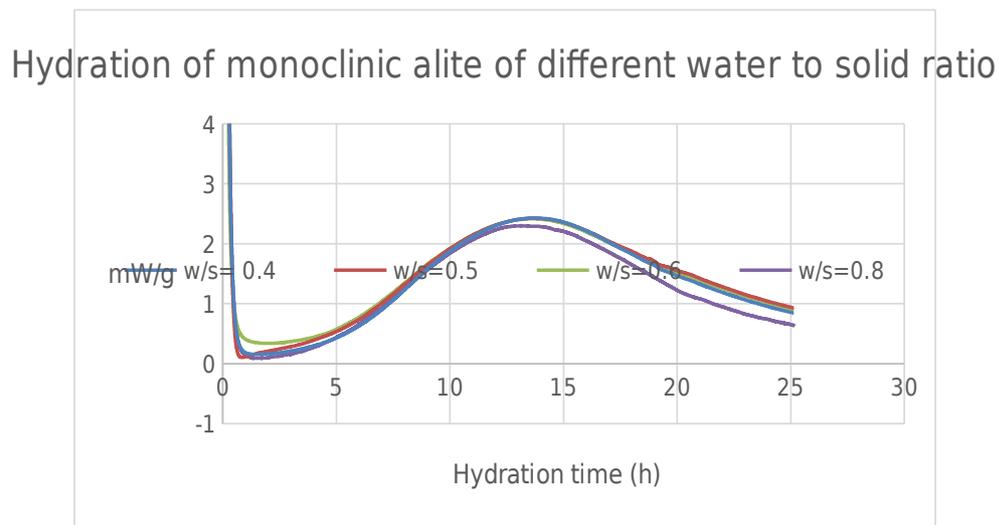

Figure 6 Calorimetry: Hydration of monoclinic alite with different amounts of water available

Figure 7 shows the hydration diagram of triclinic alite with different water to solid ratio. As can be seen all the curves have a similar shape and the total amount of heat release is almost the same within the first 24 hours. The local maximum is between 14-17 h.

At local minimum (the induction period) there is no big difference between the different water to solid ratio with respect to the shape and the amplitude of the curves.
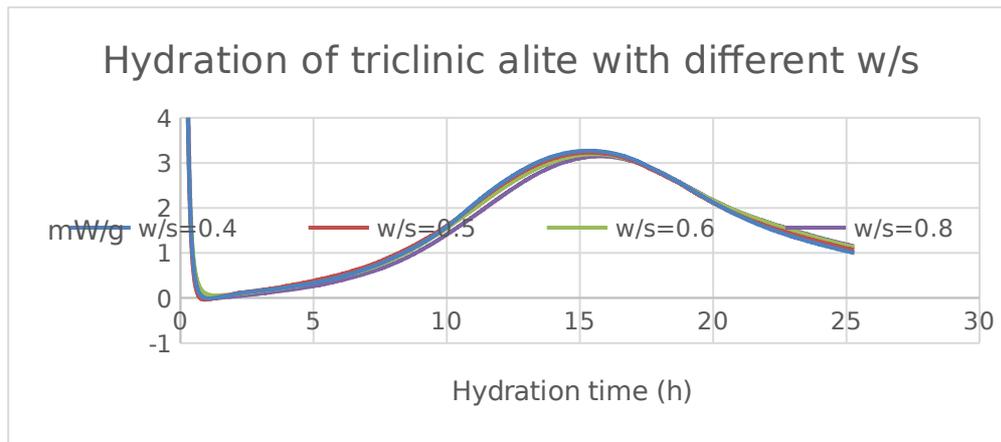
Figure 7 Calorimetry: Hydration of triclinic alite with different amounts of water available

The above investigations show that higher water to solid ratio has little effects on the appearance of the hydration curves of monoclinic and triclinic alite.

According to [13], the cement system with higher water contents will slow down the onset of the acceleration period (the setting), which cannot be seen in the hydration of alite system. Cement system is more complex compared to alite system and there may have other components in cement that slow down the onset of the acceleration period when water content is increased.

5.3.2 Calorimetry: A comparison of hydration of monoclinic and triclinic alite without additives

When water to solid ratio is 0.8 the hydration curves of monoclinic and triclinic alite have different appearance as can be seen in figure 8. The monoclinic alite has a shorter induction period compared to triclinic alite. The maximum for the two curves arises at different time-periods. Triclinic alite has its maximum at 15-20 h whereas monoclinic alite has its maximum at 12-15 h. The height of the maximum of the two curves is also different. The height of the maximum for triclinic alite is clearly higher than that of monoclinic alite.
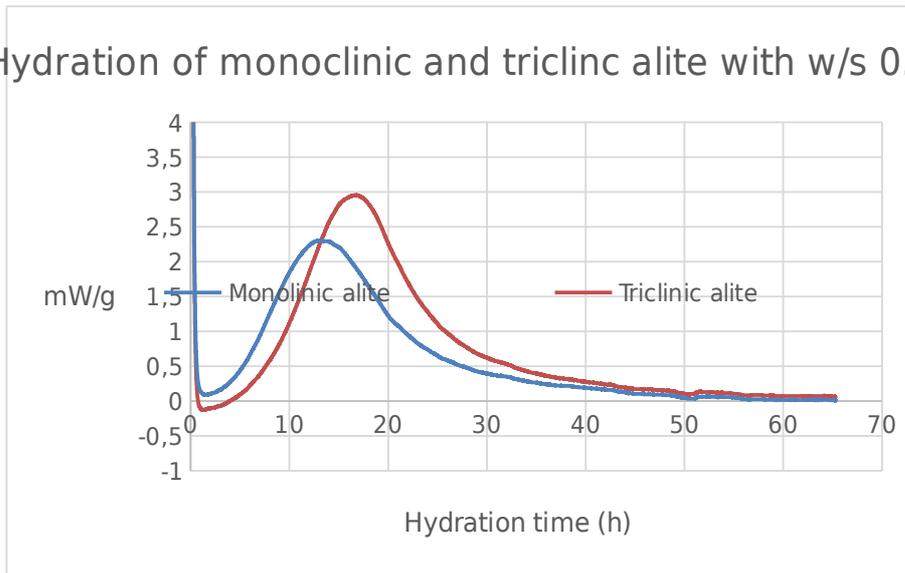
Figure 8 Calorimetry: Hydration of monoclinic and triclinic alite when w/s is 0.8

The reason to the different appearance of the hydration curves of monoclinic and triclinic alite when w/s is 0.8 can be the presence of MgO and Al_2O_3 in monoclinic alite. This addition makes the monoclinic alite system not as pure as triclinic alite and the presence of these impurities seems to accelerate the C-S-H formation in the beginning of hydration and to decrease the amount of heat released within the first 50 hours. The surface area of monoclinic alite is larger than that of triclinic alite. A large surface area may provide a more extended reaction surface. The larger surface area may therefore cause the formation of C-S-H or heat release to be more accelerated for monoclinic alite compared with that of triclinic alite in the beginning of hydration.

5.4 Hydration of monoclinic and triclinic alite with different carboxylate ether based superplasticizers

The calorimetry results of hydration of monoclinic and triclinic alite with carboxylate ether based superplasticizers, M.G. SKY 558, M.G. ACE 410 and Sikament H-D 10 are described, compared and discussed in this section.

5.4.1 Calorimetry: The influence of MasterGlenium SKY 558 on the hydration of monoclinic and triclinic alite

Different amount of MasterGlenium SKY 558 is added to monoclinic and triclinic alite when w/s is 0.4.

As can be seen in figure 9 when the M.G. SKY 558 to solid ratio are 1 % and 2.5 % the induction period are prolonged to more than 25 h. The 0.2 % SKY 558 curve (the solid content of SKY 558/solid phase of monoclinic alite is 0.002) starts to "grow" after 20 hours (figure 10), which may indicate the formation of C-S-H after a long induction period; the induction period is prolonged when the content of SKY 558 is increased. This is in agreement with some earlier reports [11, 13, 14].
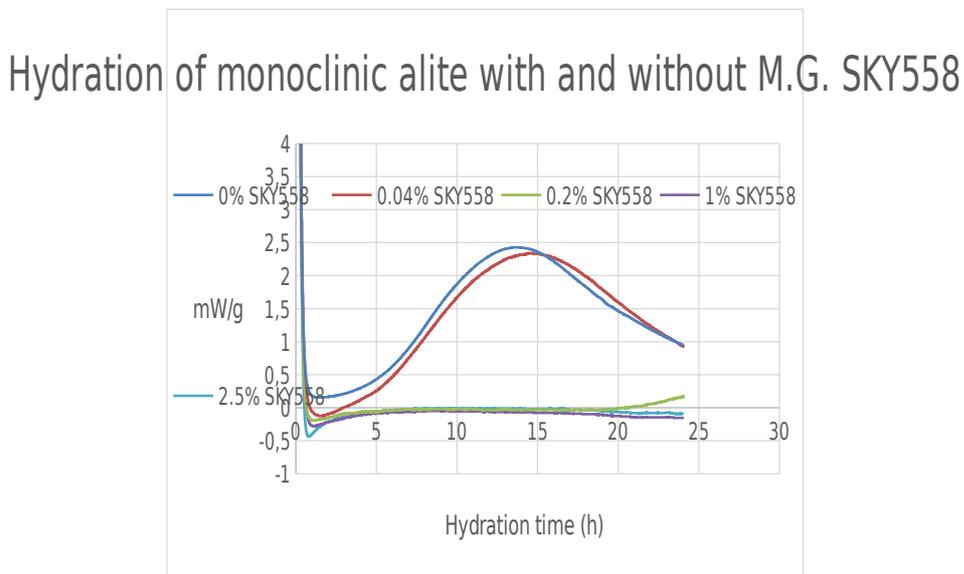

Figure 9 Calorimetry: Hydration of monoclinic alite with 0%, 0.04%, 0.2%, 1% and 2.5% MasterGlenium SKY 558 when w/s is 0.4

The 0.04 % SKY 558 curve coincides with the 0 % SKY 558 curve, which indicates that the addition of 0.04 % SKY 558 has almost no effect on the hydration of monoclinic alite (figure 10).
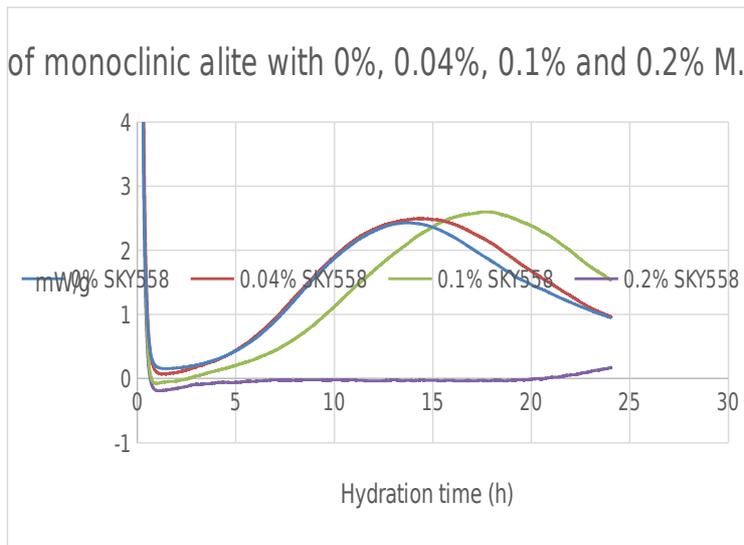
Figure 10 Calorimetry: Hydration of monoclinic alite with 0 %, 0.04%, 0.1 % and 0.2 % MasterGlenium SKY 558 when w/s is 0.4

The influence of 0.04 % and 0.1 % of M.G. SKY 558 on triclinic alite is shown in figure 11. The induction period is prolonged to about 5 h in the case of 0.04 % of SKY 558 and is prolonged to more than 25 h in the case of 0.1 % of SKY 558.
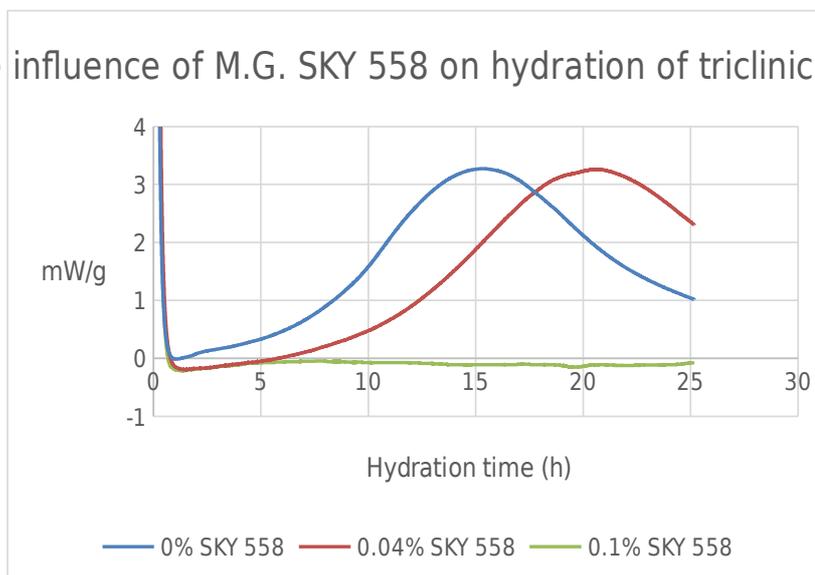

Figure 11 Calorimetry: Hydration of triclinic alite with 0 %, 0.04 % and 0.1 % MasterGlenium SKY 558 when w/s is 0.4

5.4.2 Calorimetry: The influence of MasterGlenium ACE 410 on the hydration of monoclinic alite and triclinic alite

As can be seen in figure 12 and 13 the MasterGlenium ACE 410 affects the monoclinic and the triclinic alite differently. In the presence of ACE 410 the hydration curve of triclinic alite is shifted much more to the right with respect to the hydration curve of monoclinic alite, thus the induction period is prolonged to about 10 h for triclinic alite, whereas the induction period for monoclinic alite is prolonged to about 5 h. The 0 % and the 0.05 % ACE 410 curves for monoclinic alite are almost the same, thus the addition of 0.05 % ACE 410 has little effect on the hydration of monoclinic alite.

The dosage of M.G. ACE 410 for monoclinic and triclinic alite is: the same amount ACE 410 will affect triclinic alite more; if a similar delayed acceleration period as for triclinic alite is desired the amount ACE 410 should be increased in the case of monoclinic alite; if a shortened induction period is preferred in the case of triclinic alite the amount ACE 410 should be decreased.
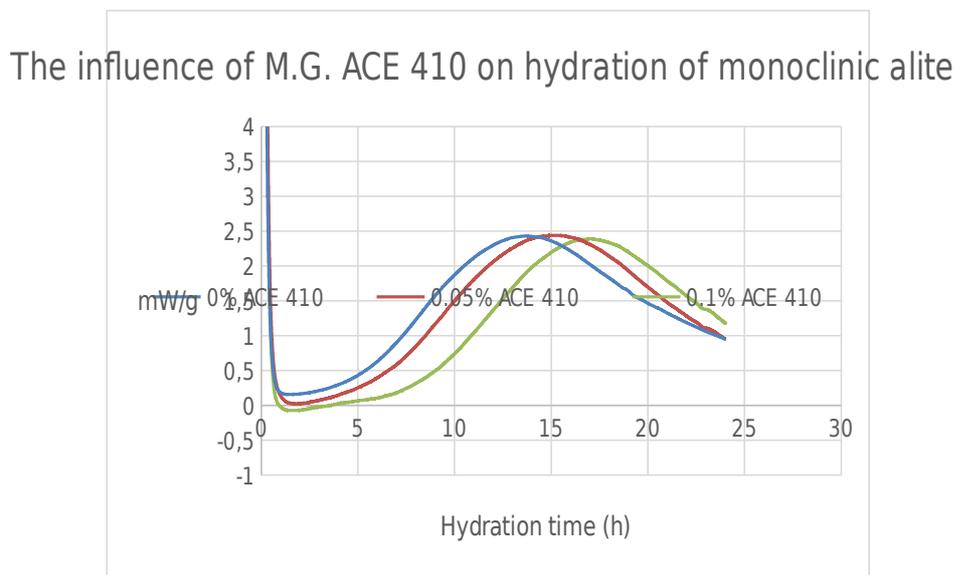

Figure 12 Calorimetry: Hydration of monoclinic alite with 0 %, 0.05 % and 0.1 % MasterGlenium ACE 410 when w/s is 0.4
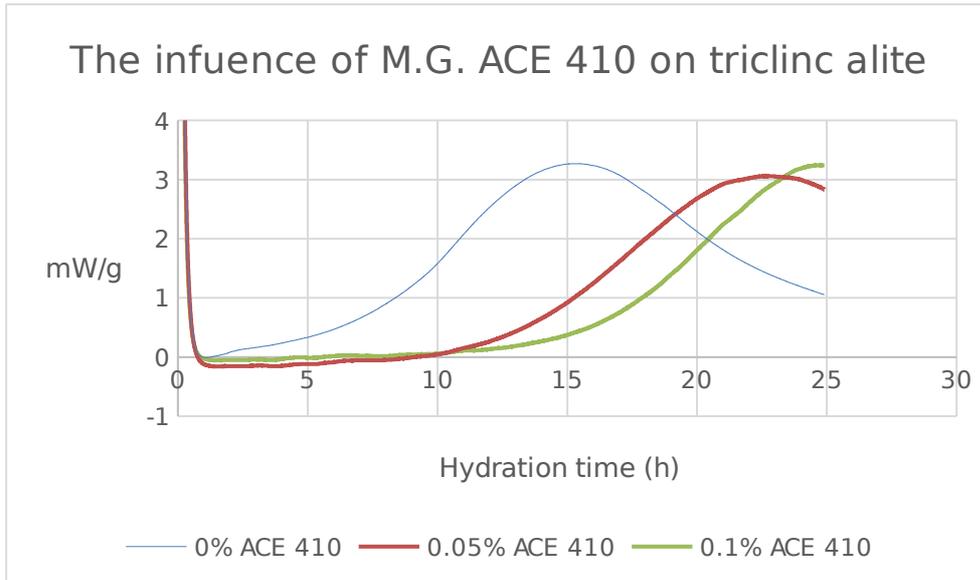
The infuence of M.G. ACE 410 on triclinc alite

mW/g

Hydration time (h)

—— 0% ACE 410 —— 0.05% ACE 410 —— 0.1% ACE 410

Figure 13 Calorimetry: Hydration of triclinic alite with 0 %, 0.05% and 0.1 % MasterGlenium ACE 410 when w/s is 0.4

5.4.3 Calorimetry: The influence of Sikament H-D 10 on the hydration of monoclinic and triclinic alite

As can be seen in figure 14 and 15, Sikament H-D 10, as the other superplasticizers, influences triclinic alite more than monoclinic alite. The induction period is prolonged to 5 h and 10 h when 0.05 % and 0.1 % H-D 10 is used in case of triclinic alite. In contrast, the induction period is almost unaffected in the case of monoclinic alite.
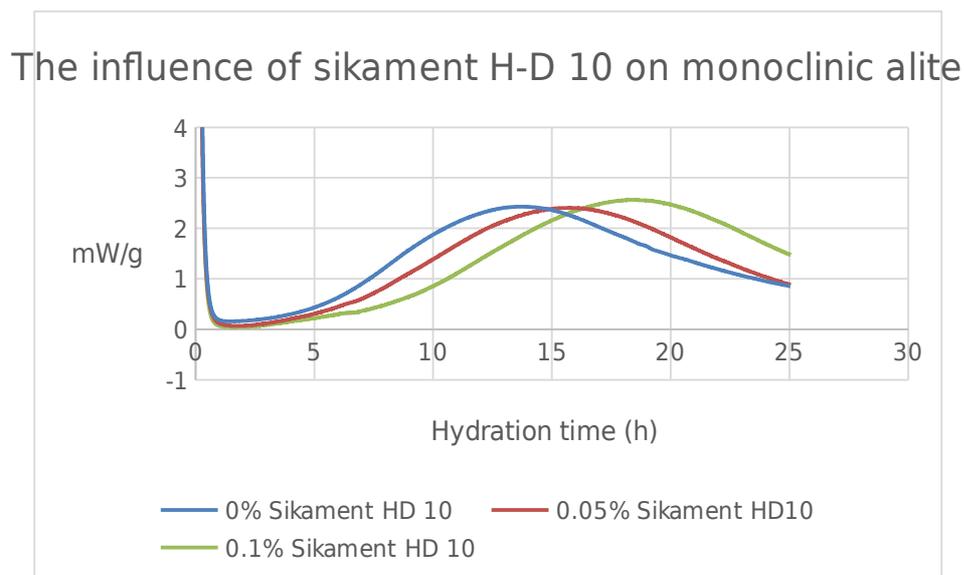

The influence of sikament H-D 10 on monoclinic alite

mW/g

Hydration time (h)

—— 0% Sikament HD 10 —— 0.05% Sikament HD10
—— 0.1% Sikament HD 10

Figure 14 Calorimetry: Hydration of monoclinic alite with 0 %, 0.05 % and 0.1 % Sikament HD-10 when w/s is 0.4
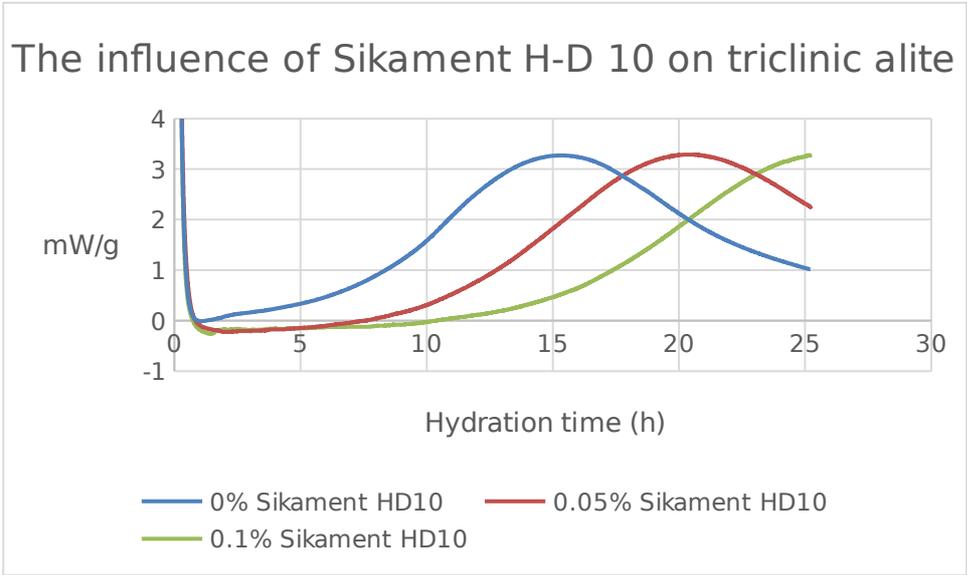
Figure 15 Calorimetry: Hydration of triclinic alite with 0 %, 0.05 % and 0.1 % Sikament HD-10 when w/s is 0.4

5.4.4 Calorimetry: The influence of different superplasticizers on the hydration of monoclinic and triclinic alite when the dosage is 0.1 % of solid weight and the water to solid ratio is 0.4

The influences of M.G. SKY 558, M.G. ACE 410 and Sikament H-D 10 on hydration of monoclinic and triclinic alite when superplasticizer content to solid ratio is 0.1 % are shown in figure 16 and 17. All three additives have a similar effect on monoclinic alite, with the respect to induction, acceleration and the second deceleration period. In the case of triclinic alite, M.G. ACE 410 and Sikament H-D 10 have a similar effect, but M.G. SKY 558 gives more effect. The induction period is prolonged to about 10h when M.G. ACE 410 and Sikament H-D 10 are used. In the case of M.G. SKY 558 the induction period is prolonged to more than 25 h, which makes the acceleration period not visible within the first 25 h. This may due to SKY 558 has a higher charge density compared with ACE 410 and Sikament H-D 10. The prolonged effect is more significant on triclinic alite than that of monoclinic alite when same additives and same amounts are used. This may be due to monoclinic alite contains small amount of MgO and Al_2O_3 that can mitigate the effect of additives.

One theory of the prolonged induction period is that the negatively charged carboxylated backbones are adsorbed on the positively charged calcium ions and delay the further formation of C-S-H. According to the Charge-Controlled-Reaction-Model [14, 15], calcium ions usually forms a bilayer with negatively charged surfaces, such as C-S-H, in the earlier stage of hydration of cementitious materials. Alite and C-S-H have a negative potential when the concentration of CaO is low and are positively charged at higher CaO concentration. The presence of negatively charged superplasticizer may create a trilayered configuration with the calcium ions in the middle. This configuration may inhibit further hydration. [13, 14, 15]

Another theory is that there are other additives/components in the as received superplasticizers that make the delayed formation of C-S-H. The blenders can blend polycarboxylated ethers (PCEs) with different structures or different types of superplasticizers to meet different applications. Many PCE based superplasticising products may contain up to 15 different components; the detailed information to the commercial superplasticizers is often not available to the users. [13]
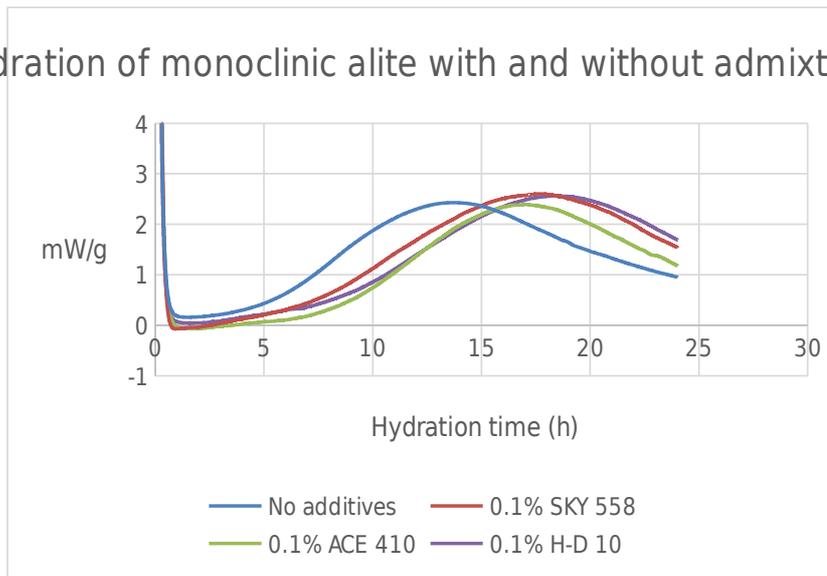
Figure 16 Calorimetry: Hydration of monoclinic alite with and without additives when w/s is 0.4
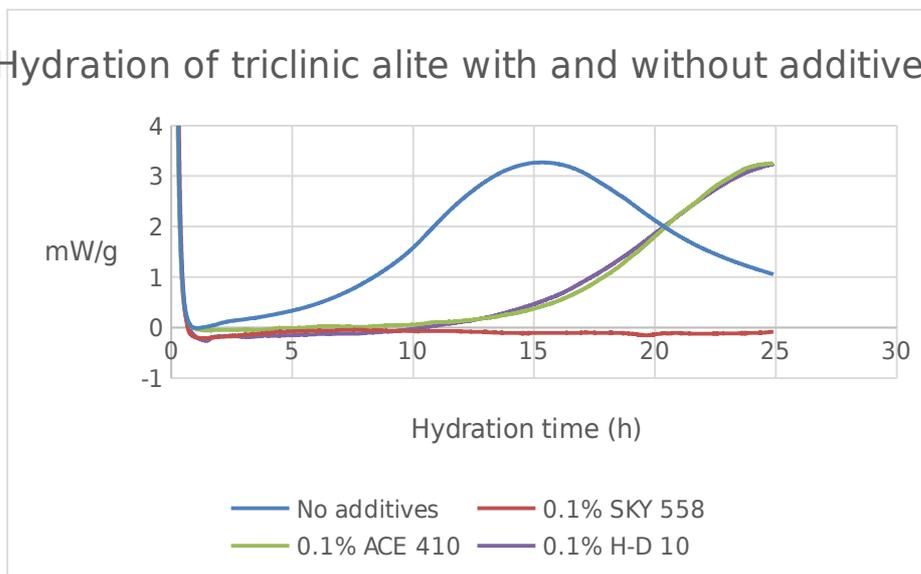

Figure 17 Calorimetry: Hydration of triclinic alite with and without additives when w/s is 0.4

5.5 In-situ FTIR

The IR-results of hydration of monoclinic and triclinic alite with and without superplasticizers are described, compared and discussed in this section.

5.5.1 IR: Hydration of monoclinic alite with and without superplasticizer

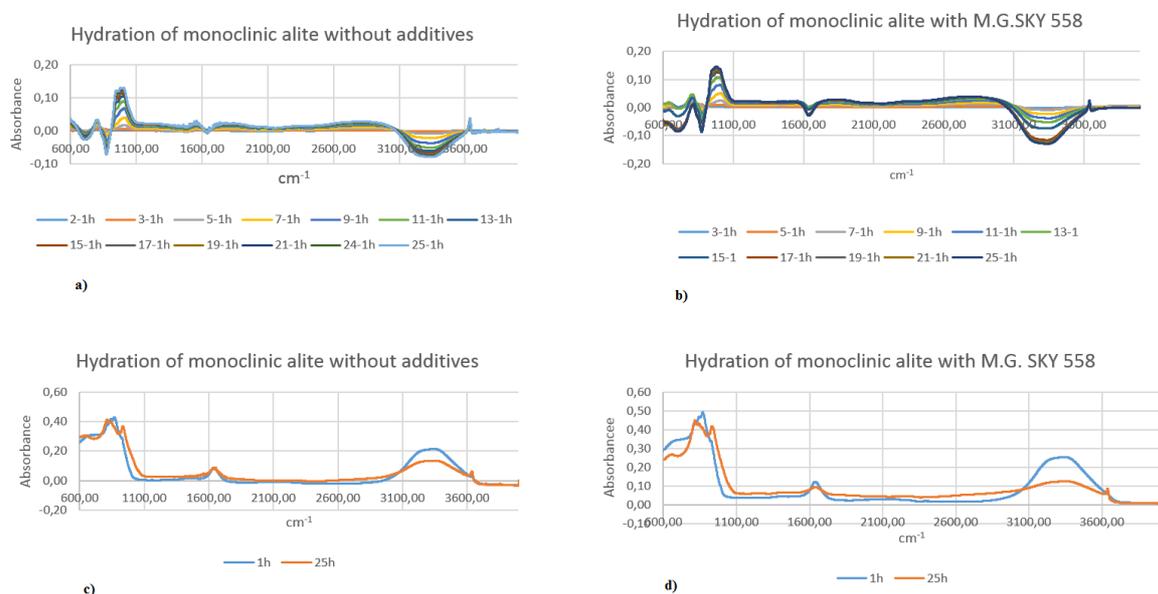Figure 18 shows the subtracted in-situ FTIR result of hydration of monoclinic alite.

Figure 18 In-situ FTIR: Hydration of monoclinic alite with and without additives a) is the subtracted in-situ FTIR of hydration of monoclinic alite without additives; b) is the subtracted in-situ FTIR spectra of hydration of monoclinic alite with M.G. SKY 558; c) is the raw spectra of hydration of monoclinic alite without additives and d) is raw spectra of hydration of monoclinic alite with M.G. SKY 558.

There are no big differences that can be seen between a) and b) in figure 18 (1h is subtracted from the other time intervals) with exception at about 1000 cm^{-1}, 1500 cm^{-1} and 3700 cm^{-1}. The peak at about 1000 cm^{-1} in figure 18b seems to be a little higher than that in figure 18a. In contrast, the peak at about 3700 cm^{-1} in figure 18b is a little shorter than that in figure 18a. At about 1500 cm^{-1} there is a dip in figure 18a whereas it is flat in figure 18b.

According to [16] the intensity between about 1080-1011 cm^{-1} and the intensity between 3641-3644 cm^{-1} represent the formation of C-S-H and Ca(OH)$_2$ respectively. The time derivative of peak area at these intervals will therefore represent the formation rate of C-S-H and Ca(OH)2. The integration of these peaks will present the total formation of C-S-H and

Ca(OH)$_2$. The intensities at 1650 cm^{-1} are associated with the stretching water molecules. The dips at this interval is the losing of water molecules during hydration.

According to [16] the dip at about 1400-1500cm^{-1} (figure 18a) is associated with CO$_3^{2-}$; but when M.G. SKY 558 is used it is more flat at this interval (figure 18b). This may indicate that the interactions between SKY 558 and the alite system absorb energies at this region or the carboxylate groups of SKY 558 absorb energies at this region.

The peaks at 920-1100 cm^{-1} and 3600-3660 cm^{-1} are analyzed with time derivative of peak area and integration of these peaks. This will be presented in the discussion below.

5.5.1.1 Analyze of the peaks at 1100-920 cm^{-1} and 3660-3600 cm^{-1}

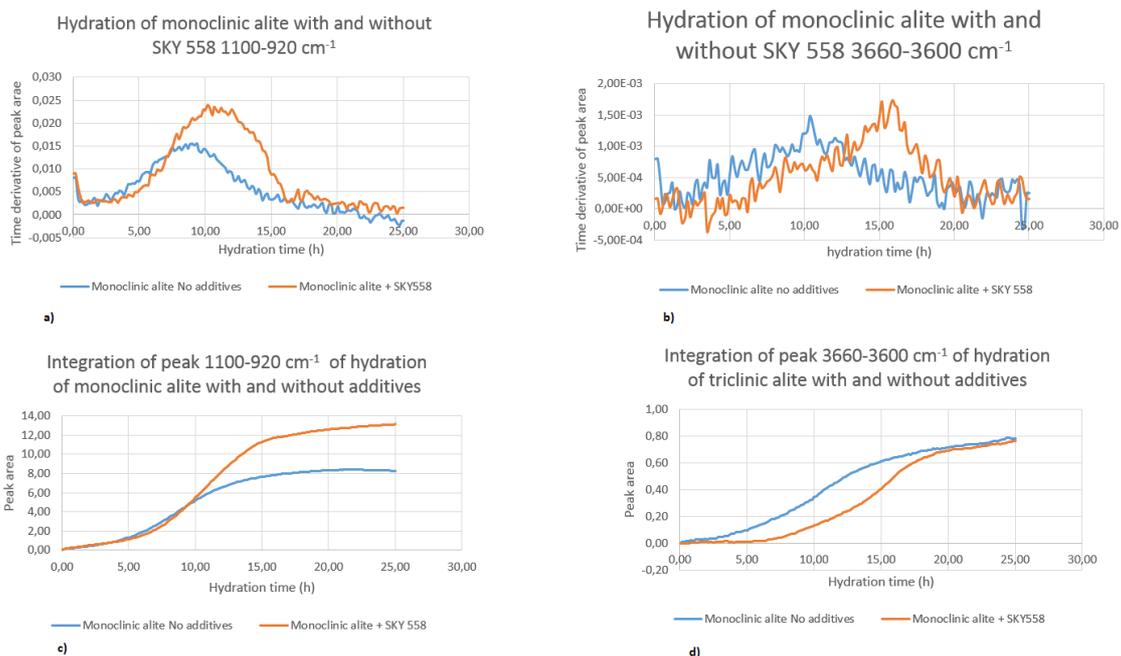*Figure 19a is the time derivative of peak area at 1100-920 cm^{-1} of hydration of monoclinic alite with and without SKY 558; figure 19b is the time derivative of peak area at 3660-3600 cm^{-1} of hydration of monoclinic alite with and without SKY 558; figure 19c is the integration of peak at 1100-920 cm^{-1} of hydration of monoclinic alite with and without SKY 558 and figure 19d is the integration of peak at 3660-3600 cm^{-1} of hydration of monoclinic alite with and without SKY 558.*

From figure 19a-b it can be seen that the addition of SKY 558 makes the formation rate of C-S-H and Ca(OH)$_2$ to slow down in the beginning of hydration compared with hydration of monoclinic alite with no additives. Figure 19c shows that the total formation of C-S-H is

increased within the first 25 hours and figure 19d shows that the total formation of $Ca(OH)_2$ is deceased within the first 25h when SKY 558 is used compared with hydration of monoclinic alite with pure water.

It is possible that there are H^+ in SKY 558 that react with OH^-, to decrease the formation of $Ca(OH)_2$ and the released calcium ions from $Ca(OH)_2$ can form more C-S-H, to increase the formation of C-S-H. There can also be other positively charged ions in SKY 558 that can stabilize the negatively charged backbone of SKY 558 which in turn inhibit the trilayered configuration to form. Because the trilayered configuration can hinder the further formation of C-S-H. The SKY 558 used may also contain excess calcium and silicate ions that can contribute the formation of C-S-H.

5.5.1.2 A comparison of the calorimetry result and the IR-result

Figure 20a-b are a comparison of the calorimetry result and the time derivative of peak area at 1100-920cm^{-1} and 3660-3600 cm^{-1} of hydration of monoclinic alite without additives. Figure 20c-d are a comparison of the calorimetry result and the time derivative of peak area at 1100-920cm^{-1} and 3660-3600 cm^{-1} of hydration of monoclinic alite with SKY 558.
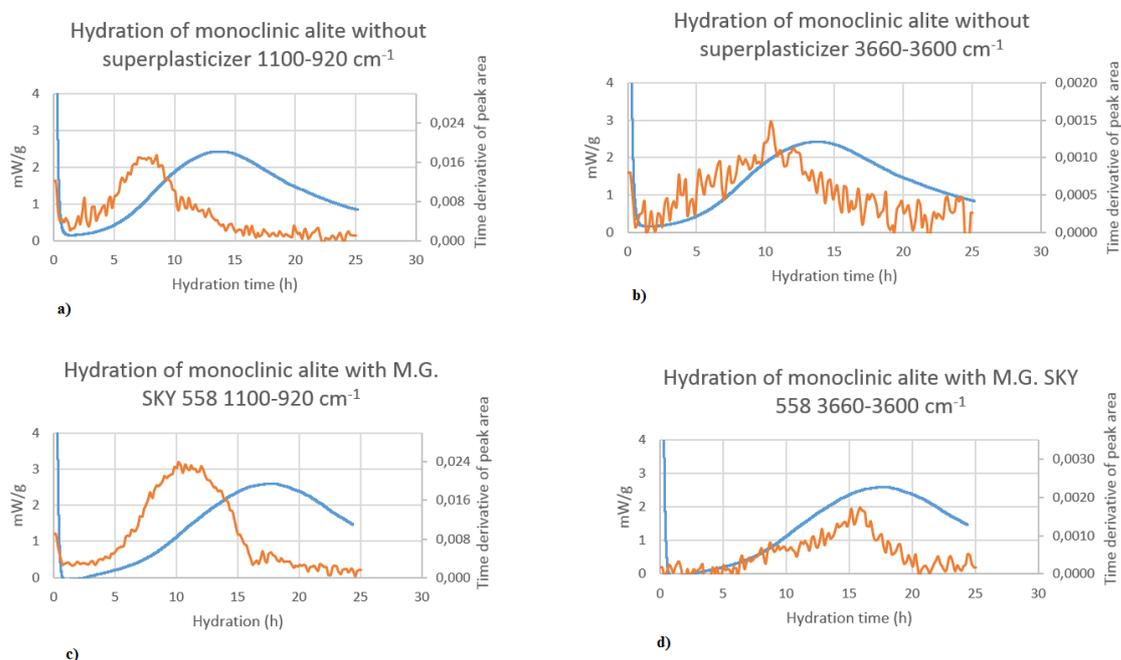

Figure 20 A comparison of calorimetry result and IR result

Figure 20b and figure 20d show that the calorimetry curves (blue curves) and the IR curves (red curves) are in good correspondence (at the $Ca(OH)_2$ region) regardless if the SKY 558 is

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used whereas the calorimetry curves and the IR curves in figure 20a and figure 20c are not in agreement (at the C-S-H region) regardless if the SKY 558 is used.

The calorimetry curves in figure 20a and figure 20c are shifted to right with respect to the IR curves regardless if SKY 558 is used. When the monoclinic alite is synthesized small amount of Al_2O_3 and MgO is added to stabilize the monoclinic structure. The structure of monoclinic alite or the unreacted Al_2O_3 and MgO in the monoclinic alite may shift the calorimetry curves to right compared to IR curves (figure 20a and figure 20c). It can for example be that the stabilizing ions in the monoclinic structure alite somehow take up some of the heat in the beginning of the hydration and release it later. The heat flux seems to follow the formation rate of $Ca(OH)_2$ better regardless if the SKY 558 is used (figure 20b and figure 20d). Because IR-result shows a surface reaction whereas the calorimetry result shows a bulk reaction [17], the calorimetry curves may not follow the formation of C-S-H.

5.5.2 IR: Hydration of triclinic alite with and without superplasticizer

Figure 21 is the in-situ FTIR result of hydration of triclinic alite.
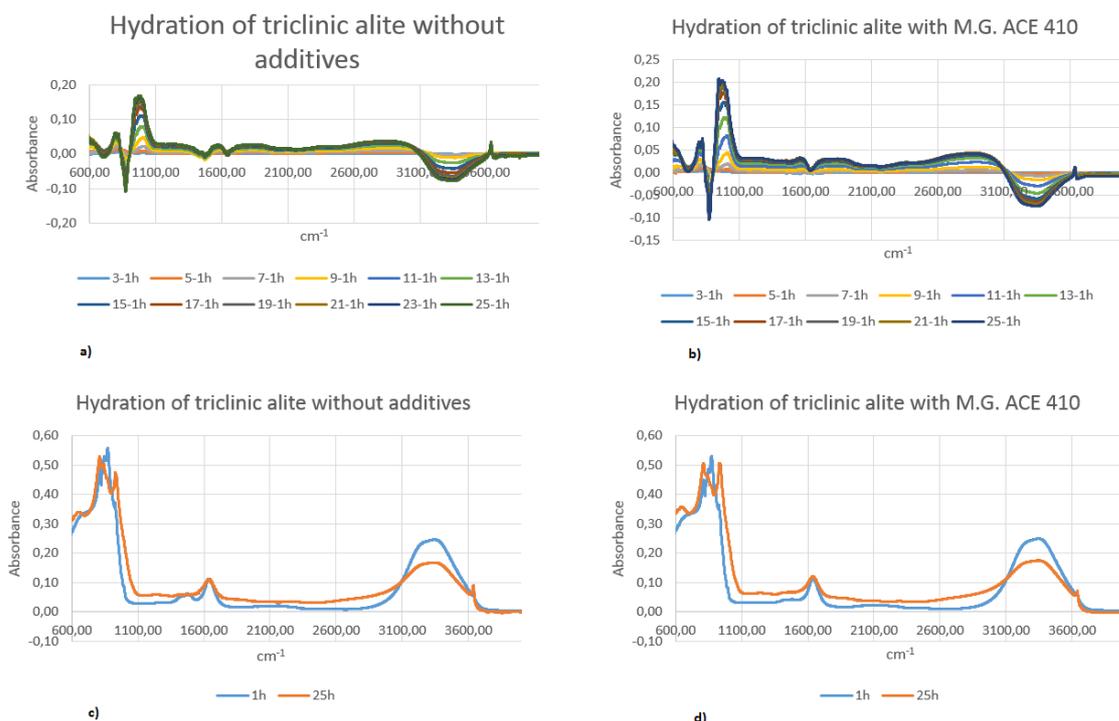

Figure 21 a) is the subtracted in-situ FTIR of hydration of triclinic alite without additives; b) is the subtracted in-situ FTIR spectra of hydration of triclinic alite with M.G. ACE 410; c) is the raw spectra of hydration of triclinic alite without additives and d) is raw spectra of hydration of triclinic alite with M.G. ACE 410.

Even here the subtracted spectra of hydration of triclinic alite with pure water shows more noise than that of hydration of triclinic alite with M.G. ACE 410. As for hydration of monoclinic alite the intervals at about 1000 cm^{-1}, 1500 cm^{-1} and 3700 cm^{-1} are not exactly

same in these figures (figure 21a vs figure 21b). At about 1000 cm^{-1} the peak in figure 21b (with ACE 410) is a little higher than that in figure 21a, but the peak at about 3700 cm^{-1} in figure 21a is higher than that in figure 21b.

As for monoclinic alite at about 1500 cm^{-1} there is a dip in figure 21a whereas it is flat in figure 21b at this region. The interactions between ACE 410 and the alite system may absorb energies at this region or the carboxylate molecules in ACE 410 may absorb energies at this region.

The peak at 920-1100 cm^{-1} and at 3600-3660 cm^{-1} are discussed further in the following section.

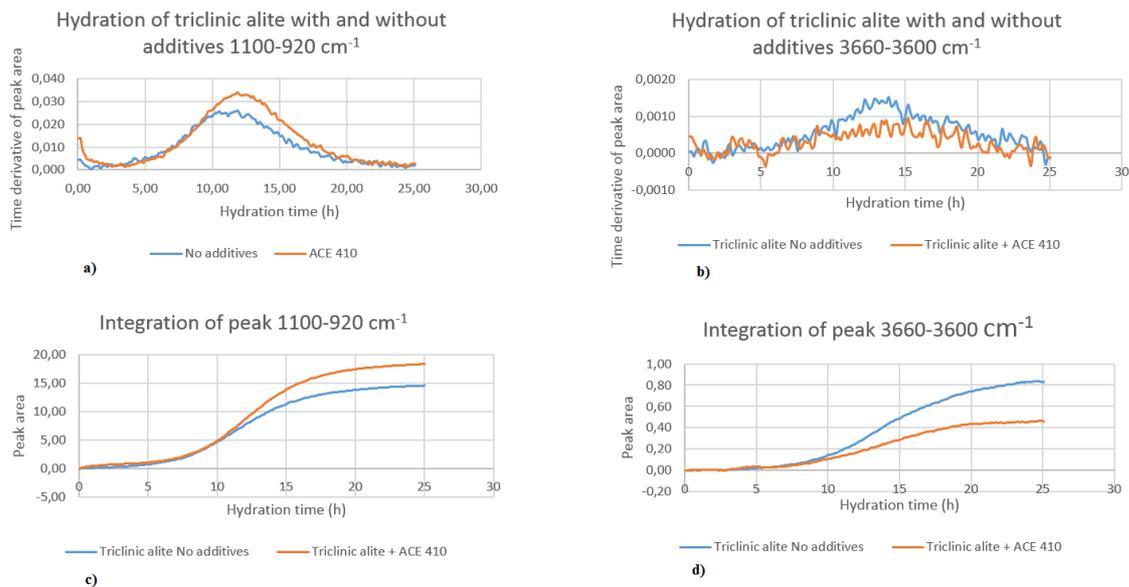### 5.5.2.1 Analyze of the peaks at 1100-920 cm^{-1} and 3660-3600 cm^{-1}

Figure 22a is the time derivative of peak area at 1100-920 cm^{-1} of hydration of triclinic alite with and without ACE 410; figure 22b is the time derivative of peak area at 3660-3600 cm^{-1} of hydration of triclinic alite with and without ACE 410; figure 22c is the integration of peak at 1100-920 cm^{-1} of hydration of triclinic alite with and without SKY 558 and figure 22d is the integration of peak at 3660-3600 cm^{-1} of hydration of triclinic alite with and without ACE 410.

Figure 22a-b show that the addition of ACE 410 in the hydration of triclinic alite has no effect on the formation rate of C-S-H and Ca(OH)$_2$ in the beginning of the hydration compared with no additives. Figure 22c shows that the total formation of C-S-H is increased within the first 25 hours when ACE 410 is used compared with when additives are absent. Figure 22d shows that the total formation of Ca(OH)$_2$ is decreased when ACE 410 is added to the hydration of triclinic alite system within the first 25 hours.

As for monoclinic alite the increased formation of C-S-H and the decreased formation of $Ca(OH)_2$ may because there are protons in ACE 410 that react with hydroxides. This reaction may in turn increase the formation of C-S-H and decrease the formation of $Ca(OH)_2$.

ACE 410 may as SKY 558 contain excess calcium ions or other positively charged ions that stabilizing the negatively charged backbone of ACE 410 and hinder the trilayered configuration to form. The ACE 410 used may also contain excess calcium and silicate ions that can contribute the formation of C-S-H.

5.5.2.2 A comparison of the calorimetry result and the IR-result

Figure 23a-b are a comparison of the calorimetry result and the time derivative of peak area at 1100-920cm^{-1} and 3660-3600 cm^{-1} of hydration of triclinic alite without additives. Figure 23c-d are a comparison of the calorimetry result and the time derivative of peak area at 1100-920cm^{-1} and 3660-3600 cm^{-1} of hydration of triclinic alite with ACE 410.
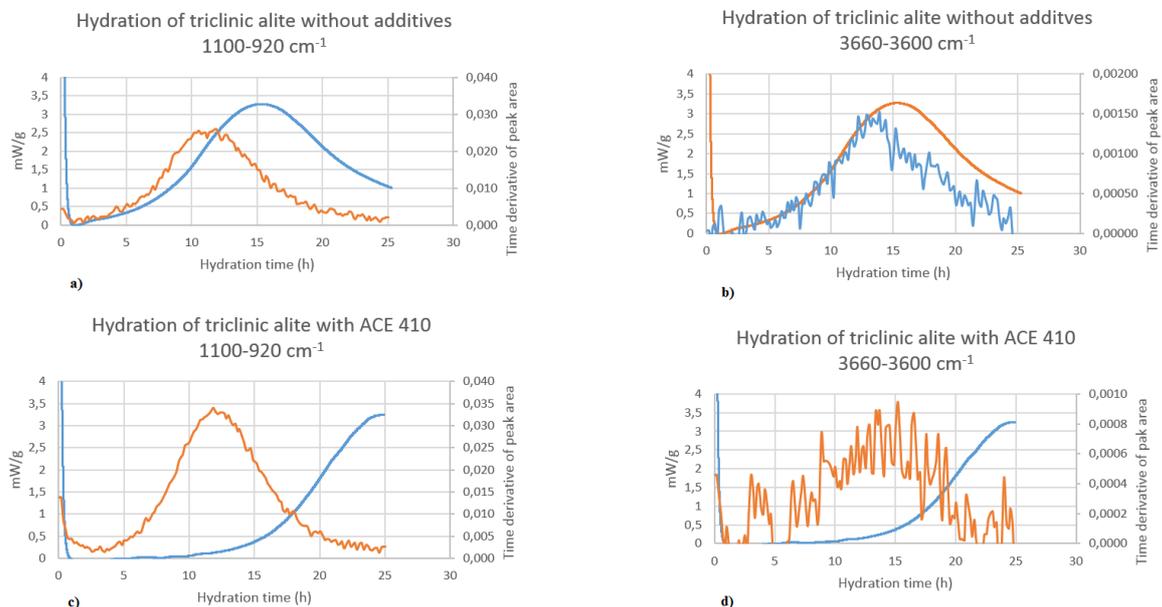
Figure 23 Calorimetry and in-situ FTIR of hydration of triclinic alite wirh and without additives

Figure 23a-b show that the calorimetry result and the IR-result are in good correspondence when additives are absent. The calorimetry curves follow the IR curves which means the heat flux follows the formation rate of C-S-H and $Ca(OH)_2$. In contrast when ACE 410 is used the calorimetry curves are shifted to right with respect to the IR curves. This may be due to the components in ACE 410 or the interactions between ACE 410 and triclinic alite absorb some

of the heat and release the absorbed heat later. It is important to note that the IR shows a surface reaction whereas calorimetry shows a bulk reaction, so the calorimetry curves may not follow the IR curves.

5.5.3 IR: A comparison of hydration of monoclinic and triclinic alite with pure water

Figure 24a is the time derivative of peak area at 1100-920 cm^{-1} of hydration of monoclinic and triclinic alite without additives; figure 24b is the time derivative of peak area at 3660-3600 cm$^{-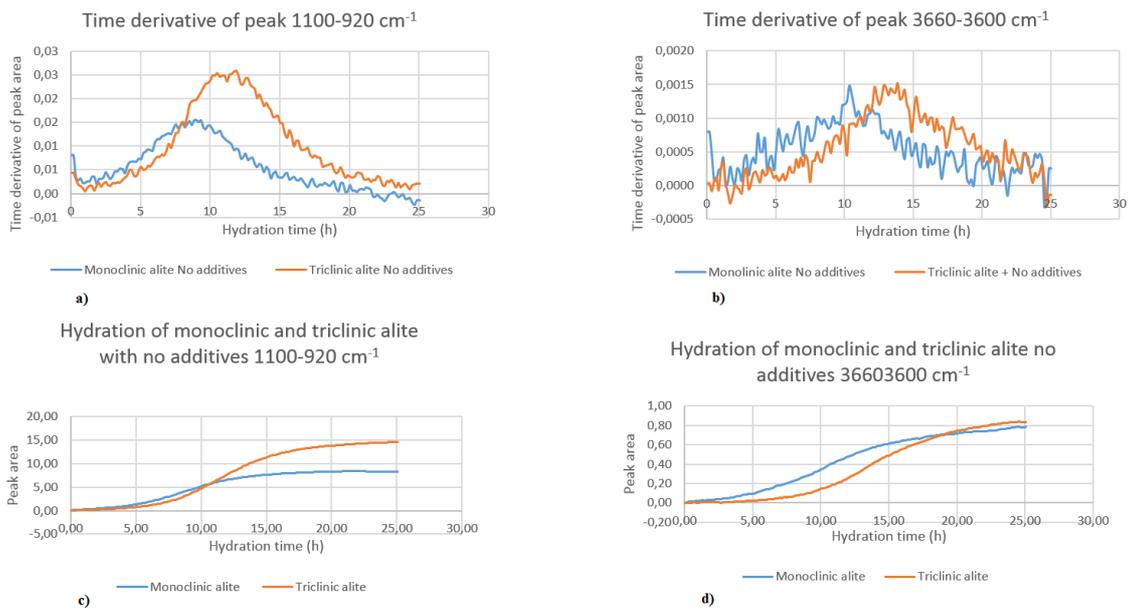1}$ of hydration of monoclinic and triclinic alite without additives; figure 24c is the integration of peak at 1100-920 cm^{-1} of hydration of monoclinic and triclinic alite without additives and figure 24d is the integration of peak at 3660-3600 cm^{-1} of hydration of monoclinic and triclinic alite without additives.

Figure 24a shows that the formation rate of C-S-H of monoclinic alite is faster than that of triclinic alite in the beginning of hydration and figure 24c shows that the total amount of formed C-S-H is higher for triclinic alite compared with monoclinic alite (within the first 25 hours). Figure 24b shows that the formation rate of $Ca(OH)_2$ of monoclinic alite is faster than that of triclinic alite in the beginning of hydration and figure 24d shows the total amount of formed $Ca(OH)_2$ of monoclinic alite is higher than that of triclinic alite (within the first 25 hours).

The addition of MgO and Al_2O_3 in synthesis of monoclinic alite to stabilize the structure of monoclinic alite may accelerate the formation of C-S-H and $Ca(OH)_2$, in the beginning of hydration with respect to triclinic alite.

The larger surface area of monoclinic alite compared to triclinic alite may be another reason to the earlier formation of C-S-H and $Ca(OH)_2$ in the beginning of hydration.

According to early studies the contents of CaO will affect the formation of $Ca(OH)_2$ [18]. CaO reacts with water and forms $Ca(OH)_2$. The monoclinic alite may contain more CaO compared to triclinic alite.

5.6 The influence of adipic acid on hydration of triclinic alite
In this section the calorimetry and in-situ FTIR result of hydration of triclinic alite with adipic acid are described and discussed. The results are also compared with those of hydration of triclinic alite with pure water and with ACE 410.

5.6.1 Calorimetry result
Figure 25 shows the calorimetry result of hydration of triclinic alite with pure water, with adipic acid and with ACE 410 when superplasticizer to solid ratio is 0.1%.
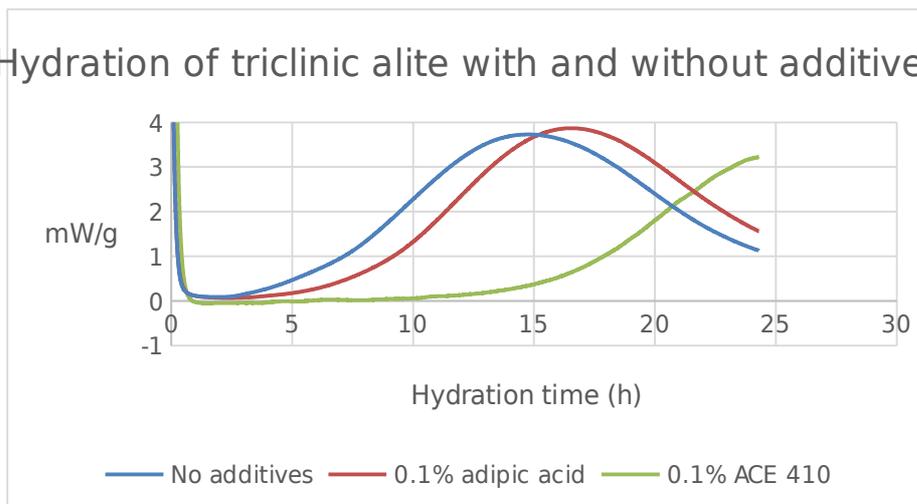
Figure 25 Calorimetry: hydration of triclinic alite with and without additives

As can be seen the effect of addition of adipic acid is less than that of addition of ACE 410.The adipic acid used is pure and there may not have other components/other functional groups in adipic acid that may absorb heat from the hydrating system and release it later compared with when ACE 410 is used.

5.6.2 In-situ FTIR result

Figure 26 is the subtracted in-situ FTIR spectra of hydration of triclinic alite with adipic acid.

Figure 26 IR: Hydration of triclinic alite with adipic acid and the 1h spectrum has been subtracted from all the other

The interval at about 1500 cm^{-1} in figure 26 is not as deep as the one in figure 21a (when pure water is used) and is not 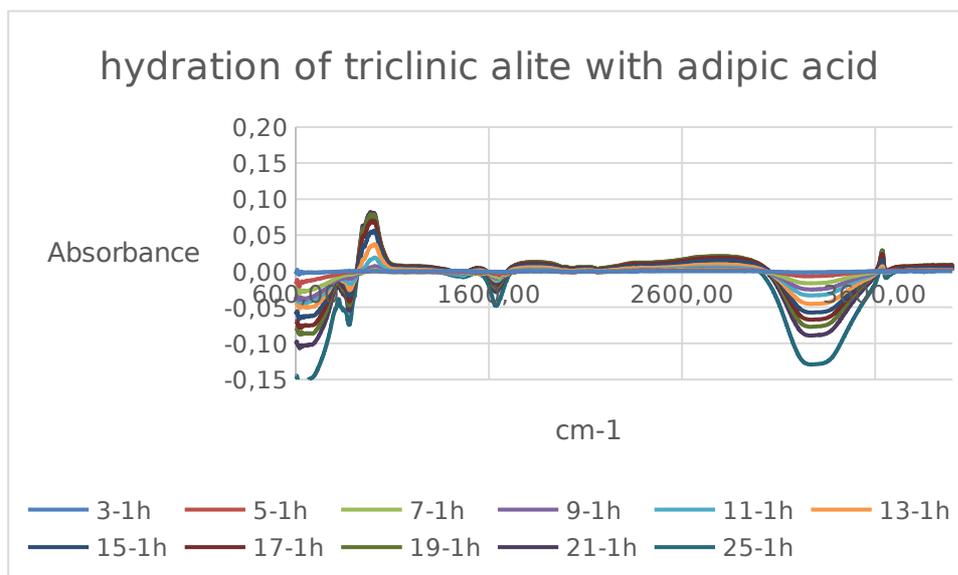as flat as the one in figure 21b (when ACE 410 is used). This may indicate that the interactions between triclinic alite and the adipic acid are not as strong as these between triclinic alite and ACE 410, if these interactions absorb energy at this region. This may also indicate that there is other components than carboxylate groups in ACE 410 that absorb energies at this region.

The peak at 920-1100 cm^{-1} and at 3600-3660 cm^{-1} are analyzed further in the following discussion.

5.6.2.1 Analyze of the peaks at 1100-920 cm^{-1} and 3660-3600 cm^{-1}
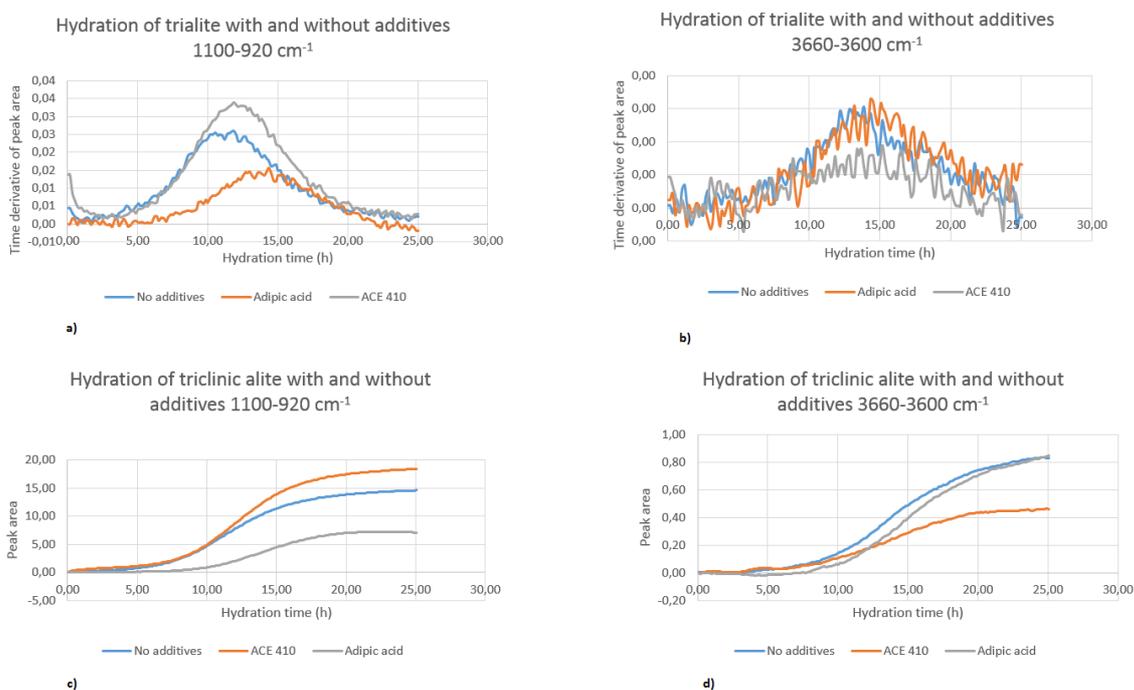
Figure 27a is the time derivative of peak area at 1100-920 cm^{-1} of hydration of triclinic alite without additives, with ACE 410 and with adipic acid; figure 27b is the time derivative of peak area at 3660-3600 cm^{-1} of hydration of triclinic alite without additives, with ACE 410 and with adipic acid; figure 27c is the integration of peak at 1100-920 cm^{-1} of hydration of triclinic alite without additives, with ACE 410 and with adipic acid and figure 27d is the integration of peak at 3660-3600 cm^{-1} of hydration of triclinic alite without additives, with ACE 410 and with adipic acid.

Figure 27a shows that the addition of adipic acid makes the formation rate of C-S-H is the lowest within the first 15h compared with no additive and with ACE 410. It is difficult to say (from figure 27b) about the formation rate of $Ca(OH)_2$ when adipic acid is used compared with no additives and with ACE 410. Figure 27c shows the total formation of C-S-H is the lowest when adipic acid is used and the total formation of C-S-H is highest when ACE is used within the first 25h. In figure 27d, the total formation of $Ca(OH)_2$ is the lowest between 4h and 12h when adipic acid is used, though the differences are quite insignificant. Between 12h and 25h the total formation of $Ca(OH)_2$ is the lowest when ACE 410 is used.

The addition of adipic acid seems to decrease the total formation of C-S-H (within the first 25 h) compared with when no additive is used and when ACE 410 is used. The hydrogen ions in the adipic acid may react with OH^- and decrease the formation of $Ca(OH)_2$. The adipic acid used is pure and it probably does not contain other positively charged ions that can stabilize the negatively charged "backbone" if the hydrogen ions are reacted with OH^-. This leads to the limited reaction between H^+ and OH^-, which in turn leads to the formation of $Ca(OH)_2$ is not as decreased as when ACE 410 is used. The charge density of "the backbone" of adipic acid is probably high with respect to ACE 410, because the chain of adipic acid is relatively short and there are no side chains that can share the charge. This higher charge density compared with the backbone of ACE 410 may contribute more calcium ions are trapped in the trilayered configuration which in turn leads to the total formation of C-S-H is the lowest when adipic acid is used. The ACE 410 used may contain excess calcium and silicate ions that can contribute the formation of C-S-H.

5.6.2.2 A comparison of the calorimetry result and the IR-result

Figure 28a-b are a comparison of the calorimetry result and the time derivative of peak area at 1100-920cm^{-1} and 3660-3600 cm^{-1} of hydration of triclinic alite with adipic acid.
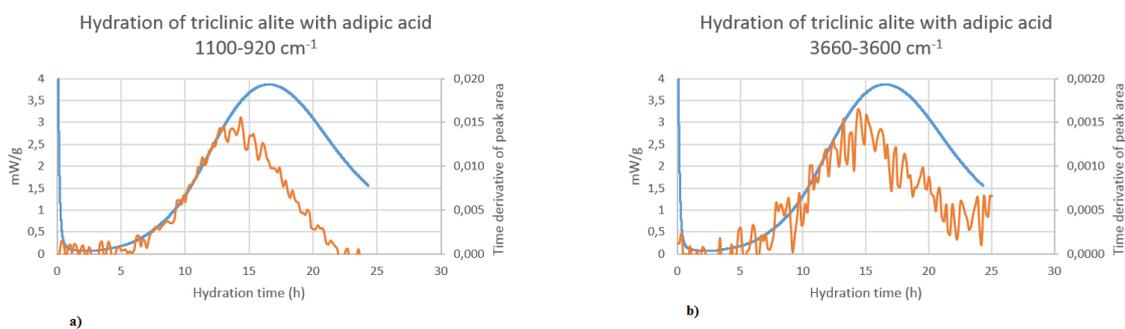
Figure 28 A comparison of calorimetry result and IR result

As can be seen in figure 28a-b the IR-result and the calorimetry result are in good agreement in the beginning of hydration (0-15 h), the calorimetry curves follow the IR curves.

Because the adipic acid used is pure and there is probably no other component that "steals" heat from the hydration system with respect when ACE 410 is used (figure 28 vs figure 23c and figure 23d). So the calorimetry curve follows the formation of C-S-H and the formation of $Ca(OH)_2$ within the first 15 hours (the blue curve follows the red curve in figure 28).

6 Discussion

The monoclinic and triclinic alite are successfully synthesized, though they contain small amount of unreacted CaO and the hydration of the two forms alite with and without additives are studied by using calorimetry and in-situ FTIR.

The calorimetry result of hydration of the two forms alite with different water to solid ratio shows that the different amount water added has almost no effect on the appearance of the calorimetry curves. The calorimetry curve of monoclinic alite is somewhat shifted to left with respect to triclinic alite. This may be due to the presence of the minor amount of MgO and Al_2O_3 in monoclinic alite. The larger surface area of monoclinic alite compared to triclinic alite may also accelerate the formation of C-S-H or the heat release in the beginning of the hydration.

When M.G. SKY 558, M.G. ACE 410 and Sikament H-D 10 are used, it is seen from calorimetry curves that the hydration of triclinic alite is more affected compared to monoclinic alite. The addition of Al_2O_3 and MgO in the synthesis of monoclinic alite makes it not as pure as triclinic alite and this impurity may mitigate the effect of the additives. An increasing dosage of the additives will prolong the induction period of the two forms of alite, which is in correspondence with early studies on hydration of cement system when additives are used [11]. M.G. SKY 558, M.G. ACE 410 and Sikament H-D 10 have a similar effect on monoclinic alite whereas M.G ACE 410 and Sikament H-D 10 have a similar effect on triclinic alite and M.G SKY 558 gives a stronger effect on triclinic alite.

According to the Charge-Controlled-Reaction-Model, calcium ions, the negatively charged C-S-H and the negatively charged backbone of the superplasticizer can form a trilayered configuration. This configuration may contribute to the delayed formation of C-S-H and thereby prolonging the inductions period. The charge density of the backbone of SKY 558 may be higher than that of ACE 410 and that of Sikament H-D 10.

There may have other components in the additives that contribute the prolonged induction period. The manufactures can blend polycarboxylated ethers (PCEs) with different structures or different types of superplasticizers to meet different applications. Many PCE based superplasticising products may contain up to 15 different components; the detailed information to the commercial superplasticizers is often not available to the users.

The time derivative of peak area of in-situ FTIR results of hydration of monoclinic alite show a delayed formation of C-S-H and $Ca(OH)_2$ when SKY 558 is used in the beginning of hydration. This is in agreement with the calorimetry results. In contrast the time derivative of peak area of in-situ FTIR results of hydration of triclinic alite with ACE 410 is not showing delayed formation of C-S-H and $Ca(OH)_2$. The trilayered configuration may be more significant on monoclinic alite which has a larger surface area compared with triclinic alite. This trilayered configuration in turn can inhibit the formation of C-S-H in the beginning of

hydration. The charge density of SKY 558 may be higher than that of ACE 410. However it is difficult to give a comparison of the IR-result of hydration of monoclinic alite with SKY 558 and the hydration of triclinic alite with ACE 410, because the structure and components of monoclinic alite and triclinic alite are not exactly same.

When additives are used the calorimetry curves and IR curves are not in very good agreement. The calorimetry curves are shifted to right compared to IR curves. The components in the additives or interactions between the components in the additives and the alite system may absorb heat from the hydrating system and release the absorbed heat later. This is due to the IR-results show a surface reaction and the calorimetry results show reactions in the bulk.

A comparison of the time derivative of peak area at 1100-920 cm^{-1} and 3660-3600 cm^{-1} of in-situ FTIR curves of hydration of the two forms of alite without additives shows that the formation rate of C-S-H and $Ca(OH)_2$ is accelerated in the beginning of the hydration in the case of monoclinic alite. The total formation of C-S-H is higher for triclinic alite and the total formation of $Ca(OH)_2$ is higher for monoclinic alite within the first 25 hours. The minor amount of MgO and Al_2O_3 in monoclinic alite and the larger surface area of monoclinic alite compared to triclinic alite may accelerate the formation rate of C-S-H and $Ca(OH)_2$ in the beginning of hydration. The formation of C-S-H and $Ca(OH)_2$ competes for calcium ions. If there is a component that increases the total formation of $Ca(OH)_2$ this component will at the same time decrease the total formation of C-S-H within the first 25 hours. The impurities in monoclinic alite seem to increase the total formation of $Ca(OH)_2$ and to decrease the total formation of C-S-H compared with hydration of triclinic alite, which is purer. According to earlier studies, CaO that is presented in the hydration system accelerates the formation of $Ca(OH)_2$ [18]. CaO reacts with water and forms $Ca(OH)_2$. The monoclinic alite may contain more CaO compared to triclinic alite and this in turn leads to the total formation of $Ca(OH)_2$ is higher for monoclinic alite within the first 25 hours.

According to in-situ FTIR result the formation of C-S-H is increased and the formation of $Ca(OH)_2$ is decreased when additives, such as M.G. SKY 558 and M.G. ACE 410 are used during the hydration of monoclinic and triclinic alite. The decreased formation of $Ca(OH)_2$ may be due to the additives containing hydrogen ions. These hydrogen ions react with OH$^-$ which in turn decrease the formation of $Ca(OH)_2$. The reason to the increased formation of C-S-H can be the additives contain excess Ca^{2+} ions or other positively charged ions that can stabilize the negatively charged backbone of the additives which in turn hinder the formation of the trilayered configuration. The SKY 558 and ACE 410 used may contain excess calcium and silicate ions that can contribute the formation of C-S-H.

The investigation of the influence of adipic acid on the hydration of triclinic alite shows that the addition of adipic acid seems to decrease the total formation of C-S-H (within the first 25h) compared with when no additive is used and when ACE 410 is used. The addition of adipic acid makes the formation of $Ca(OH)_2$ is lower than when pure water is used and is higher than when ACE 410 is used. The hydrogen ions in the adipic acid react with OH$^-$ and

decrease the formation of $Ca(OH)_2$ (4-12 h). The adipic acid used is pure and it probably does not contain other positively charged ions that can stabilize the negatively charged "backbone" if the protons are reacted with OH^-. This leads to the limited reaction between H^+ and OH^-, which in turn leads to the formation of $Ca(OH)_2$ is not as deceased as when ACE 410 is used (12-25 h). The charge density of "the backbone" of adipic acid is probably high with respect to ACE 410, because the chain of adipic acid is relatively short and there are no side chains that can share the charge. This higher charge density compared with the backbone of ACE 410 may contribute more calcium ions are trapped in the trilayered configuration which in turn leads to the total formation of C-S-H is least when adipic acid is used.

7 Conclusion

The influence of carboxylate ether based superplasticizer on hydration of monoclinic and triclinic alite are investigated in this project. Even the influence of adipic acid (pure) on the hydration of triclinic alite is investigated.

The techniques are used in the investigation are calorimetry and in-situ FTIR. Calorimetry result shows the heat flux during hydration. The released heat follows the C-S-H and the $Ca(OH)_2$ formation if there is no other component that take up or release heat at the same time, thus the calorimetry results show a bulk reaction. In-situ FTIR result shows the change of bindings on surfaces during hydration. The formation of C-S-H and $Ca(OH)_2$ can therefore be detected by this technique.

According to the calorimetry results: The different water to solid ratio has no effect of the hydration of the two forms of alite. The addition of M.G. SKY 558, M.G. ACE 410, Sikament H-D 10 and adipic acid prolongs the induction period, though the influence is stronger on triclinic alite. The increased dosage of additives gives a more prolonged induction period.

According to the in-situ FTIR results: The addition of SKY 558 on hydration of monoclinic alite decreases the formation rate of C-S-H and $Ca(OH)_2$ in the beginning of hydration. In contrast, the addition of ACE 410 on the hydration of triclinic alite has no effect of the formation rate of C-S-H and $Ca(OH)_2$ in the beginning of the hydration. The total formation of C-S-H is increased and the total formation of $Ca(OH)_2$ is decreased when SKY 558 is used on hydration of monoclinic alite and ACE 410 is used on hydration of triclinic alite within the first 25 hours. The investigation of the influence of adipic acid on the hydration of triclinic alite shows that the addition of adipic acid seems to decrease the total formation of C-S-H (within the first 25h) compared with when no additive is used and when ACE 410 is used. The addition of adipic acid makes the total formation of $Ca(OH)_2$ is lower than when pure water is used and is higher than when ACE 410 is used.

A comparison of the calorimetry result and the time derivative of peak area of in-situ FTIR result at 920-1100 cm^{-1} and 3600-3660 cm^{-1} shows: The calorimetry curves and the IR curves are not in good agreement at the C-S-H region regardless if SKY 558 is used on hydration of monoclinic alite, however the calorimetry curves seem to follow the formation rate of $Ca(OH)_2$ regardless if SKY 558 is used on hydration of monoclinic alite. In the case of hydration of triclinic alite, the calorimetry curves seems to follow the formation rate of C-S-H and $Ca(OH)_2$ when pure water is used, but when ACE 410 is used the calorimetry curves are shifted to right with respect to the IR curves. In the case of hydration of triclinic alite with adipic acid, the calorimetry curves follow the IR curves within the first 15 hours.

8 Future work

1. Investigation of the influence of superplasticizer (pure form) on alite system. Because the information of the superplasticizers (structure/components) that used in this project are not available it is difficult to give a discussion or conclusion about what is influencing the delayed calorimetry curves when additives are used.
2. Investigation of the influence of superplasticizer (pure form) on the blended system (alite, aluminate or some of other substances). A blended system is more like the cement system. Cement system is more complex compared to alite system and there are different parts with different charges on a clinker phase that may form interactions with additives. These interactions may be detected by IR.
3. Monitoring the changing of pH during the hydration process when superplasticizer is used. If the protons presents in the additives react with the OH^- the pH will also change.

9 Acknowledgements

I would like to thank the fowling people:

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