



**CHALMERS**

# **Early hydration of Portland Cement Compounds**

## **Synthesis and Hydration of Alite and Calcium Aluminate**

Bachelor Thesis Högskoleingenjörprogrammet Kemiteknik

**MATTHIAS MOLÈN**

## **Abstract**

Cement is an adhesive substance primarily used as the bonding agent in concrete. Concrete is one of the most commonly used building materials and is formed when water, cement and an aggregate (usually sand or gravel) is mixed. The most used cement is called Portland cement. It is hydraulic cement which means it hardens even if it is under water. Portland cement consists mainly of five components which are gypsum and the four clinker phases: alite, belite, aluminate and ferrite.

In this work alite and aluminate were synthesized and their hydration reaction studied by using infrared spectroscopy and isothermal calorimetry. The main hydration reaction of alite occurs during the first 24 hours and peaks after 10-15 hours. The hydration reaction of aluminate is very fast and occurs immediately. The addition of gypsum leads to a slower reaction rate. With 10 wt% gypsum added the reaction occurred after 2-3 hours and with 20 wt% gypsum it occurred after 10 hours.

# Contents

Abstract .....	2
1 Introduction.....	4
2 Aim.....	4
3 Theory.....	5
3.1 Notations.....	5
3.2 Portland Cement .....	5
3.3 Alite .....	6
3.4 Belite.....	7
3.5 Aluminate .....	7
3.6 Ferrite .....	7
3.7 Reaction Products of Alite and Belite.....	7
3.8 Reaction Products of Aluminate and Ferrite.....	7
3.8.1 AFm Phases.....	7
3.8.2 AFt Phases .....	7
3.9 Infrared Spectroscopy .....	8
3.10 Isothermal Calorimetry .....	8
3.11 X-Ray Diffraction.....	8
4 Experimental .....	9
4.1 Synthesis.....	9
4.1.1 Aluminate .....	9
4.1.2 Alite .....	9
4.2 Hydration of the Synthesized Phases.....	10
4.2.1 Calorimetry.....	10
4.2.2 IR.....	10
5 Results and Discussion.....	11
5.1 Synthesis.....	11
5.2 Hydration of the Synthesized Phases.....	13
5.2.1 Calorimetry.....	13
5.2.2 Infrared Spectroscopy .....	15
6 Conclusion .....	20
7 Acknowledgements .....	21
8 References .....	22

## 1 Introduction

Cement is an adhesive substance primarily used as the bonding agent in concrete. Concrete is one of the most commonly used building materials and is formed when water, cement and an aggregate (usually sand or gravel) is mixed. The most used cement is called Portland cement. It is a hydraulic cement which means it hardens even if it is under water. Portland cement got its name in 1824 when Joseph Aspdin took patent for it.

2013 was the cement production in the world about 4 billion tonnes, where China accounted for 2.3 billion tonnes <sup>[1]</sup>. The environmental impact from the cement production is big. To produce one tonne of cement is about 4-5 GJ required and the CO<sub>2</sub> emission from the process is approximately 0.7-0.8 tonnes.

Portland cement contains of five main components: alite, belite, aluminate and ferrite, which are the clinker phases, and gypsum. Alite, aluminate and ferrite are the most important components during the early phases of the cement hydration and belite is more important for the final strength in the cement. The gypsum is added to the cement to delay the hydration reaction of aluminate and ferrite and to make it less exothermic.

## 2 Aim

Cement have been used for a long time and is today one of the most building materials, still there are much to learn about the chemistry behind it. This is because of the complexity of the cement-water system which makes it very hard to study and understand. The aim in this work is to synthesize the triclinic form of alite and the cubic form of aluminate and study their hydration reaction using infrared spectroscopy and isothermal calorimetry.

## 3 Theory

### 3.1 Notations

Abbreviations used in this work:

Alite ( $\text{Ca}_3\text{SiO}_5$ ) =  $\text{C}_3\text{S}$

Belite ( $\text{Ca}_2\text{SiO}_4$ ) =  $\text{C}_2\text{S}$

Calcium Aluminate/Aluminate ( $\text{Ca}_3\text{Al}_2\text{O}_6$ ) =  $\text{C}_3\text{A}$

Ferrite  $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$  =  $\text{C}_4\text{AF}$

C-S-H = Calcium Silicate Hydrate

w/s = water-to-solid ratio

### 3.2 Portland Cement

Portland cement contains five main components which are alite, belite, aluminate, ferrite and gypsum. To produce Portland cement limestone and clay/shale are crushed and grinded and then mixed together. Sometimes are  $\text{Fe}_2\text{O}_3$  (iron oxide) and  $\text{SiO}_2$  (quartz) also added. The material is then heated in a kiln (figure 1) to about  $1450^\circ\text{C}$  where it forms clinkers <sup>[2]</sup>.

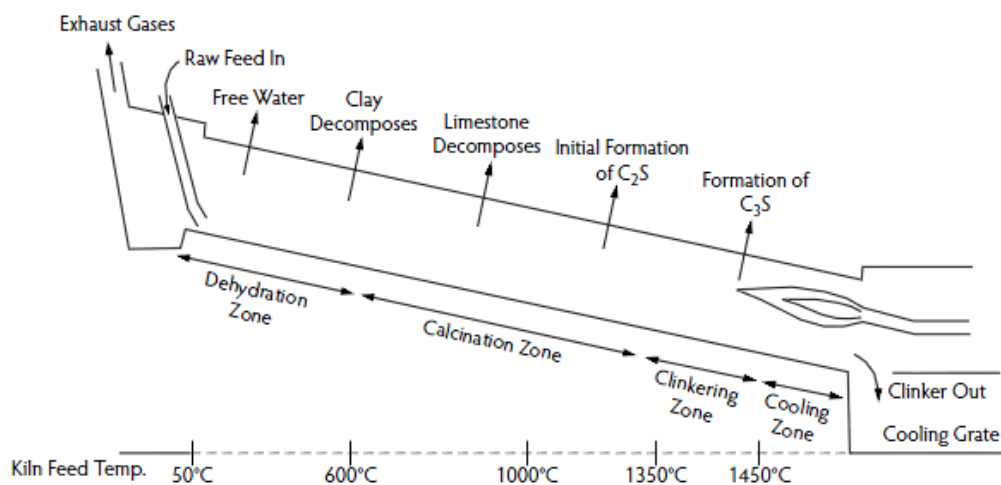


Figure 1 - Rotating cement kiln <sup>[2]</sup>

The material is subjected to an increasing temperature in the kiln and following reactions take place:

- In temperatures below  $1000^\circ\text{C}$  calcite and clay are decomposed.
- In temperatures between  $1000$ - $1300^\circ\text{C}$  is  $2\text{CaO}\cdot\text{SiO}_2$  formed from the decomposed calcite and clay and  $\text{SiO}_2$ .
- In temperatures between  $1300$ - $1450^\circ\text{C}$  are clinkers formed.

After the kiln, gypsum is added and it is grinded to finished cement. An overview of the whole process is shown in figure 2.

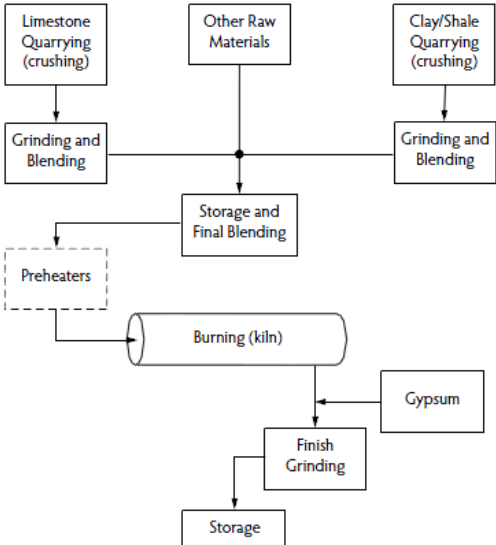


Figure 2 - Cement manufacturing process [2]

### 3.3 Alite

Portland cement contains between 50-70%  $C_3S$  ( $Ca_3SiO_5$ ), which makes it the most common component in ordinary Portland cement. The hydration reaction of  $C_3S$  lasts several months but most of it reacts within the first 24 h, with a peak around 10-15 h [3]. In figure 3 is the hydration reaction of  $C_3S$  shown. Its hydration rate compared to belite is very high, therefore it plays a more important role in the early stages of cement hardening. The high reaction rate depends on lower thermodynamic stability and holes in the molecule structure which makes it easier for the water to react [4].

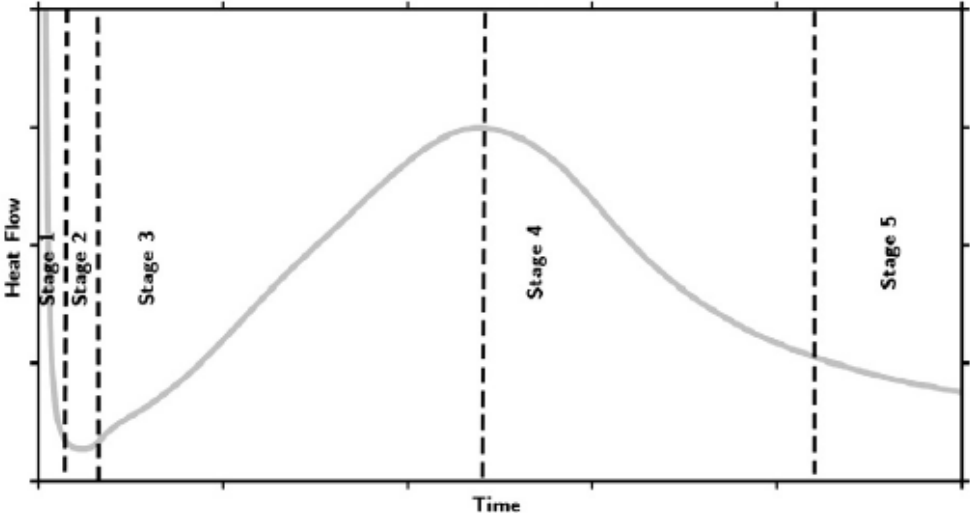


Figure 3 - Heat flow in the hydration reaction of alite during the first 30 h [5]

### 3.4 Belite

Portland cement contains about 15-30%  $C_2S$  ( $Ca_2SiO_4$ ).  $C_2S$  occurs most often in 4 different polymorphic states:  $\alpha$  (a hexagonal phase),  $\alpha'$  (an orthorhombic phase),  $\gamma$  (an orthorhombic phase) and  $\beta$  (a monoclinic phase) which is called larnite<sup>[6]</sup>. The most common phase in cement clinkers is  $\beta$ -belite. The reaction rate of  $\beta$ -belite is very slow compared with the one of alite. Therefore it is not very important for the early strengthening phase in cement. On the other hand, it is important for the strength of the final hardened cement.

### 3.5 Aluminate

$C_3A$  has a cubic structure and its chemical formula is written  $Ca_3Al_2O_6$ .  $C_3A$  is one of the main components in Portland cement, about 5-10% of ordinary Portland cement is  $C_3A$ . Its reaction with water is very exothermic and occurs immediately. This leads to a phenomenon called flash-setting, meaning that the cement hardens too quick, which is prevented by adding calcium sulphate (gypsum).

### 3.6 Ferrite

$C_4AF$  exists in many possible compositions and that is why its molecular formula is written  $Ca_2(Al_xFe_{1-x})_2O_5$ , where  $x$  varies from 0 to 0.7<sup>[8]</sup>. Portland cement contains about 5-15%  $C_4AF$ . The hydration reaction of  $C_4AF$  is very similar with the one of aluminate and forms AFm and AFt phases.

### 3.7 Reaction Products of Alite and Belite

The reaction products of alite and belite is calcium hydroxide, called portlandite, and C-S-H which stands for calcium silicate hydrate and where C, S and H has a varying composition. C-S-H is an amorphous material and is the most important component for the strength of the cement because it is about 70-80% of the total hydrated cement<sup>[9]</sup>. The main formation of C-S-H in the hydration reaction of alite occurs in stage 3 and 4 in figure 3.

### 3.8 Reaction Products of Aluminate and Ferrite

#### 3.8.1 AFm Phases

The AFm phase is a generic name for a group of hydrated calcium aluminates. The group has the same base, which is  $[Ca_2(Al,Fe)(OH)_6] \cdot X \cdot xH_2O$ .  $X$  stands either for an exchangeable singly charged anion or for a half of a doubly charged anion<sup>[10]</sup>. The AFm phases are formed from  $C_3A$  and  $C_4AF$  in the presence of carbonates, sulphates, chlorides and hydroxides. Hydrated cement often consists of different AFm phases, because most of the compositions do not form solid solutions and they behave like separate phases. The only exceptions from this are some replacements (50mol%, maximum) of sulfate by hydroxide<sup>[10]</sup>.

#### 3.8.2 AFt Phases

The AFt phases has the general formula  $C_3(A,F) \cdot 3CaX \cdot xH_2O$ . The AFt phases are formed at the beginning of the hydration of  $C_3A$  and  $C_4AF$  in the presence of gypsum and make the cement harden slower<sup>[11]</sup>. When  $C_3A$  reacts with water it forms AFm phases which leads to an unwanted phenomena called flash-setting. To prevent this gypsum is added and ettringite is formed, which is an AFt phase. The formation of AFt phases is a slower and less exothermic reaction and prevents flash-setting.

### **3.9 Infrared Spectroscopy**

Infrared spectroscopy is a measuring method of electromagnetic radiation. The molecules absorb the radiation and goes from a vibrational state to another. Different molecules absorb radiation of different frequency. This can be used to determine the composition of a sample.

The result from a measure is a spectrum that shows the absorption at different wavelengths. Depending on how the absorption of a certain wavelength varies over time, the formation and dissolution of a compound can be monitored.

### **3.10 Isothermal Calorimetry**

A calorimeter is used to measure the heat in a reaction. The calorimeter used in this work was an isothermal calorimeter which means it holds a constant temperature. It had four sample holders were two of the sample holders contained references. The reference is used to reduce the noise. This is done by subtracting the reference measure from the samples measure.

### **3.11 X-Ray Diffraction**

X-ray diffraction is a method used for identification of crystalline materials. The technique is using a X-ray beam hitting the sample and then diffracting into many directions. The angles and intensity of the diffracted beams gives the information needed to identify what compounds or substances the samples contains.



## 4 Experimental

### 4.1 Synthesis

#### 4.1.1 Aluminate

$\text{Al}_2\text{O}_3$  and  $\text{CaCO}_3$  were weighed and then mixed and grinded thoroughly for about 30 minutes to a fine powder. About 0.5-1.0 gram of the powder were then pressed into tablets in a pellet press with about 8 tonnes of pressure for 10 minutes. The finished tablets were then put in a platinum container and then into a box furnace. The furnace was running a program with three segments; during the first segment the temperature was increased to  $1200^\circ\text{C}$  with a rate of  $5^\circ\text{C}/\text{min}$ , during the second segment the temperature was kept at  $1200^\circ\text{C}$  for 10 hours and during the last segment the furnace was cooled from  $1200^\circ\text{C}$  degrees to room temperature. To verify that aluminate had formed, XRD was run on the sample. Before the XRD measurement, all the burned tablets were mixed and grinded to a fine powder. This to make the measurement possible since it requires a powder, but also to get an average of the content in all tablets. If not pure aluminate had been obtained the whole process was repeated.

Aluminate was made in four different batches. The following table shows the size and composition of the batches.

Batch nr	$\text{CaCO}_3$	$\text{Al}_2\text{O}_3$	Total weight
1	5.5562 g	1.8868 g	7.443 g
2	5.5562 g	1.8868 g	7.443 g
3	5.5562 g	1.8868 g	7.443 g
4	22.225 g	7.547	29.772 g

#### 4.1.2 Alite

The procedure to synthesize alite is similar to the aluminate synthesis, but  $\text{SiO}_2$  is used instead of  $\text{Al}_2\text{O}_3$ . To produce alite a higher temperature is needed than for aluminate. So instead of a box furnace, a tube furnace was used. The tube furnace program had the following three segments: the first segment was ramping to  $1400^\circ\text{C}$  with a rate of  $5^\circ\text{C}/\text{min}$ , the second segment was dwelling for 13 hours at  $1400^\circ\text{C}$  and the third segment was cooling to room temperature for three hours. The cooling process should go as fast as possible to prevent alite to dissociate into belite and  $\text{CaO}$ , this is because alite is only metastable in temperatures below  $1250^\circ\text{C}$ <sup>[12]</sup>.

Alite was made in two different batches. The following table shows the size and composition of the batches.

Batch nr	$\text{CaCO}_3$	$\text{SiO}_2$	Total weight
1	6.5753 g	1.3158 g	7.8911 g
2	8.767 g	1.754 g	10.521 g

## 4.2 Hydration of the Synthesized Phases

### 4.2.1 Calorimetry

The following tables show the size and composition of the different samples that were measured with calorimetry. In all the tests the solid compounds were mixed together before the water was added. The samples were then mixed for a minute before the measurements were started.

#### *Aluminate*

Name	Aluminate (g)	Gypsum (g)	Total solid weight (g)	Water (g)	w/s
Aluminate	0.700	0	0.700	0.560	0.8
Aluminate with 10 wt% gypsum	0.749	0.083	0.832	0.666	0.8
Aluminate with 20 wt% gypsum	0.500	0.125	0.625	0.500	0.8

#### *Alite*

Name	Alite (g)	Water (g)	w/s
Alite	1.000	1.000	1.0

#### *Alite and Aluminate*

This sample was meant to represent typical Portland cement.

Name	Alite (g)	Aluminate (g)	Gypsum (g)	Total solid weight (g)	Water (g)	w/s
Alite 86 wt%, aluminate 11 wt% and gypsum 3 wt%	0.700	0.0860	0.0260	0.812	0.700	0.8

### 4.2.2 IR

The following tables show the size and composition of the samples measured with infrared spectroscopy. In this work an infrared spectrometer called Nicolet 6700 ftir was used. It measures mid-IR. In all the tests were the solid compounds mixed together before the water was added. The samples were then mixed for a minute before the measures were started. To prevent the water to evaporate during the measure, the sample was covered with a plastic lid with a hole (where the clamp to the ATR could fit in to press the sample against the diamond) and a plastic film attached with tape.

#### *Aluminate*

Name	Aluminate (g)	Gypsum (g)	Total solid weight (g)	Water (g)	w/s
Aluminate	0.700	0	0.700	0.560	0.8
Aluminate with 10 wt% gypsum	0.500	0.056	0.556	0.444	0.8
Aluminate with 20 wt% gypsum	0.500	0.125	0.625	0.500	0.8

### Alite

Name	Alite (g)	Water (g)	w/s
Alite	0.500	0.300	0.6

### Alite and Aluminate

This sample was meant to represent typical Portland cement.

Name	Alite (g)	Aluminate (g)	Gypsum (g)	Total solid weight (g)	Water (g)	w/s
Alite 86 wt%, aluminate 11 wt% and gypsum 3 wt%	0.700	0.0860	0.0260	0.812	0.700	0.8

## 5 Results and Discussion

### 5.1 Synthesis

Figure 4 shows the XRD measure of aluminate batch 4. As can be seen it is not completely pure aluminate. There are small amounts of unreacted CaO and also mayenite, a calcium aluminate oxide mineral.

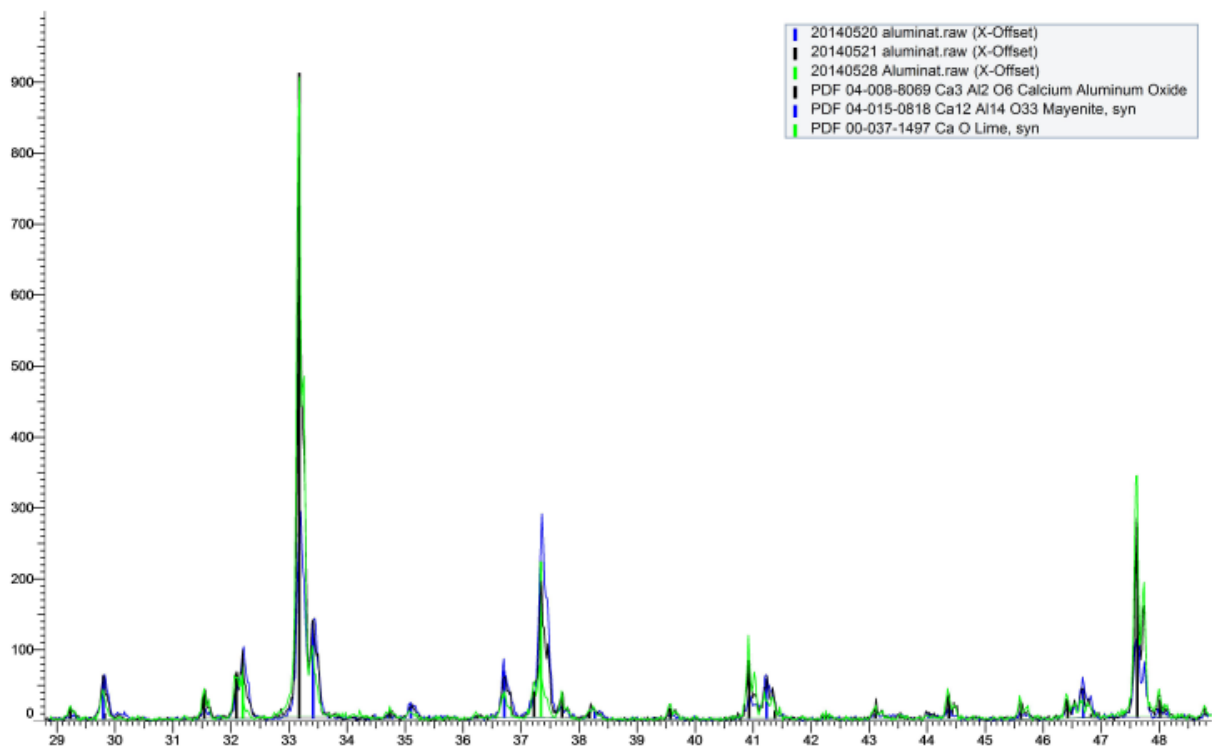


Figure 4 - XRD: Aluminate batch 4

Figure 5 shows the XRD measure of Alite batch 1. This sample is almost pure alite. There is only a small amount of unreacted CaO.

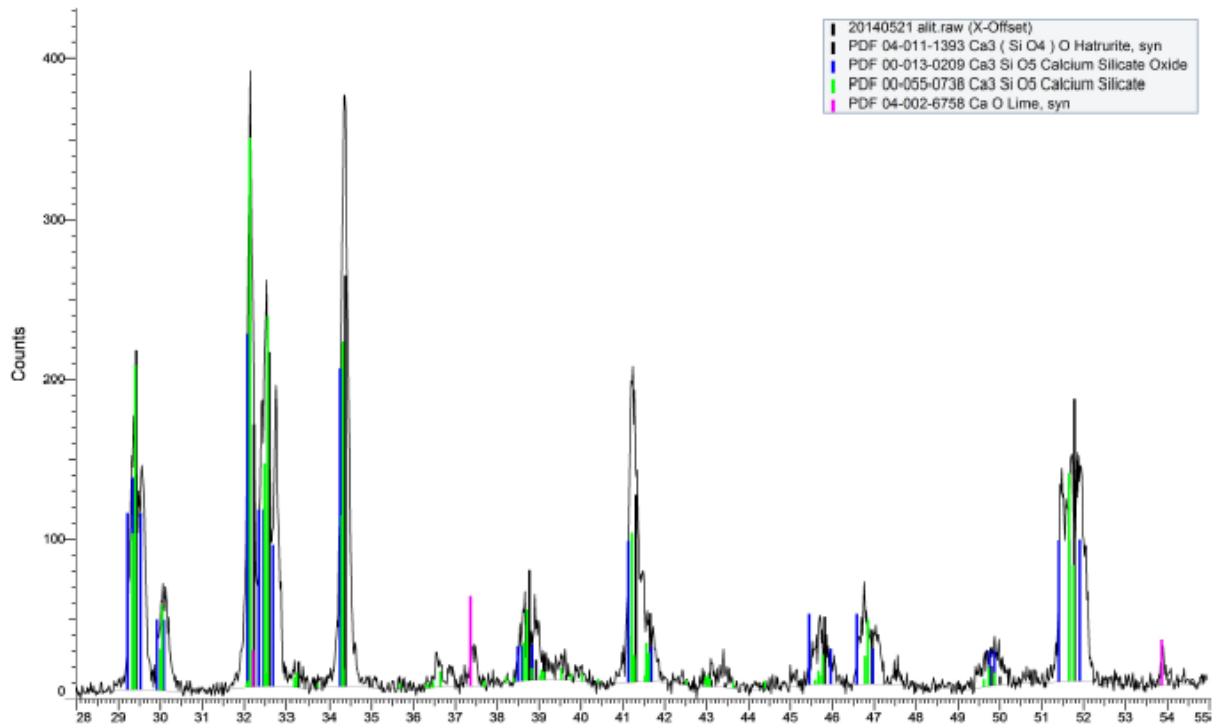


Figure 5 - XRD: Alite batch 1

Aluminate was much more difficult to synthesize than alite, although the literature said the opposite. To synthesize aluminate the tablets needed to be burned at least five times, while alite only needed to be burned one or two times. The best results from both aluminate and alite synthesis were given when the tablets were burned for about 10 hours, longer than that did not give better results. One batch each of aluminate and alite were not pressed into tablets, instead it was burned as a powder. The results were better when the powder was pressed into tablets. No tests were made without grinding.

## 5.2 Hydration of the Synthesized Phases

### 5.2.1 Calorimetry

Figure 6 shows the heat development when alite is hydrated. The maximum of the reaction peak is between 10-15 h. The peak shows the formation of C-S-H. The result is consistent with the literature [3] [5].

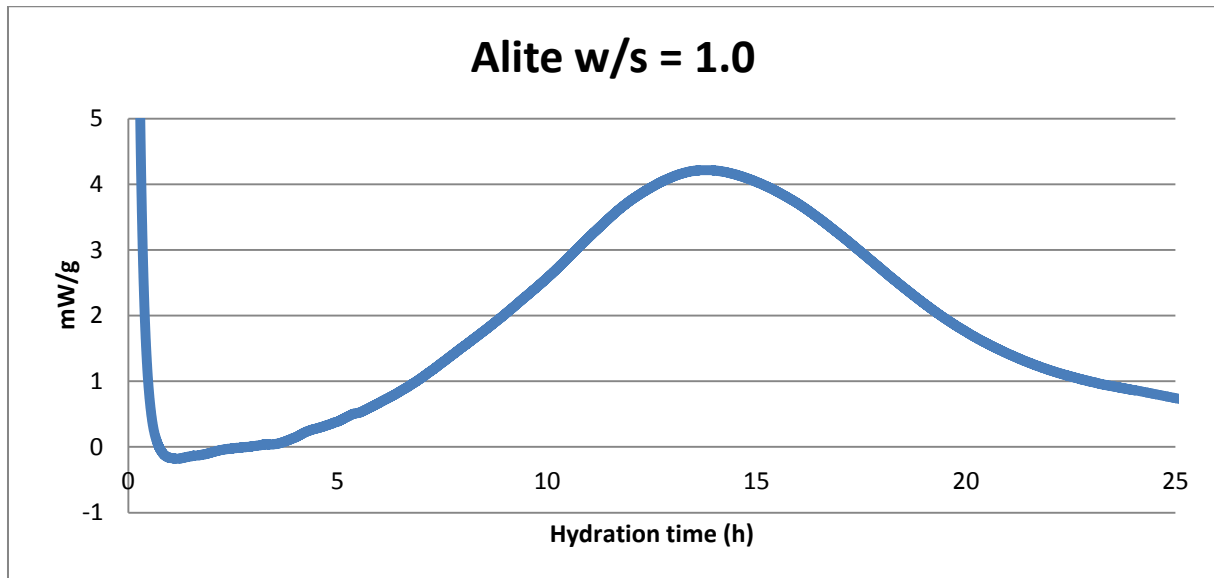


Figure 6 – Calorimetry: Alite mixed with water

Figure 7 shows the hydration reaction of aluminate and gypsum. The reaction peaks just after a few minutes when it is pure aluminate, after 2-3 h with 10 wt% gypsum and after 10 h with 20 wt% gypsum. The delay of the reaction is caused by the formation of AFt phases [11].

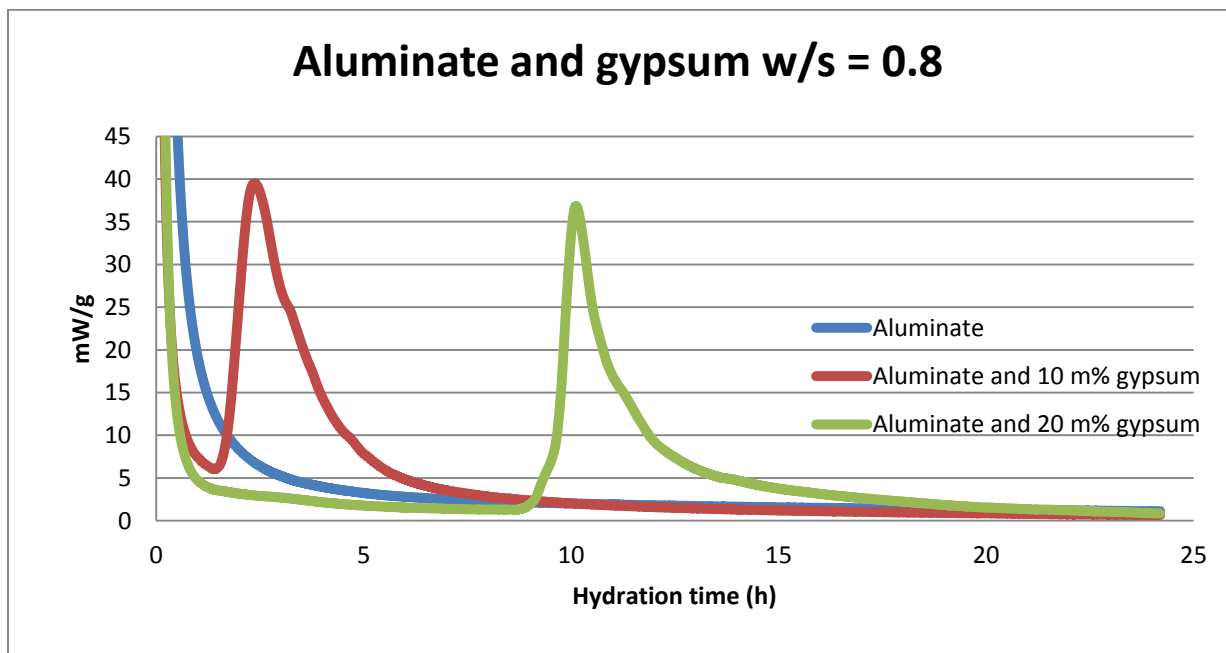


Figure 7 - Calorimetry: Aluminate and gypsum mixed with water

Figure 8 shows the hydration reaction of alite, aluminate and gypsum. The reaction has two peaks, one smaller around 11 h and another bigger one around 15 h. The curve mostly depends on the alite reaction but the peak after 15 hours is due to the aluminate/gypsum reaction. The aluminate reaction with 20 wt% gypsum peaks after 11 hours and in this sample it is 23 wt% gypsum (relative the aluminate) which makes it peak after 15 hours.

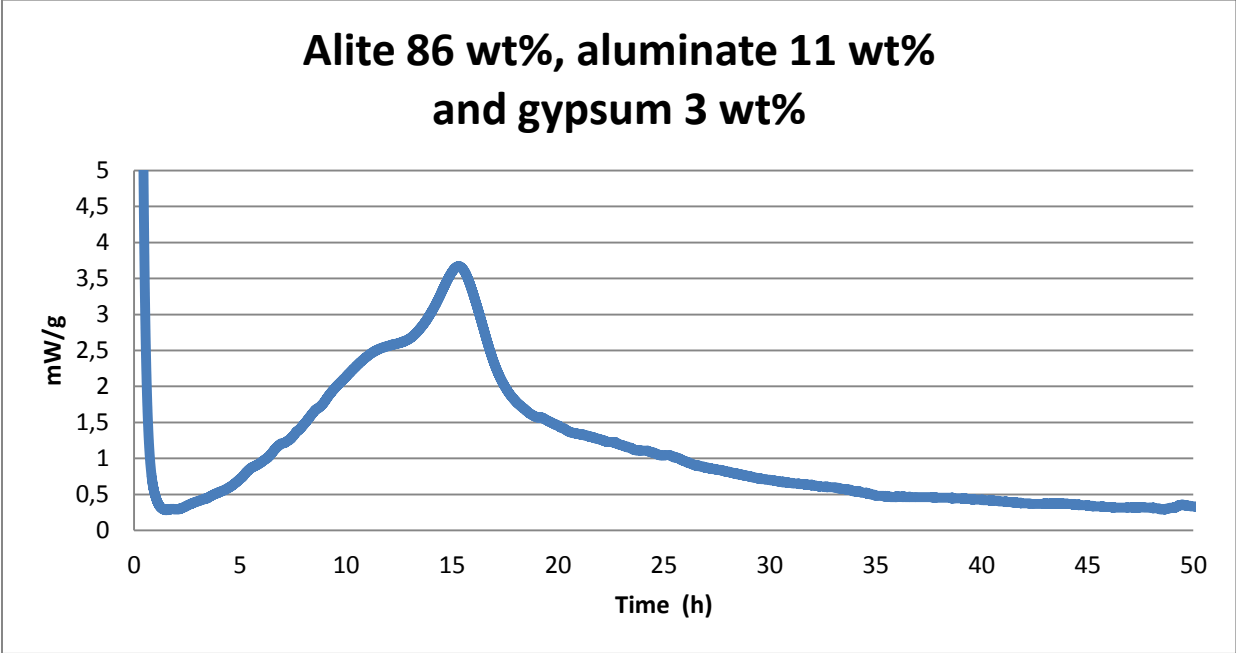


Figure 8 – Calorimetry: Alite, aluminate and gypsum mixed with water

### 5.2.2 Infrared Spectroscopy

Figure 9: The peaks in the range 500-900  $\text{cm}^{-1}$  are probably showing the formation silicates in the first 13 h and after that the reaction of water, with a big decrease between 15-17 h. A broad peak at 900-1100  $\text{cm}^{-1}$  can be observed. This shows the polymerization of silica and the formation of C-S-H and is most active between 5-13 h [13]. The dip at  $\sim 1625 \text{ cm}^{-1}$  shows the disappearing of water in the sample. The big dip at 3000-3600  $\text{cm}^{-1}$  is water which reacts and forms C-S-H. The peak around 3600  $\text{cm}^{-1}$  shows the formation of  $\text{Ca}(\text{OH})_2$ , portlandite.

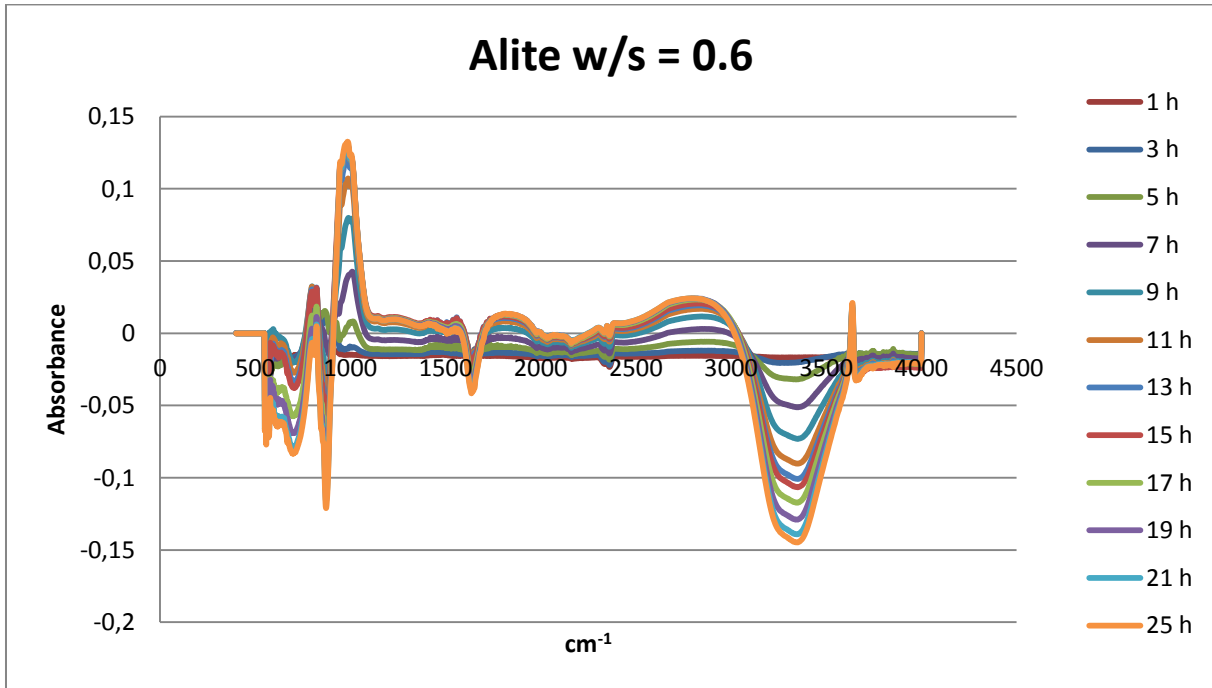


Figure 9 - IR: Alite mixed with water. ATR difference spectra in the range 550-4000  $\text{cm}^{-1}$ . The absorbance spectra have been subtracted from the spectrum acquired after 1 minute.

Figure 9 shows that the formation of C-S-H is most active after 5-13 h, which is consistent with the calorimetry data in figure 6.

Figure 10: The peaks in the range of 700-900  $\text{cm}^{-1}$  show the dissolution calcium aluminate. The dissolution rate is especially high between 5 and 14 h. The small dip around  $\sim 1600 \text{ cm}^{-1}$  and the dip at 3200-3400  $\text{cm}^{-1}$  is caused by the reaction of liquid water to hydroxides and incorporation of water molecules in the solid hydration products. The peak at  $\sim 3640 \text{ cm}^{-1}$  might be the formation of  $\text{Ca}(\text{OH})_2$ , portlandite, or another calcium hydroxide compound.

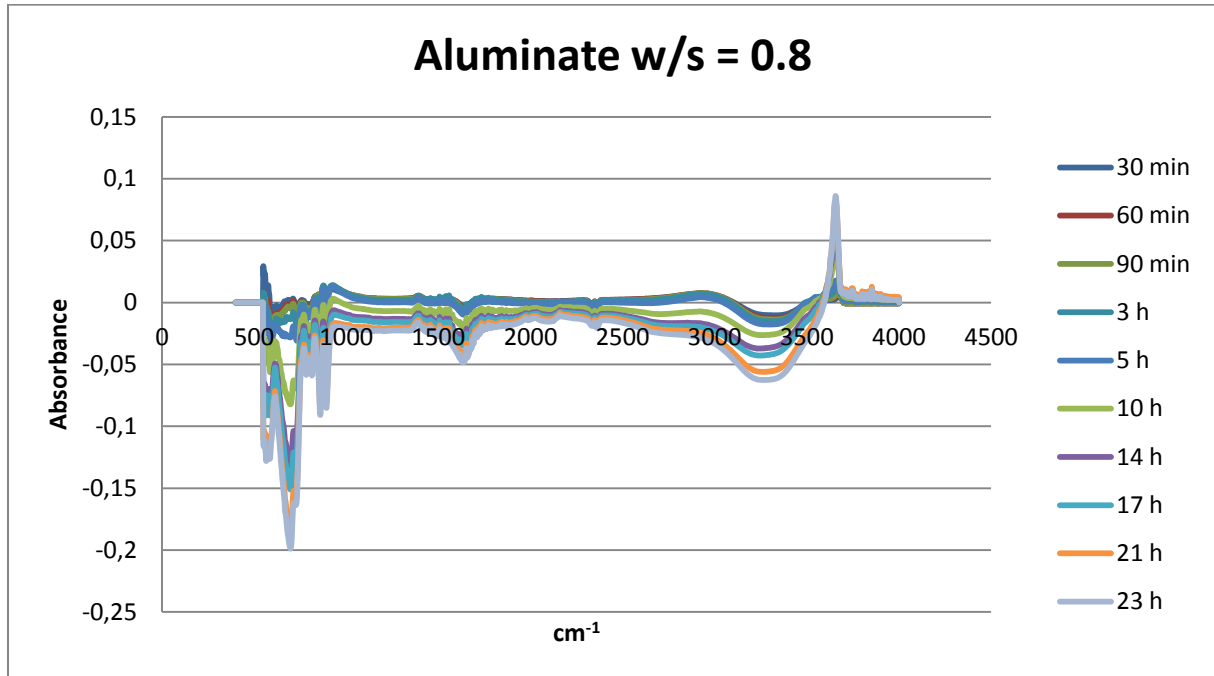


Figure 10 - IR: Aluminate mixed with water. ATR difference spectra in the range 550-4000  $\text{cm}^{-1}$ . The absorbance spectra have been subtracted from the spectrum acquired after 1 minute.

The hydration reaction of aluminate is very fast, the reaction occurs immediately after the addition of water (figure 7). The addition of gypsum to the aluminate-water system leads to a slower reaction rate and makes the reaction less exothermic. This depends probably of the formation of the Aft phase ettringite. It may also be due to that calcium- and sulphate ions attaches on the surface of the grains of the aluminate, which prevents the water from reacting and delays the reaction <sup>[15]</sup>.



Figure 11: The dips and peaks in the range 500-900  $\text{cm}^{-1}$  is the dissolution of  $\text{SO}_4^{2-}$  and calcium aluminate <sup>[14]</sup>. The peak at 1000-1200  $\text{cm}^{-1}$  is the formation of AFm and AFt phases and it goes very fast the first 3 h. The dip at  $\sim 1640 \text{ cm}^{-1}$  shows the reaction of liquid water. The dip at 3100-3400  $\text{cm}^{-1}$  probably shows the disappearing of water which reacts to form new compounds. The peak around 3600  $\text{cm}^{-1}$  is very likely the formation of OH-groups in the AFm- or AFt phases (from the peak at 1000-1200  $\text{cm}^{-1}$ ) but can also be the formation of  $\text{Ca}(\text{OH})_2$ .

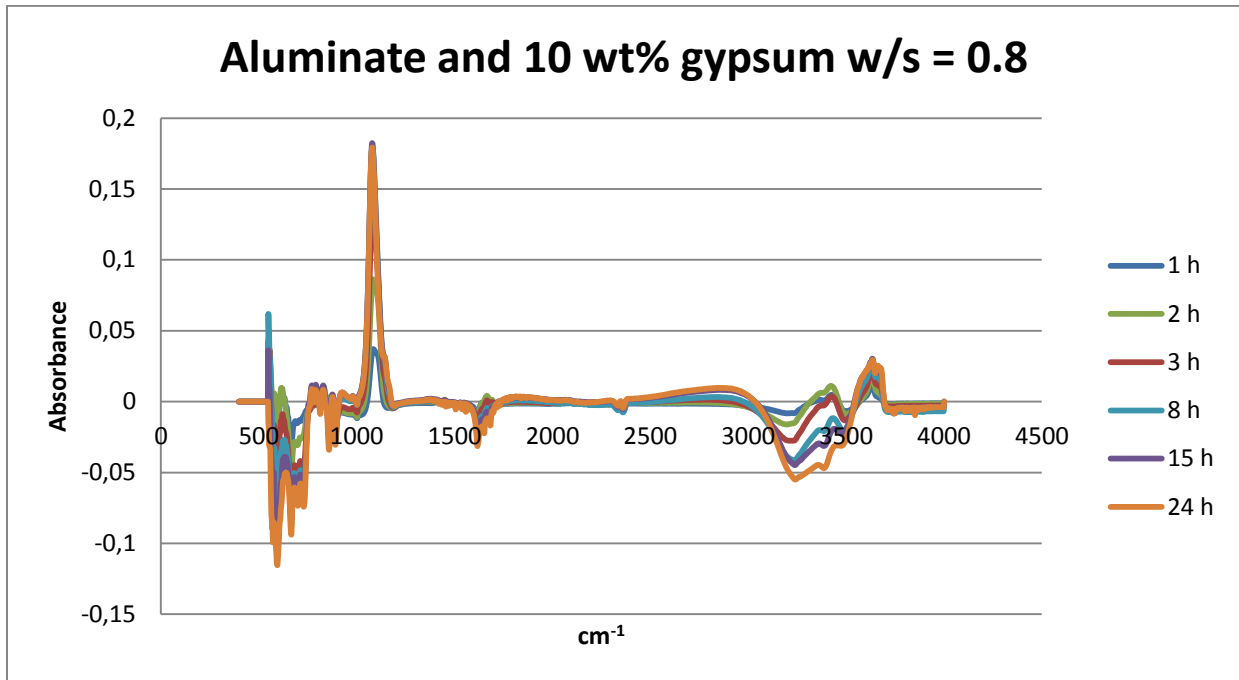


Figure 11 - Aluminate and gypsum mixed with water. ATR difference spectra in the range 550-4000  $\text{cm}^{-1}$ . The absorbance spectra have been subtracted from the spectrum acquired after 1 minute.

Figure 12: The small peaks at  $600\text{ cm}^{-1}$  and  $662\text{ cm}^{-1}$  is probably from the vibrations of  $\text{SO}_4^{2-}$  and calcium aluminate<sup>[14]</sup>. The peak around  $850\text{ cm}^{-1}$  shows the dissolution of calcium aluminate. The big peak at  $1000\text{-}1150\text{ cm}^{-1}$  is the formation of AFm and Aft phases. The dip at  $3000\text{-}3300\text{ cm}^{-1}$  shows the disappearing of water. The peak after  $3400\text{ cm}^{-1}$  is very likely vibration of water in the AFm- or Aft phases. The peak around  $3600\text{ cm}^{-1}$  is due to the formation of  $\text{Ca}(\text{OH})_2$ .

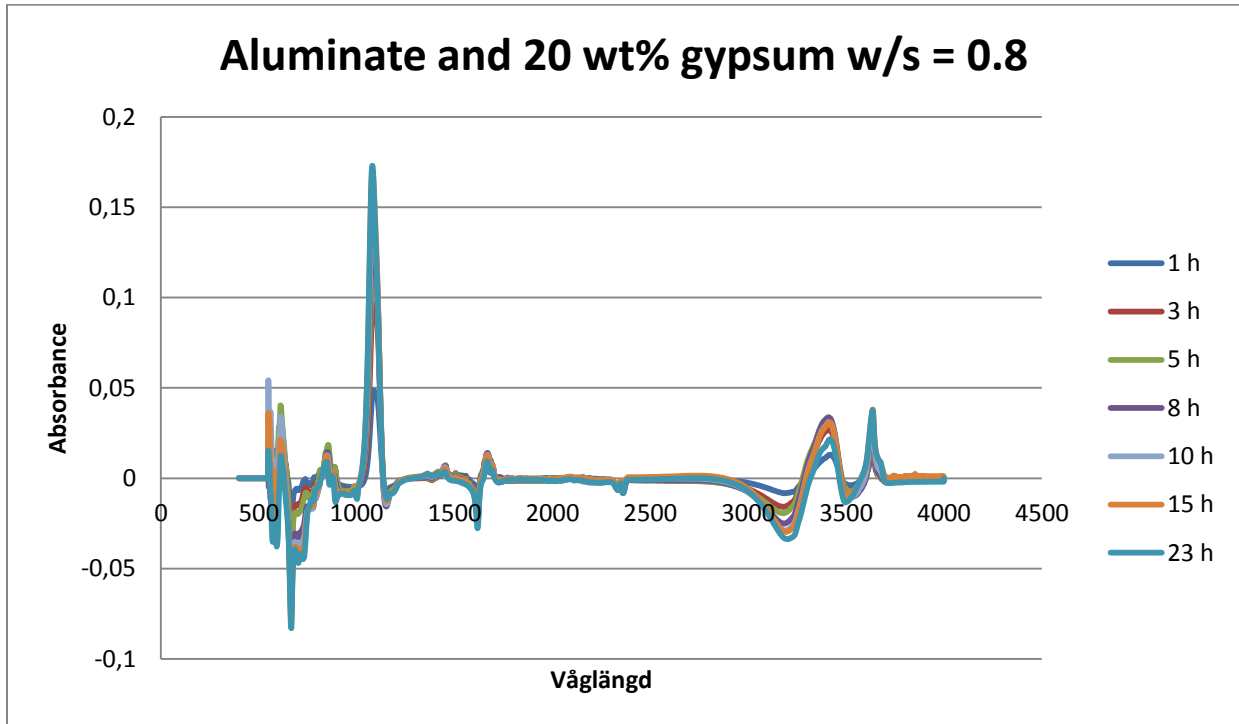


Figure 12 - Aluminate and gypsum mixed with water. ATR difference spectra in the range  $550\text{-}4000\text{ cm}^{-1}$ . The absorbance spectra have been subtracted from the spectrum acquired after 1 minute.

The samples with gypsum have a peak at  $500\text{-}600\text{ cm}^{-1}$  which doesn't exist in the aluminate sample without gypsum. This means it depends on the gypsum and might therefore be the vibrations of  $\text{SO}_4^{2-}$ . The dip at  $\sim 1600\text{ cm}^{-1}$  and  $3100\text{-}3400\text{ cm}^{-1}$  exists in all calcium aluminate samples and is showing the reaction of water. The peak at  $3400\text{ cm}^{-1}$  only exists in the presence of gypsum and might therefore be caused by the Aft phases.

Figure 13: The broad peak at 550-800  $\text{cm}^{-1}$  is due to either sulphates or silicate. The peak increases the first 5 h and decreases after that, with the biggest decrease rate between 5-7 h. This means it forms sulphates/silicate during the first 5 h and then it is being dissolved. The dip around 860  $\text{cm}^{-1}$  is related to the  $\text{C}_3\text{S}$  phase, because it can be seen in figure 11 where pure  $\text{C}_3\text{S}$  were hydrated, and is probably some kind of silicate compound related to the silicate polymerization and the formation of C-S-H. The big peak in the range of 900-1200  $\text{cm}^{-1}$  must be the formation of C-S-H and AFm and AFt phases. The round peaks in the range 1500-2000  $\text{cm}^{-1}$  and 2400-3000  $\text{cm}^{-1}$  might show the crystallization of water in the sample. The big dip at 3000-3600  $\text{cm}^{-1}$  exists in all mixtures and is showing the disappearing of water, however it is much bigger in the presence of  $\text{C}_3\text{S}$ . The last peak around 3600  $\text{cm}^{-1}$  shows the formation of  $\text{Ca}(\text{OH})_2$  or another kind of OH-compound.

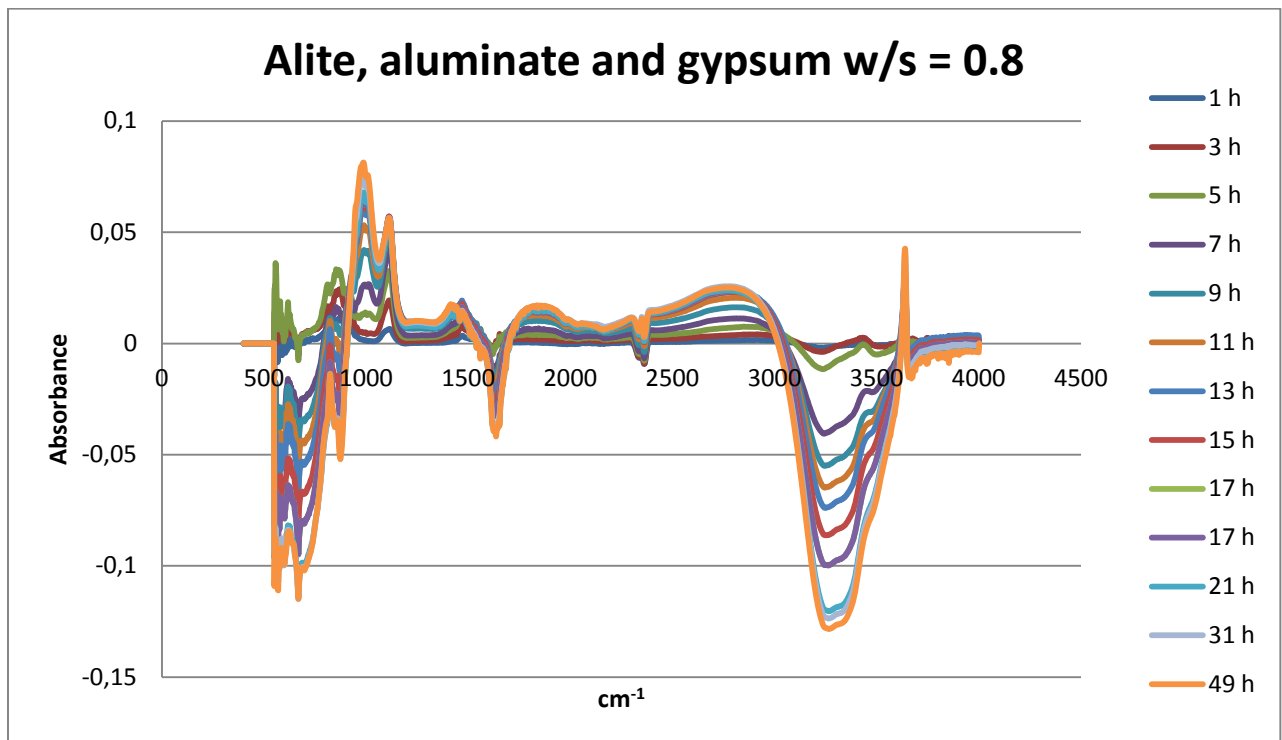


Figure 13 - Alite, aluminate and gypsum mixed with water. ATR difference spectra in the range 550-4000  $\text{cm}^{-1}$ . The absorbance spectra have been subtracted from the spectrum acquired after 1 minute.

## 6 Conclusion

The triclinic form of alite and the cubic form of calcium aluminate were successfully synthesized and their hydration reaction was studied by using isothermal calorimetry and infrared spectroscopy. The study gave an insight of the mechanisms behind the early hydration of the cement compounds alite and calcium aluminate.

The hydration reaction of aluminate is very fast, the reaction occurs immediately after the addition of water. The addition of gypsum to the aluminate-water system leads to a slower reaction rate and makes the reaction less exothermic. This depends probably of the formation of the AFt phase ettringite.

The main reaction of alite occurs around 5-20 hours after the addition of water. The C-S-H formation is the most active 5-13 hours after the addition of water.

The synthesis of calcium aluminate was much harder than alite, even if a higher temperature is needed for alite.

## **7 Acknowledgements**

I would like to thank the following persons for contributing to my work:

My examiner Ulf Jäglid and my supervisor Rikard Ylmén for the help and support during my work.

Habibur Rahman and Nico Torino for the help with the furnaces.

Johan Hjelmgren for the support and help.

## 8 References

- [1]: van Oss H.G. <http://minerals.usgs.gov/minerals/pubs/commodity/cement/>, February 2014. Available: <http://minerals.usgs.gov/minerals/pubs/commodity/cement/mcs-2014-cemen.pdf>
- [2]: Mindess S. Concrete Construction Engineering Handbook. 2008.
- [3]: Jansen D, Bergold T. S, Goetz-Neunhoeffer F, Neubauer J. The hydration of alite: a time-resolved quantitative X-ray diffraction approach using the G-factor method compared with heat release. Journal of Applied Crystallography 2011;44:895-901.
- [4]: N.B Singh. Hydrothermal synthesis of  $\beta$ -dicalcium silicate ( $\beta$ -  $\text{Ca}_2\text{SiO}_4$ ). Progress in Crystal Growth and Characterization of Materials 2006;52:77-83.
- [5]: Kumar A, Bishnoi S, Scrivener K.L. Modelling early age hydration kinetics of alite. Cement and Concrete Research. 2012;42:903-918.
- [6]: G W Groves. Twinning in  $\beta$ -dicalcium silicate. Cement and Concrete Research 1982;12:619-624.
- [7]: Merlino M, Artioli G, Cerulli T, Cella F, Bravo A. Tricalcium aluminate hydration in additive systems. A crystallographic study by SR-XRPD. Cement and Concrete research 2008;38:477-486.
- [8]: Landa-Cánovas Angel R, Hansen S. Transmission electron microscopic study of ferrite in sulfate-resisting Portland cement clinker. Cement and Concrete Research 1999 January 21;29:679-686.
- [9]: Sáez del Bosque I.F, Martínez-Ramírez S, Blanco-Varela M.T, FTIR study of the effect of temperature and nanosilica on the nanostructure of C-S-H gel formed by hydrating tricalcium silicate. Construction and Building Materials 2014;52:314-323.
- [10]: Matschei T, Lothenbach B, Glasser F.P. The AFm phase in Portland cement. Cement and Concrete Research 2007 October 27;37:118-130.
- [11]: Odler I, Abdul-Maula S. POSSIBILITIES OF QUANTITATIVE DETERMINATION OF THE AFt-(ETTRINGITE) AND AFm-(MONOSULPHATE) PHASES IN HYDRATED CEMENT PASTES Cement and Concrete Research 1984 November 21;14:133-141.
- [12]: Wesselsky A, Jensen O.M. Synthesis of pure Portland cement phases. Cement and Concrete research 2009 July 2009.
- [13]: Ylmén R, Jäglid U, Steenari B, Panas I. Early hydration and setting of Portland cement monitored by IR, SEM and Vicat techniques. Cement and Concrete Research 2009 May;39:433-439.
- [14]: Mollah M.Y.A, Wenhong Y, Schennach R, Cocke D.L. A Fourier transform infrared spectroscopic investigation of the early hydration of Portland cement and the influence of sodium lignosulfonate. Cement and Concrete Research 2000 February;30:267-273.
- [15]: Minard H, Garrault S, Regnaud L, Nonat A. Mechanisms and parameters controlling the tricalcium aluminate reactivity in the presence of gypsum. Cement and Concrete Research 2007 June;37:1418-1426.