



## HEAT OF HYDRATION OF CALCIUM SULFOALUMINATE CEMENT – A LITERATURE REVIEW

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**Abstract:** Calcium sulfoaluminate (CSA) cement is a sustainable alternative to Ordinary Portland Cement (OPC). The manufacturing of CSA has a lower carbon dioxide emission compared to OPC. This is attributed to the lower temperature needed to calcinate the raw materials and less energy consumed during the pulverization process, which reduces the carbon footprint. However, in many cases, the production process of CSA can be more expensive than OPC. The Heat of Hydration (HH) of cement can affect the properties of concrete. In mass concrete structure, high HH can lead to thermal stresses and delayed ettringite that may lead to the expansion, thermal cracking, and failure of the structure. Several factors affect the amount of heat released during the hydration of cement, such as: the cement mineralogical composition, curing temperature, water/cement (w/c) ratio, and cement fineness. This study presents a review of previous studies that focused on the assessment and quantification of the HH of CSA. This paper serves as a succinct guide for future researchers that aim to conduct advanced studies on the HH of CSA.

### 1 INTRODUCTION

Calcium sulfoaluminate (CSA) cement was mentioned for the first time in a French patent in the 1930's, but it was only in the 1970's and 1980's that its production started to become important (Garcia-Mate 2013). CSA cement can reach a compressive strength of 5000 psi in 24 hours, while Ordinary Portland Cement (OPC) achieves it in 28 days. The initial setting time of the CSA cement begins after approximately 20 minutes and its final setting time is then arrived to after ten more minutes. With the use of retarders, the processing time can be considerably extended. Therefore, even in low temperature environments, CSA cement maintains its reactivity unlike other cement types (Zhou et al. 2006). For these reasons, CSA cement is commonly used in airport start and runways, bridge reparations, and any other application where time is vital.

A key advantage of CSA cement is that it has a smaller impact on the environment in comparison to OPC; CSA can be produced at about 1200°C, making it 200-250°C lower than OPC, because it is relatively softer and more friable, making it easier to grind. As a result, the entire process will save more energy (Kasselouri et al. 1995).

When water makes contact with cement an exothermic reaction liberates heat, called heat of hydration. The release of excessive heat is a concern in mass concrete constructions, such as: dams, bridges, raft foundations, etc. Mass concrete elements generate substantial thermal gradients between the core and the

surface that pose a considerable risk of thermal damage. This phenomenon is called Thermal Cracking (Bernardo et al. 2006).

Sufficient literature review exists regarding the heat of hydration and the early hydration phases of Calcium Sulfoaluminate cement. Common methods to quantify the heat of hydration- Isothermal Calorimetry, Semi-Adiabatic Calorimetry, Differential Calorimetry, nonisothermal-nonadiabatic differential BMR Calorimetry, which are discussed in this literature review. The objective of this study is to provide a comprehensive literature review on the Heat of Hydration of CSA cement that could serve as a guide for the scientific community for future references.

## **2 PROBLEM STATEMENT**

Even though CSA is relatively new when compared to OPC, a great amount of research has been done. However, most previous studies are quite fragmented in the sense that they do not have continuity or fully cover CSA topics in depth. The fact that there is not a single paper that combines all this literature suggests that a comprehensive paper of all previous HH of CSA articles is needed.

## **3 OBJECTIVE**

The main objective of this literature review to provide a tool to the scientific community that will facilitate future research on HH of CSA as it takes time and effort to know what has been done in the past. This literature review will compare results between different publications to look for discrepancies and similarities in their findings.

## **4 METHODOLOGY**

The methodology adopted in this study is comprised of two steps. First, a thorough search was conducted to compile all previous research publications related to the HH of CSA. Second, the collected studies with classified according to the method used in assessing and quantifying the HH of CSA and organized chronologically for comprehensive review. Two categories were used to classify the studies based on the methods used to quantify the heat of hydration, which are: 1) Isothermal calorimetry, and 2) Semi-Adiabatic calorimetry.

## **5 ISOTHERMAL CALORIMETRY**

The literature included eight studies that utilized isothermal calorimetry to assess and quantify the heat of hydrations of CSA. One of the first studies on the HH of CSA goes back to Dová et al. (2005). The authors presented a study on the heat evolution and mechanism of the hydration of  $\text{CaO-Al}_2\text{O}_3\text{-SO}_3$  using an isothermal conduction calorimeter. The study addressed the hydration behavior of  $\text{CaO-Al}_2\text{O}_3\text{-SO}$  at different temperatures range of 25, 40, 60 and 80°C, and different water-solid(w/s) ratios of 0.5, 0.7 and 1.0. For the calorimeter test, the authors made a combination of  $\text{CaCO}_3$ ,  $\text{Al(OH)}_3$  and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . Then, they calcined it twice for two hours at 1250°C to synthesize  $\text{C}_4\text{A}_3\text{S}$ . A first experiment was conducted to study the influence of the temperature on the rate of hydration. The results of the calorimeter test indicated that when the temperature increases the hydration intensity also increases and the duration of the induction period becomes shorter, as shown in Figure 1.

The second experiment focused on assessing the influence that w/s ratio has on the HH at different temperatures. The results showed that when w/s ratio increases at low temperatures (25°C and 40°C), the heat flow peaks increases slightly, and the induction period is shorter- see Figure 2a. However, at high temperatures (60°C and 80°C), the heat flow peaks and the length of induction period decrease by increasing the w/s ratio, see Figure 2b. As such, it is concluded that the hydration reaction of  $\text{C}_4\text{A}_3\text{S}$  is accelerated with increasing temperatures at w/s ratios of 0.5, 0.7, and 1.0. Also, the hydration accelerates if w/s ratio increases at 25°C and 40°C, but at higher temperatures the intensity of hydration decreases.

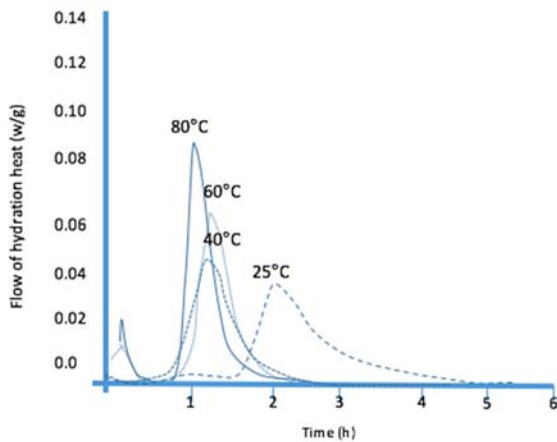


Figure 1a. Influence of temperature on the HH at w/s of 0.7 (Dová et al. 2005)

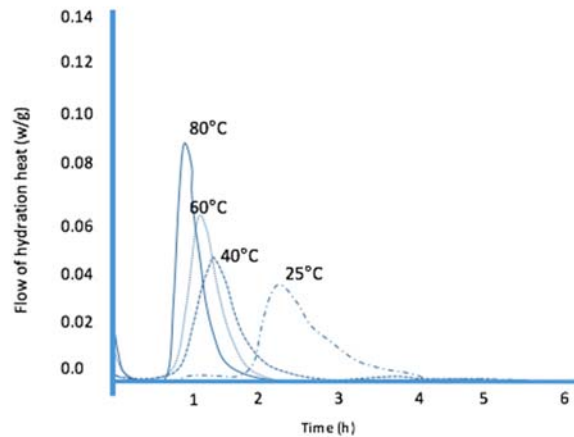


Figure 1b. Influence of temperature on the HH at w/s of 1 (Dová et al. 2005)

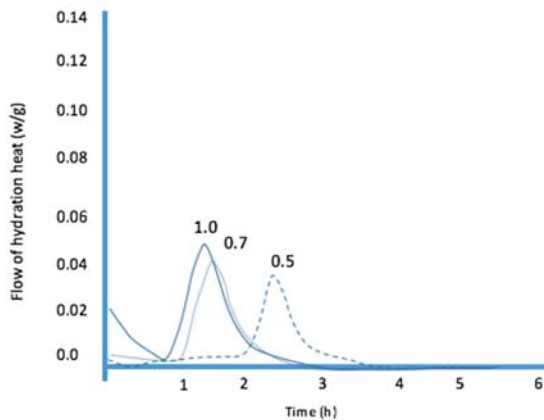


Figure 2a. Influence of w/s/ on the HH at W/S at 40°C (Dová et al. 2005)

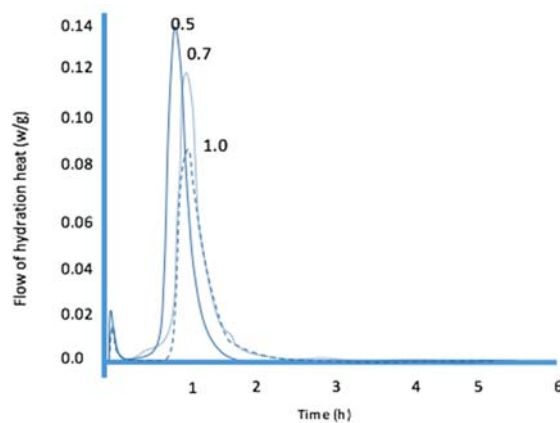


Figure 2b. Influence of w/s/ on the HH at W/S at 80°C (Dová et al. 2005)

Lura et al. (2010) conducted a set of experiments using isothermal calorimetry and chemical shrinkage measurements to assess the heat of hydration of Ordinary Portland Cement (OPC) and CSA. In this study, three experiments were conducted applying the two methods in order to determine the heat of hydration of PC samples and a mixture of CSA and anhydrite. The first setup is called a sole calorimetry, where a commercial conduction calorimeter with eight measuring cells was used. The time period used to get the heat flow was about 80 hours and a temperature of  $\pm 0.02$  °C was set to keep the measuring cells in the calorimeter. The second experiment is a sole chemical shrinkage; a thin layer of demineralized water was placed on top of the three pastes. Regular intervals were chosen for three days to determine the corresponding measurements done by reading the oil level of each graduated pipettes.

Lastly, the third experiment is a combined calorimetric/chemical shrinkage, here several mixtures were conducted, and parallel measurements were used to measure the heat of hydration and chemical shrinkage. The results show that measuring the chemical shrinkage inside the calorimeter is as efficient as the sole measurement using the ASTM C-1608-07 procedures.

Gartner et al. (2011) studies the hydration of Belite-Calcium Sulfoaluminate-Ferrite cement paste using XRD-Rietveld, TGA, Differential Thermal Analysis (DTA), Isothermal calorimetry, and pycnometry. For isothermal calorimetry, the cement paste was studied at 20°C with a water-cement ratio of 0.5. The composition of the cement was as follows: 48% of belite (C<sub>2</sub>S), 28% of ye'elimite (C<sub>4</sub>A<sub>3</sub>S), 18% of ferrite solid solution (C<sub>2</sub>(AF)), and 6 % of anhydrite. The previous mentioned methods were implemented at the early hydration ages, which is between the first 28 days, and after 28 days (Gartner et al. 2011).

The specimens used in these procedures were prepared with different raw materials, such as: limestone, clay, bauxite, iron ore and anhydrite. All previous materials were ground together in the desired proportions and pelletized at 1280°C. The results from the hydration at very early ages for the calorimeter showed three peaks. The first one happened at 15 minutes, which is the beginning of the ye'elimite dissolution. The second one appeared at 2 hours, which is the main dissolution period of ye'elimite. Lastly, the third one appeared at 3.5 hours (Gartner et al. 2011).

In a different research, the hydration of two CSA cements (CSA-1 and CSA-2) was investigated at a range of 1 hour and 28 days with a w/c ratio of 0.72 (CSA-1) and 0.80 (CSA-2) (Winnefeld et al. 2010a). The chemical composition of CSA-1 was ye'elimite (50%), gehlenite (15%), calcium aluminate (8%), gypsum (22%) and others (5%). For CSA-2, its chemical composition consisted of ye'elimite (54%), belite (19%) and anhydrite (21%). All hydration experiments were carried out at 20 °C. The methods implemented were isothermal calorimetry, X-Ray Diffraction (XRD), Thermo-Gravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM) (Winnefeld et al. 2010a).

Isothermal calorimeter was used to determine the rate of hydration heat liberated during the first 72 hours. The results showed that the main hydration peak of CSA-1 occurs at 7 hours and has a dormant period between 3-4 hours during hydration. The results showed that the main hydration peak of CSA-1 occurs at 7 hours with a dormant period between 3-4 hours during hydration. For CSA-2, the main hydration peak occurred after 7 hours and a second at 26 hours, with a dormant period similar to CSA-1 (Winnefeld et al. 2010a).

In a separate publication, the same authors studied the main phase of hydration in CSA, ye'elimite (calcium sulfoaluminate), with two calcium sulfates along with different reactivities (gypsum, and anhydrite) (Winnefeld et al. 2010b). The methods implemented were isothermal conduction calorimetry, TGA, and XRD. All the experiments were done at 20°C, and they used ye'elimite blended with different quantities of gypsum/anhydrite at different molar ratios (1:1, 1:2, 1:3 and 1:4) (Winnefeld et al. 2010b).

Isothermal calorimetry was used to determine the influence in the hydration heat flow of gypsum in ye'elimite. Without the addition of gypsum in ye'elimite, the results showed that there were two maxima peaks in the heat flow curve (Figure 3a). The first peak occurred after water was added, and the second one at 15 hours of hydration (Figure 3b). When gypsum was added to the mixtures, the graphs behaved similarly to the ones with pure ye'elimite. Nevertheless, it is important to notice that heat is more intense in the mixtures with the presence of gypsum, and its dormant period is shortened to about 3 hours. After the dormant period, the samples with lower amount of gypsum (1:1 and 1:2) showed two maximum peaks, the first one at 5 hours (1:1 and 1:2) and the second one was at 10.5 hours (1:1) and at 15.5 hours (1:2). The samples with higher amount of gypsum showed only one maximum peak (Winnefeld et al. 2010b).

When the anhydrite was added to the ye'elimite, the results showed that anhydrite has less impact on the very early reactions. The first peak shown in Figure 3a is caused by the addition of water. The results indicated that the addition of anhydrite in the samples accelerates the hydration of ye'elimite phase as gypsum does. In comparison to samples with gypsum, anhydrite's dormant period is shortened to about 4 hours, and its curves behave differently, see Figure 4b (Winnefeld et al. 2010b).

When the authors used potassium hydroxide (KOH) on the hydration kinetics of ye'elimite, the results showed that the initial peak increased significantly because there is an enhanced dissolution and precipitation of more hydrated phases in the first minute of hydration. The addition of KOH to the sample showed that the hydration of ye'elimite is accelerated with alkaline solutions. When gypsum and KOH were used in the samples, the results showed that the initial peak increases, and the hydration accelerates (Winnefeld et al. 2010b).

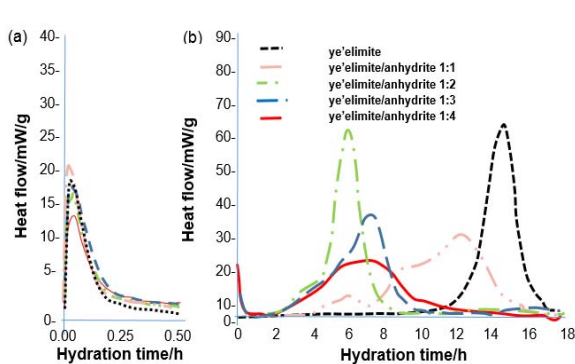


Figure 3a: Conduction calorimetry of ye'elimitite pastes: influence of gypsum addition. q) first 30 minutes, b) from 0-18 hours (Winnefeld et al. 2010b).

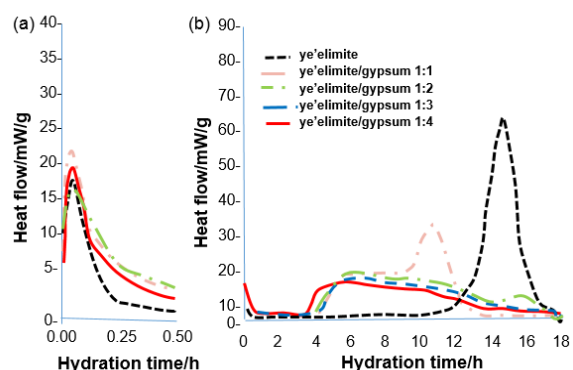


Figure 3b: Conduction calorimetry of ye'elimitite pastes: influence of anhydrite addition. a) first 30 minutes, b) from 0-18 hours (Winnefeld et al. 2010b).

Another study presents a documentation for the synthesis of calcium sulfoaluminate-belite (CSB); three different CSAB clinkers were made using reagent-chemicals and different gypsum amounts (Chen and Juenger 2011). as study to analyze the dependency of temperature of calcium sulfoaluminate-belite cement hydration. A period of three days with a temperature of 23 °C was used to determine the hydration of pastes with a w/c of 0.45. Also, the phase composition was refined using a proposed proportioning method and an equation for calculating the minimum amount of gypsum needed for the synthesis of CSAB (Chen and Juenger 2011).

A specific rheometric cell was created to characterize hydration at early ages of CSA cement using demineralized water or a borate solution (Champenois 2013). One of the main advantages of this cell is the possibility to collect data simultaneously avoiding any bias due to slight temperature differences between two experiments. The objective of the study was the characterization of the early hydration ages of CSA using complementary techniques, such as: semi-adiabatic calorimetry and isothermal conduction calorimetry. The hydration of the cement was found using a micro-calorimeter under isothermal conditions at  $24.0 \pm 0.5$  °C. The temperature recorded in the samples for rheometry and conductometry were compared to the progress of the heat flux (Champenois 2013).

One study investigated the hydration phases of CSA (ye'elimitite) mixed with two different forms of calcium sulphate, namely, gypsum and anhydrite. Two samples were added using the CSA clinkers with gypsum (CGy) and another one with anhydrite (CAn). There was a fast hydration on both samples within the first minutes. After that, the entire hydration for both samples decreased. The sample made of CSA and anhydrite had an initial slow stage than the one made with gypsum. Subsequently, there was an acceleration within the next two hours and a maximum heat flow was shown after 40 hours. The hydration rate for the CGy specimen is faster than the CAn. There were two peaks within the first 7 hours and the maximum heat flow was shown after 15 hours. This experiment showed that there is a higher reactivity in the system when the samples are mixed with gypsum after 8hours. The results also show that the hydration reaction is dependent on the availability of sulphates.

## 6 SEMI-ADIABATIC CALORIMETRY

The literature included only one study that used semi-adiabatic calorimetry to assess the HH of CSA. Berger et al. (2009) presented a study to investigate hydration of CSA cement at an early age with respect to gypsum content, the thermal history, and  $ZnCl_2$  concentration. The CSA cements used in these tests were prepared by mixing a ground industrial CSA clinker with gypsum. The mortars and pastes used were made with a w/c ratio of 0.55, and with an increasing amount of gypsum from 0 to 35%. Also, in some of the

solutions it was added  $ZnCl_2$ . The pastes were cured for 7 days at  $20^\circ C$  or submitted to a thermal cycle for 7 days Berger et al. (2009).

The heat curves were generated to assess the influence of gypsum on the HH of CSA – see Figure 4a. The results indicate that the cumulative heat decreases when the amount of gypsum in the mortars increases. Another interesting result is changing the amount of gypsum from 0 to 3% of gypsum did not significantly change the total HH, but reduced the timing for the maximum heat fluxes. In the mortars with a 3-7% gypsum content, it was observed that the times for maximum heat fluxes decreased as the gypsum content increases. The mortars with a 7-10% gypsum content behave similarly by having the same minimum induction period, the time for maximum heat flux, and cumulated heat. In mortars with a gypsum content from 10-35% the results show that the induction period increases slightly when the gypsum increases Berger et al. (2009).

The results from the hydration of CSA with  $ZnCl_2$  solution experiments were also determined by the semi-adiabatic calorimetry method, see Figure 4b. It was demonstrated that salt tends to retard the hydration process, but it becomes even more with the binders that did not contain gypsum. When the binders reach 20% of gypsum the retardation in hydration process is only observed at 0.5 Mol/L Berger et al. (2009).

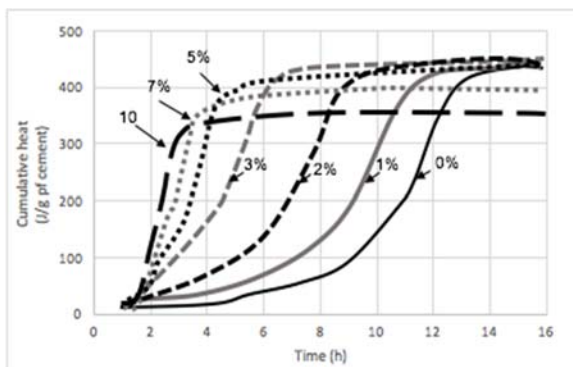


Figure 4a: Influence of the gypsum content on the heat produced by CSA mortars (Berger et al. 2009)

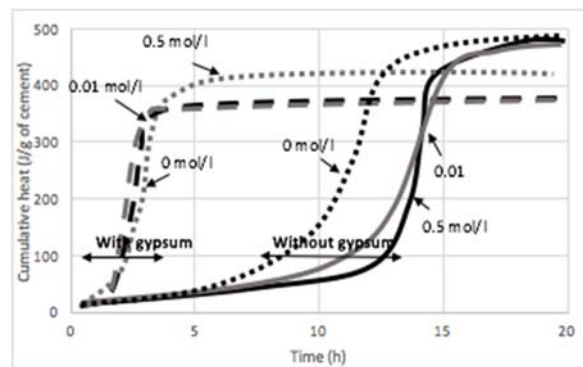


Figure 4b: Influence of the  $ZnCl_2$  concentration in on the heat produced by CSA mortars (Berger et al. 2009)

## 7 FINDINGS

The review of previous studies shows some interesting findings about the HH of CSA. It was found that the hydration of CSA increases by increasing the temperature in general. Also, increasing the w/s ratio at temperature ranging between  $25^\circ C$ - $40^\circ C$  will increase the hydration of CSA. However, increasing the w/s ratio at a temperature above this limit will slow the hydration of CSA (Doval et al. 2005).

Also, it was found that CSA made with gypsum behaves differently from the one made with anhydrite. It was found that gypsum accelerates the hydration reaction and shortens the dormant period more than the anhydrite (Winnefeld et al. 2010 a, b). One disadvantage of using excess gypsum in the CSA is that when the gypsum amount increases, the setting time in the cement decreases (Champenois 2013). Also, it is important to notice that the induction period is shorter when adding anhydrite to the CSA solution compared when gypsum is added, and the hydration is faster with gypsum compared with anhydrite (S. Allevi 2016).

In addition, it is found that when gypsum is not added to the CSA in the phase of ye'elimitite, two maximum peaks are found in the heat flow curve. In the other hand, when gypsum is added to the solution of CSA at ratios of 1:1, 1:2, 1:3 and 1:4 the results show that the initial peaks increased. When anhydrite was used in the CSA solution, the results showed that anhydrite has less impact on the very early reactions compared with gypsum and the dormant period is shorter (Winnefeld 2010).

## 8 CONCLUSION

This study presents a summary review of the previous research that has been conducted to assess the HH of CSA and the factors that influence it. The review shows that the HH of CSA varies based on the chemical composition. Factors such as temperature and w/s ratios have different effects on the HH. The utilization of gypsum versus anhydrite in the synthesis of CSA affect the peak of the HH and the dormant period. As such, there is a need for future studies that standardize the different types of CSA based on the chemical composition and properties similar to the four main types of OPC.

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