

# Thermal Stability of Ettringite in Microwave-cured Calcium Sulphoaluminate Cement

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## ABSTRACT

The paper investigates the thermal stability of ettringite in calcium sulphoaluminate cement (CSA) paste cured by microwaving, compared with that under thermal curing. After mixing CSA clinker, gypsum and water, the paste was cast into different moulds for pre-setting 1 hour before being cured at 60 and 70 °C by a tailor-made microwave oven and in an ICC machine (simulating thermal curing). The products obtained were characterized by TG/DTG, XRD and SEM. The DTG results show that the decomposition temperatures of ettringite-formed in the CSA paste are lower than those cured in the ICC machine. The XRD results demonstrate that above 60 °C, ettringite begins to decompose with the ettringite peak intensity under microwaving lower than that cured in the ICC machine at the same curing temperature. The SEM results show that as the temperature is increased from 60 to 70 °C, the degree of damage of the ettringite in CSA paste cured by microwaving increases significantly, while the degree of damage on the ettringite in CSA paste cured in the ICC machine remains the same, which agrees with the results of DTG and XRD.

## 1. INTRODUCTION

In modern construction, precast concrete (PC) has become increasingly popular due to its advantages in terms of shortened construction period, improved quality and reduced cost. Steam curing has been a popular curing method to assure large-scale production of precast concrete products. Although it can enhance the productivity of precast concrete, more than 10 hours at less than 75 °C is required to complete the curing process and therefore a huge amount of energy is consumed. In addition, due to its non-homogenous heating, the long-time strength of the concrete cured by conventional thermal curing is normally lower than that cured at ambient environment [1, 2]. For precast concrete with steam curing, the curing temperature is usually set to be less than 70 °C, which is mainly based on the decomposition temperature of ettringite [3], and to avoid serious durability issues caused by higher temperatures at later stage. Ettringite is an important hydration product of PC, formed from the reaction of C<sub>3</sub>A with gypsum and water. Once the temperature reaches (or even higher than) the decomposition temperature of ettringite, it decomposes to monosulfate. However, this reaction is reversible, i.e. when

exposed to a wet environment during the service period, ettringite can be reformed, causing expansion cracks – so called delayed ettringite formation (DEF) [4].

Compared to steam curing, microwave curing brings a number of benefits, including energy saving by shortening curing period, and hence enhanced productivity. Microwave curing is quite different from conventional thermal curing. In microwave curing, dipolar molecules in dielectric materials vibrate under the alternating electromagnetic field, resulting in the generation of friction between the molecules, converting microwave energy into thermal energy instantly and volumetrically [5].

Up to date, a large number of studies have been reported on the effects of microwave on the properties of cementitious materials, especially early strength [6-8]. However, there is only very limited research available on the thermal stability of ettringite under microwave curing condition. To explore the feasibility of applying microwave curing at industry-scale applications, the thermal stability of ettringite cured by microwave needs to be fully understood in order to optimise microwave curing regime. It is well-established that, in addition to thermal effect, microwave can also

produce non-thermal effect. The non-thermal effect usually refers to the coupling of microwave energy within the molecule or lattice of crystals. Hence, it is anticipated that, due to the non-thermal effect of microwave, the microstructure of ettringite might be affected, resulting, possibly, in a change of its thermal stability.

In this study, the paste formed by a CSA cement was used to study the thermal stability of ettringite, as ettringite is the main hydration product of CSA. It is expected that the finding obtained from this study can be extended to future studies on the thermal stability of ettringite formed in Portland cement (PC) system.

## 2. Experimental

### 2.1 Materials

In this paper, CSA clinker and gypsum are the main raw materials. The CSA used in this investigation is a "Type III" CSA (Hanson,UK), the phase components of which are given in Table 1. Gypsum of industrial grade with a purity of 95% was also supplied by Hanson.

Table 1 Phase components of CSA (wt%)

Ye'elimite $C_4A_3\bar{S}$	Lamite $C_2S$	Perovskite CT	Mayenite $C_{12}A_7$	Others
77.2	14.3	5.7	1.6	1.2

### 2.2 Sample preparation

The mix proportion based on the calculation of hydrated reaction products of each component in CSA clinker is shown in Table 2.

Table 2 Mix proportion

Components	CSA (g)	Gypsum (g)	Water (g)
Weight	1000	435.35	840

Two batches of CSA paste were prepared based on the mix proportion in Table 2; one batch was cast into four 25×25×25 mm<sup>3</sup> three-gang plastic moulds and a second batch was cast into four plastic ICC ampoules. To compare well with the microwave system where both temperature and humidity were controlled, an ICC machine was used to simulate conventional thermal curing as it can keep samples at a constant temperature and humidity. Both batches were pre-set for 1 hour at room temperature before being placed into a tailor-made microwave oven and the ICC machine. The samples were cured at 60 and

70°C for 4 hours; immediately after the hydration was complete, all the samples were dried in vacuum desiccators for 72 hours and stored for further analysis. The samples are detailed in Table 3.

Table 3 CSA paste cured under different conditions

Sample number	Curing condition	Curing Temperature (°C)	Curing Duration (h)
CM6004	Microwave Oven	60	4
CI6004	ICC machine	60	4
CM7004	Microwave Oven	70	4
CI7004	ICC machine	70	4

## 3 Analysis Method

All samples were characterized by thermogravimetric analysis (TG), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The derivative thermogravimetric (DTG) curve was also employed to precisely locate the reaction start temperature, the peak temperature at the maximum reaction rate and the reaction termination temperature [9].

## 3 Results and discussion

### 3.1 Thermogravimetric analysis

The TG and DTG curves of the CSA pastes cured by microwave and ICC machine at 60 and 70 °C for 4 hours are plotted in Figures 1 and 2. The first peak (about from 50 to 105 °C) on the DTG curve was attributed to the dehydration of ettringite into monosulfate and gypsum. In order to calculate the weight loss occurring at the first peak, the start point temperature and end point temperature for ettringite decomposition were then determined by the second derivative to TG [10]. Detailed information related to the first peaks is given in Table 4.

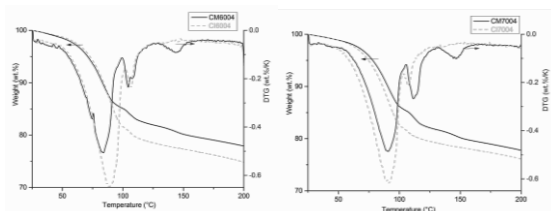


Figure 1: TG and DTG curves of CSA paste cured by microwaving and in the ICC machine at 60 °C for 4 h

Figure 2: TG and DTG curves of CSA paste cured by microwaving and in the ICC machine at 70 °C for 4 h

From Figures 1 and 2, it can be seen that for all the DTG curves of CSA pastes cured by microwave, there are at least three peaks being identified, whilst only two peaks can be recognised in the CSA pastes cured in ICC machine, with the third peak representing further dehydration of monosulfate missing. This phenomenon might be caused by the different quantities of ettringite formed in the hydrated CSA paste, as the percentage of ettringite formed in the microwave cured CSA paste is much lower than that cured in the ICC machine at the same temperature. The results of weight loss of all the samples in Table 4 also confirm this.

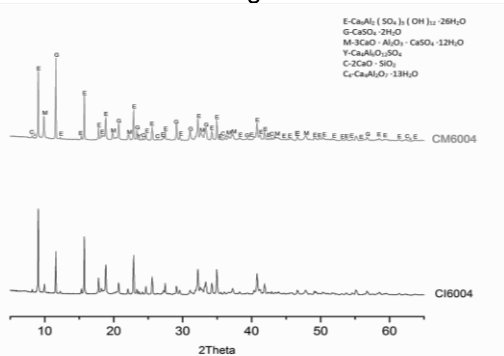
From Table 4, it can also be seen that regardless of the heating temperature, the decomposition temperature of ettringite formed in a microwave cured CSA paste is lower than that cured in the ICC machine, indicating that the ettringite formed in microwave curing is less stable than that cured in the ICC machine.

**Table 4 Detailed information related to the first peaks on DTG curves**

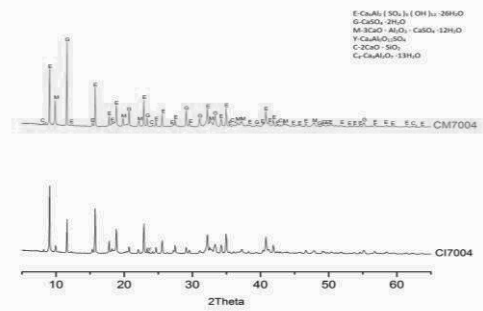
Sample number	The decomposition temperature of ettringite (°C)	Measured weight loss at the first peak (%)
CM6004	83.9	13.6
CI6004	88.8	16.9
CM7004	90.8	13.2
CI7004	91.6	15.7

### 3.2 X-ray diffraction

To demonstrate the effect that the microwave curing may have on the crystallinity of ettringite, the samples of CSA pasted cured by microwaving and in the ICC machine were further examined by XRD diffraction. The XRD patterns are shown in Figures 3 and 4.



**Figure 3 XRD patterns of CSA paste cured by microwaving and in the ICC machine at 60 °C for 4 h**



**Figure 4 XRD patterns of CSA paste cured by microwaving and in the ICC machine at 70 °C for 4 h**

From Figure 3, both types of CSA samples cured at 60°C for 4 hours show the characteristic diffraction peaks of ettringite, gypsum, monosulfate,  $\text{Ca}_4\text{Al}_2\text{O}_7 \cdot 13\text{H}_2\text{O}$ , unhydrated  $\beta\text{-C}_2\text{S}$  and Ye'elimite. The XRD intensity of monosulfate in the CSA paste cured in the ICC machine, is much lower than the intensity of monosulfate in the microwave cured CSA paste. The trend for gypsum intensity is the same as that for the monosulfate phase. These findings indicate that at 60 °C, in both microwave and ICC curing, ettringite must have begun to decompose in the CSA paste, leading to more monosulfate and gypsum being formed. Moreover, the degree of ettringite decomposition under microwave is higher than that in the ICC machine.

From Figure 4, it can be seen that the intensities of the monosulfate and gypsum peaks in the CSA paste cured by microwaving are much higher than that in the CSA paste cured in the ICC machine at 70 °C for 4 hours, suggesting that much more monosulfate and gypsum were produced in the CSA paste cured by microwave than in the ICC machine. This again suggests ettringite formed under microwaving is less stable than that cured in the ICC machine.

Comparing Figures 3 and 4, it can be concluded that with microwave curing, an increase of curing temperature leads to the intensity of both the monosulfate and gypsum peaks increasing significantly, while the intensity of ettringite peaks decreases sharply. For the CSA samples cured in the ICC machine, there is almost no change in the intensity of ettringite, monosulfate and gypsum peaks when the temperature rose from 60 to 70 °C.

### 3.3 Scanning electron microscope

To compare the morphology of ettringite formed in CSA paste under different curing conditions,

all the CSA pastes were examined by SEM and the images are presented in Figures 5 and 6.

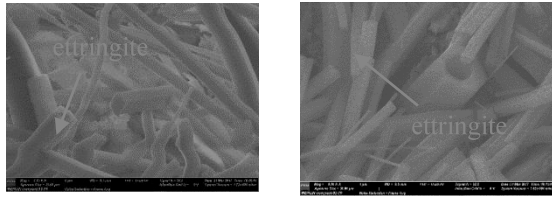


Figure 5: SEM images of CSA paste cured at 60 °C by microwaving (left) and in the ICC machine (right)

From Figure 5, it can be observed that the ettringite forms long hexagonal columns. When cured at 60 °C under microwave, some deformation of the morphology of ettringite was noticed at the end of the columns, while for the ettringite formed in the CSA pastes cured in the ICC machine, the hexagonal columnar morphology remains intact.

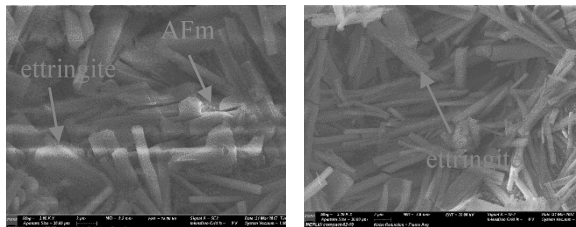


Figure 6: SEM images of CSA paste cured at 70 °C by microwaving (left) and in the ICC machine (right)

As seen in Figure 6, at 70 °C, in the microwave-cured CSA paste, a number of slim hexagonal flat plates of monosulfate appear, and a portion of the ettringite rods are seriously damaged, losing their regular hexagonal column shapes. However, the morphology of ettringite in the samples of CSA paste cured in the ICC machine is almost the same as that cured in the ICC machine at 60 °C. This indicates that as the temperature rises from 60 to 70 °C, the morphology of ettringite cured in the ICC machine does not change while there are some deterioration in the morphology of the microwave cured CSA samples.

#### 4 Conclusion

Based on the results presented in this paper, it can be concluded that under both 60 and 70 °C, the decomposition temperature of ettringite formed in microwave cured CSA pastes is always lower than that cured in the ICC machine. Moreover, the XRD results show that above 60 °C, ettringite begins to decompose. At the same curing temperature, the intensity of ettringite peak in microwave cured samples is always lower than that cured in the ICC machine. The SEM results further

confirm that with an increase in curing temperature from 60 to 70 °C, the degree of damage on the ettringite formed in the CSA pastes cured by microwaving increases significantly. There are almost no damage occurred to the ettringite formed in the CSA pastes cured in the ICC machine. All these results show that in the CSA cement system, ettringite formed under microwaving is thermally less stable than that cured in the ICC machine, implying that when cured by microwaving, in addition to thermal effect, the non-thermal effect also plays an important role in the thermal stability of ettringite formed under microwave irradiation. Further study is still needed to clearly understand how the non-thermal effect can affect the thermal stability of ettringite in the future.

#### References

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