

# A novel evidence for the formation of semi-permeable membrane surrounding the Portland cement particles during the induction period

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Received: 3 September 2012 / Accepted: 15 October 2012  
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**Abstract** This letter presents strong novel evidence for the semi-permeable membrane surrounding Portland cement during the induction period. In the cement hydration, heat curve obtained through high-resolution differential scanning calorimetry under isothermal conditions, one main and some other smaller endothermic peaks were detected. These endothermic peaks are believed to be caused by the osmotic expansion that occurs after the semi-permeable membrane forms, not the precipitation of calcium hydroxide or the imbibition of water during the induction period.

**Keywords** Semi-permeable membrane · Cement hydration · Induction period · Endothermic peak

## Introduction

Cement hydration is a complex physico-chemical process. Many studies have focused on the mechanisms since the 1880s and several detailed reviews have been published [1, 2]. A variety of techniques have been used to investigate the kinetics of cement hydration [3–9]. Among these,

isothermal calorimetry is one of the most often used one to study the overall kinetics of hydrating cement through monitoring the net reaction heat [7–9]. According to the typical heat flow monitored by isothermal calorimetry, the hydration process of alite ( $C_3S$ ) and cement has been divided into several periods. Period I is generally referred to as the initial dissolution period, during which the rate of reaction rapidly slows. This leads to period II which is characterized by a low reaction rate, generally known as the induction period [2].

Many theories have been proposed to explain why the induction period appears, as summarized by Juilland et al. [10]. One of the earliest and most widely accepted theories for the first deceleration period is the formation of a protective layer of hydration products on the surface of the reacting grains, which limits the dissolution of the anhydrous phase [1, 2, 10]. However, the critical question regarding the limited hydration of  $C_3S$  or cement that is sustained during the induction period is whether this layer is impermeable, semi-permeable or porous to water. Stein and Stevels [11] postulated that “a hydrate is formed fitting closely to the  $C_3S$  surface,” and the primary hydrate converts into another one less closely fitting the anhydrous surface and more permeable to water. Some studies on solution concentrations provide strong evidence for the existence of impermeable hydrate [12]. Double et al. [13] proposed that the protective membrane may be semi-permeable. Only calcium ions can pass into the solution once the membrane forms. The high silicate ion concentration inside the membrane sets up an osmotic pump. Water is pumped into the interior gradually, causing osmotic expansion. When the osmotic pressure is high enough, the membrane bursts locally at its weakest points. The silicate-rich content spills into the calcium-rich environment and a reaction takes place, forming the long hollow fibers. This is

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considered to be strong experimental evidence to verify the existence of the semi-permeable membrane [14]. However, little further experimental evidence has been found to support this theory [10].

In this paper, strong novel evidence to support the existence of a semi-permeable membrane around the cement particles during the induction period is reported. In the isothermal calorimetry measurements obtained through DSC with very high resolution, one main and some other small yet distinct endothermic peaks were found in the heat flow curve. These endothermic peaks were likely caused by osmotic expansion.

## Experimental procedure

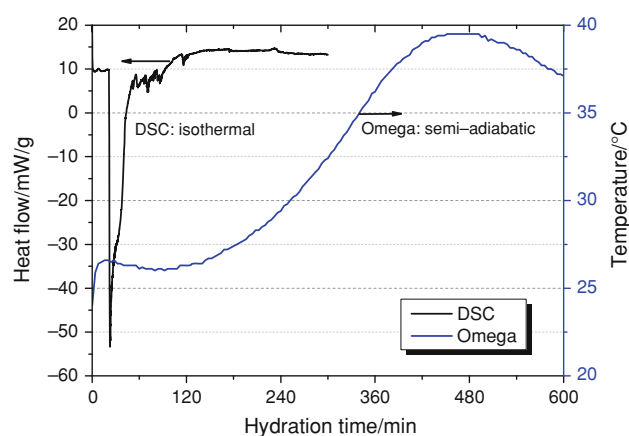
Type I Portland cement conforming to ASTM C 150 was used. The hydration kinetics of the cement was monitored using differential scanning calorimetry (DSC, Mettler-Toledo DSC 822<sup>c</sup>, calibrated with an indium standard) in an isothermal manner. This instrument had a very high resolution of 0.04  $\mu\text{W}$  at room temperature and a high temperature accuracy of  $\pm 0.2$   $^{\circ}\text{C}$ .

Before preparing the pastes, the water and cement were stored at room temperature (about 21.2  $^{\circ}\text{C}$ ) for at least 24 h. The paste with 4 g water and 10 g cement was prepared by hand-mixing for 60 s in a cylindrical plastic mold. About 50–90 mg of paste was weighed in a standard 40  $\mu\text{L}$  aluminum crucible and quickly sealed with an aluminum lid. Then the crucible was placed into the DSC cell automatically. Dry  $\text{N}_2$  was purged (50–55  $\text{ml min}^{-1}$ ) through the cell during measurements. All runs were conducted at a fixed temperature: 21.2 or 25  $^{\circ}\text{C}$ . To avoid a long waiting time for the cell to reach the experimental temperature from the historical temperature after sample loading, a run with a blank crucible was done at the experimental temperature for 60 s before the real measurement. Thus, the formal run can start soon after loading the sample, about 60 s.

The hydration temperature of each paste was also measured using a semi-adiabatic calorimeter. Cement paste with 40 ml water and 100 g cement was prepared by hand-mixing for 60 s in a cylindrical plastic mold with an inner diameter of 47 mm and a height of 97 mm. The mold containing the paste was immediately covered with a plastic lid, placed in the semi-adiabatic holder, and a thermocouple was inserted into the center of the paste. The temperature was then monitored over 20 h using an Omega data-logger.

## Results and discussions

Figure 1 shows the heat curves of cement hydration. According to the curve obtained through semi-adiabatic



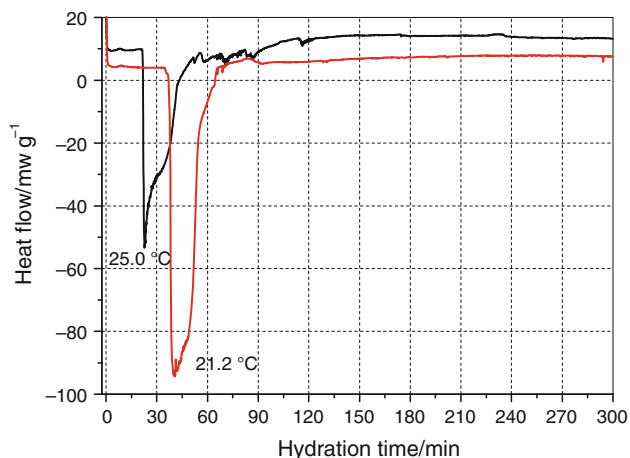
**Fig. 1** Heat curve of the cement hydration by semi-adiabatic (RT = 21.2  $^{\circ}\text{C}$ ) and isothermal calorimetry (25  $^{\circ}\text{C}$ )

calorimetry, the cement hydration process can be divided into four stages. It is generally believed that the heat release rate never reaches zero during the induction period of cement hydration [2].

However, an obvious endothermic peak was found when using DSC with a very high resolution of about 0.04  $\mu\text{W}$ . The minimum heat flow value reached as low as  $-53 \text{ mW g}^{-1}$  and the heat adsorption reached as high as  $36.67 \text{ J g}^{-1}$  paste. Further hydration showed exothermic effects overall, but there were still some small endothermic peaks. This was markedly different from the results obtained using the traditional isothermal calorimeter with relatively lower resolution, such as the TAM Air calorimeter with a resolution in the order of 2.5 mW [15] and the model 4200 isothermal calorimeter with a sensitivity of 0.4  $\mu\text{J}$  [7].

Figure 2 gives the effect of isothermal temperature on hydration heat was monitored through DSC. The curve measured at 21.2  $^{\circ}\text{C}$  also contained one main endothermic peak and other smaller endothermic peaks. This confirms the existence of endothermic effects during the cement hydration process.

Using a Tian–Calvet heat flow calorimeter (sensitivity of 0.3  $\mu\text{W}$ ) to study thermal flow variation released by  $\text{C}_3\text{S}$  suspensions stirred in water, Damidot et al. [16] observed an endothermic peak in the heat curve. However, it was much smaller than the main peak obtained in the present study. They attributed this peak to the precipitation of calcium hydroxide (CH). However, the endothermic peak in the heat curve obtained here did not result from CH precipitation. The heat of solution of CH is about  $11.2 \text{ kJ mol}^{-1}$  at 18  $^{\circ}\text{C}$  [17]. The heat of CH precipitation is accordingly about  $-151.35 \text{ J g}^{-1}$  CH. If the heat adsorption corresponding to the endothermic peak resulted from CH precipitation, the CH precipitated would be as high as 24.2 % of the paste, which is impossible during this



**Fig. 2** Effect of isothermal temperature on cement hydration heat

period. Indeed, many studies have revealed that few CH precipitate before the acceleration period [1, 2].

Dent Glasser [18] argued that the pressure that causes the swelling of gel during cement hydration may be generated by the imbibition of water rather than by osmosis. However, it has been revealed that the process of imbibition shows an exothermic effect [19]. We proposed that the endothermic peaks were likely related to the formation of a semi-permeable membrane around the cement particles to cause osmotic expansion inside the membrane, which shows an endothermic effect.

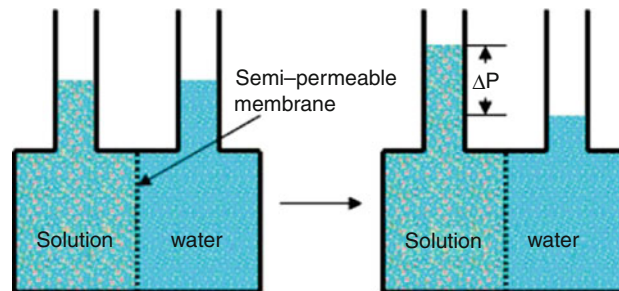
According to the first law of thermodynamics, in any incremental process, the change in the internal energy is considered to be due to a combination of heat added to the system ( $\delta Q$ ) and work done by the system ( $\delta W$ ). Taking  $dU$  as an infinitesimal (differential) change in internal energy, one writes,

$$dU = \delta Q - \delta W$$

Note that the minus sign in front of  $\delta W$  indicates that a positive amount of work done by the system leads to energy being lost by the system.

For a simple isothermal process, as seen in Fig. 3,  $dU = \delta Q - \delta W = 0$ . Thus,  $\delta Q = \delta W > 0$ . This indicates that the isothermal osmotic expansion is endothermic. While using a titration microcalorimeter to measure heat change in lipid membranes under sudden osmotic stress, Nebel et al. [20] also revealed that the osmotic expansion produced an endothermic heat change.

From Fig. 1, it can be found that the time when the main endothermic peak appeared was consistent with the time when cement hydration went into the induction period. Nevertheless, when the main peak ended hydration was still in the induction period according to the semi-adiabatic calorimetry result. Furthermore, some small endothermic peaks appeared with further hydration until the end of the



**Fig. 3** A simple osmosis process

induction period. These results implied that the hydration processes of the cement are as follows: once the cement contacts with water, the calcium ions dissolve and release heat very quickly. With further dissolution, the silicate grains begin to form a semi-permeable membrane. The difference in concentration of the ions inside and outside the membrane produces osmotic pressure and the water molecules are drawn into the membrane, leading to osmotic expansion. The system begins to absorb heat from the environment to make osmotic expansion occur once the semi-permeable membrane forms, and continues until the membrane bursts locally at its weakest points, either because of internal pressure or through mechanical weakness caused by the precipitation of  $\text{Ca}(\text{OH})_2$  at the membrane surface [18]. According to osmotic theory, this should be the end of the dormant period. However, new semi-permeable membrane may form again after the membrane bursts, which may contribute to the small endothermic peaks with further hydration.

What should be noted is that the membranes around grains with different size and activity do not necessarily have to form at the same time in the case of large sample content. They may form and rupture at different times. While new membranes form and begin to show the endothermic effect in some areas, membranes elsewhere rupture and show the exothermic effect. Statistically, the overall thermal effect is exothermic when the sample content is large enough, for example, 1 g paste or more. That may be one of the main reasons why the heat flow monitored by isothermal calorimetry never decreased to zero during the period of slow reaction. Another reason may be that the resolution of the traditional isothermal calorimeter is not high enough to detect the endothermic effect resulting from osmosis for such a large sample volume.

The curing temperature has a great influence on cement hydration. Using traditional isothermal calorimetry, it has been found that the time that the induction period starts is rarely affected but the period is prolonged when the curing temperature is lower [21]. As seen in Fig. 2, the heat release was obviously lower at 21.2 °C than at 25 °C. Although a more significant endothermic peak, which

appeared later, was found in the sample measured at 21.2 °C, the duration was nearly the same as that measured at 25 °C. The minimum heat flow value was as low as  $-94.3 \text{ mW g}^{-1}$  and the heat adsorption was as high as  $89.40 \text{ J g}^{-1}$  paste. A second main endothermic peak and some very small peaks were also found with further hydration. It reveals that the formation of the semi-permeable membrane was delayed at the lower temperature, likely due to the slower release rate of the calcium ions. However, it is difficult to explain why the endothermic peak is higher and the duration is nearly the same, which needs further research.

## Conclusions

From the previous results we can conclude that:

1. A novel evidence to support the existence of semi-permeable membrane surrounding Portland cement particles during the induction period was observed.
2. Using the DSC to monitor the net heat of hydration associated with the hydration process of Portland cement pastes under isothermal conditions indicates one obvious and some other smaller endothermic peaks in the heat curve.
3. The endothermic peaks obtained in the heat curves were caused by osmotic expansion after the formation of semi-permeable membrane, not due to the precipitation of CH.

**Acknowledgements** The authors gratefully acknowledge the financial support from Scientific Bureau of Zhejiang Province, China under Grant 2009R50022 and Infrastructure Technology Institute at Northwestern University under Grant DTRT06-G-0015. The first and the corresponding author would also like to thank China Scholarship Council (CSC) for its financial support during their stay as visiting scholars at Northwestern University.

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