Proceedings of the 3rd International Conference on Civil Engineering Fundamentals and Applications (ICCEFA'22)
~~Seoul, South Korea~~ Virtual Conference - October 24 - 26, 2022
Paper No. 139
DOI: 10.11159/iccefa22.139

Analysis of Hydration Heat in Cement Pastes with Addition of Sodium Silicate Microcapsules by Isothermal Calorimetry

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Abstract - The storage of healing agents in capsules is one of the most promising self-healing methods in cementitious materials. Incorporating microcapsules containing sodium silicate in the cement matrix aims to improve its self-healing capacity, promoting not only the sealing of cracks but also the maintenance of its physicochemical characteristics. Understanding the microstructure of a material is critical to comprehension regarding properties and performance and how they are related to the process parameters of material preparation. In this work, the Isothermal Calorimetry technique is used to analyze the heat flux that occurred during the hydration of the cement paste and the influence of the addition of sodium silicate microcapsules in the matrix. It was possible to identify that the microcapsules caused a significant decrease in heat flow, making the material excellent for applications in mass concrete structures.

***Keywords*: ** Microcapsules; Sodium silicate; Smart Material; Cement; Heat of hydration; Isothermal calorimetry; Mass concrete.

1. Introduction

Incorporating microcapsules containing sodium silicate in the cementitious matrix aims to improve its self-healing capacity by promoting not only the sealing of cracks but also the maintenance of their physique/chemical characteristics. This material is among the most promising, like smart cement-based materials. However, understanding the chemical behaviour is as important as the physical one because the improvement of a character cannot be used if the new composition brings consequences that make the use of the new material impracticable. Understanding the microstructure of a material is the key to understanding its properties and performance and how they are related to the process parameters that form the material [1]. This work will focus on analyzing the heat flow that occurred during the hydration of the cement paste and the influence of the addition of sodium silicate microcapsules in the mass in this process. The study was done in the paste (cement and water without aggregate) to avoid dilution of the signal and improve the method's accuracy. The Isothermal Calorimetry technique was applied to identify at which moments the microstructure should be evaluated in more depth during hydration in the first days.

The heat per gram of cement produced after 1, 3, or 7 days of hydration is a standardized measure of the reactivity of the cement according to ASTM C1702 (2014) [1]. Still, this experiment measured the tested samples' first 85 hours of hydration.

2. Materials

The cement used was type CP III-40 RS. Five types of samples were prepared to compare the effect of microcapsules on the cementitious matrix. The first, called group reference (G-R), was the reference sample containing only cement and water in a ratio of 1:0.48 (w/w) concerning the weight of the cement. Group 2 (G-RSS) received a solution of sodium silicate (SSS) at 1% (w/v) in place of water, maintaining the 1:0.48 ratio between water and cement. The group G-MCSS-4 and G-MCSS-16-CL received the addition of microcapsules containing sodium silicate (MC-SS) in a ratio of 4% and 16% (v/v), respectively, about the volume of cement. To G-MCA-16, microcapsules containing only water (MC-A) were added in the proportion of 16% (v/v) of cement. Water in groups G-MCSS-4, G-MCSS-16-CL, and G-MCA-16 was decreased in the amount of 70% of the volume of the microcapsules. Group G-MCSS-16-SL was not the target of this paper.

A mass with approximately 400g of cement was prepared for each sample group, and Table 1 describes the exact composition of each one. Fig.1 shows the preparation of the samples in the workbench.

Table 1: Sample compositions.

Sample Group	Cement (g)	Water (g)	SSS 1% (g)	MC-SS (g)	MC-A (g)
G-R	400,01	192,10	-	-	-
G-RSS	400,00	-	193,95		-
G-MCSS-4	400,01	176,02	-	16,02	-
G-MCSS-16-CL	400,00	128,04	-	64,09	-
G-MCA-16	400,01	128,03	-	-	64,00

Fig. 1: Separation of raw materials for sample preparation.

3. Methodology

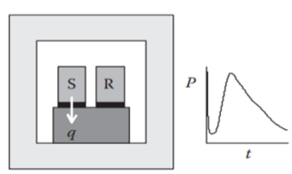
Usually, the processes, whether chemical or physical, cause a change of enthalpy. The hydration process of cement does not escape the rule, and Calorimetry is applied in studying this phenomenon. Among the possible Calorimetry techniques, isothermal (also called heat conduction Calorimetry) is the most versatile in the cementitious materials field because it can be used to analyze pastes, mortars, or even small aggregates of concrete [1]. Exploring small samples up to 100g ends up being the most used technique in the research and development of cementitious materials.

The analytical method of isothermal Calorimetry is also more advantageous than others because its energy signal provides directly, in addition to the hydration heat produced, the rate of heat production (thermal power) without the need for derivative or integral calculations [1].

The experiment here in focus used the technique of Isothermal conduction Calorimetry, where small samples of paste were hydrated and measured the heat production rate of each of them directly. The equipment used was an eight-channel TAM Air isothermal calorimeter (TA Instruments, USA) seen in Fig. 2.

In this equipment, a heat flow sensor measures the heat production (P) rate in the sample (S) while the heat is dissipated in a thermostat environment. The scheme in Fig. 3 best explains how it works.

Fig. 2: TAM Air Thermostat with 8-Channel Calorimeter.



P: potência térmica;
R: referência;
S: amostra;
q: dissipador
t: tempo

Each sample tested was inserted in a chamber (type A chamber). In contrast, a sample of another material of the same thermal properties, but without heat production, was positioned in an adjacent chamber (type B chamber) to serve as a reference in the experiment. Two pairs of chambers were not used.

To find the accumulated and differential heat produced (thermal power) by the cement pastes, the procedure followed the standards ASTM C 1679 [2] and ASTM C 1702 [3]. Was maintained the temperature at 21 °C for 85 h. The calorimeter has dual chamber test channels (sample and reference) for each one of the 8 samples. The reference sample used was an inert quartz powder. The difference between the signals emitted by the sensors generated a spreadsheet with results of heat produced and heat flow as a function of time [4]. The laboratory environment was prepared in advance for a week at a constant temperature of 21ºC, uniform, and controlled from the beginning of the experiment, minimizing its influence on heat measurements within the channels. In addition, external temperature effects are, in fact, minimized by the equipment itself which has a circulating air-based thermostat and an advanced regulation system to keep the temperature stable. TAM Air maintains Temperature accuracy of $\pm$0.15ºC, Thermostat Stability of $\pm$0,001ºC, and detection up to 2 µW [5].

4. Results

The samples were under measurement for approximately 85 hours within the calorimeter, generating an output of results containing the heat flow and the accumulated heat produced, in addition to the temperatures. The measurements were normalized, that is, to relate it to the actual mass of the cement used in each blend. This way, it is possible to compare the results between the different folders evaluated correctly. The results obtained can be seen in Fig. 4 and Fig. 5.

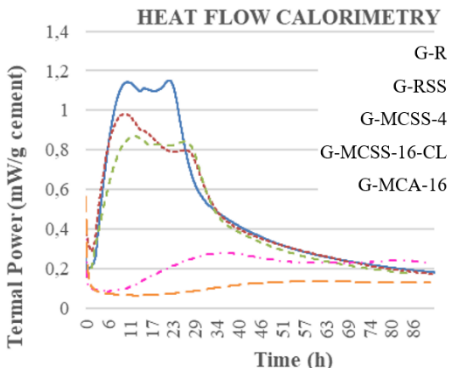


Fig. 4: Thermal power as a function of time. Overlapping sample curves.

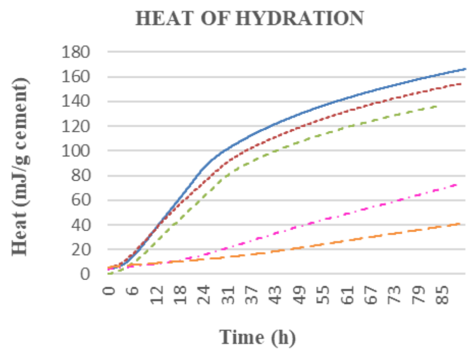


Fig. 5: Heat of Hydration as a function of time. Overlapping sample curves.

The overlap of the traces shows the significant variation of the thermal power depending on the sample's composition. It is noticed that the increase in the concentration of microcapsules causes a reduction in the curve. The reference sample presented a higher maximum rate compared to all samples tested. The incorporation of 16% (v/v) of microcapsules caused a significant decrease in the rate of heat flow of hydration on the first day compared to other samples, even when its active core contained only water.

The reference sample already produces a lower heat rate than other Portland cement pastes since blast furnace slag leads to a slower and longer-lasting reaction [6]. The addition of microcapsules further decreased this factor.

In Fig. 5, it is seen that the heat produced in all samples started at zero. While samples G-R, G-RSS, and G-MCSS-4 showed a faster initial increase (up to 2 hours), samples G-MCSS-16-CL and G-MCA-16 took longer to begun raise the temperature (between 16 and 18 hours). These last samples do not reach the temperatures reached by the first three during the analyzed hours. After 85 hours of testing, the heat produced by the weight of cement was 161.86J/g in sample G-R, 150.86J/g in G-RSS, 136.51 in G-MCSS-4, 68.88J/g in G-MCSS-16-CL, and 38.4 in G-MCA-16.

The thermal power curve during hydration of a cementitious mass manufactured with Common Portland Cement (CPC) can usually be divided into phases: 1) early reactions (or initial period); 2) induction or dormant period; 3) accelerating period; 4) decelerating period, and 5) slow hydration [1].

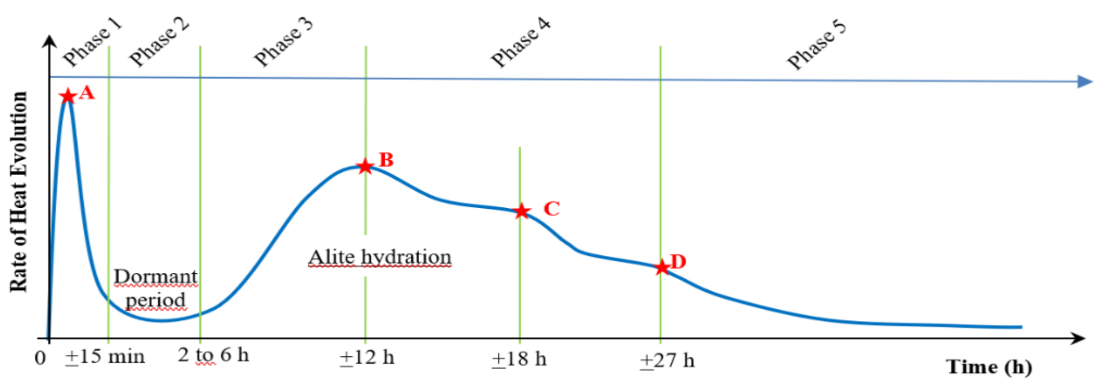


Fig. 6: Heat Release during hydration of a CPC. (A) early stage reaction, C_3A initial dissolution; (B) middle-stage reaction, C_3S hydration, CSH and CH formation; (C) C_3A hydration, Ettringite formation; (D) Ettringite-monosulfate conversion [6]–[8].

Analyzing individually the thermal power curves obtained from this experiment (Fig. 4) compared to a standard for CPC (Fig. 6), we perceive a decrease in all angles concerning the graph of an ordinary Portland cement being more remarkable in the G-MCSS-16-CL and G-MCA-16 samples. The peak formation of secondary ettringite is accompanied by an increase in heat flow in sample G-R (reference sample), compared to tracing the curve in a CPC. The first peak, which points to the formation of CHS (Hydrated Calcium Silicate) and CH (portlandite), reaches lower heat flow in all studied pastes about CPC, but this was already expected to come from a CP-III since the insertion of blast furnace slag in the composition of the cement leads to a lower heat flow. In addition to the high decrease in the curves of the groups of samples G-MCSS-16-CL and G-MCA-16, it is also noticed that the peaks are almost not detected, having been "moved" for many hours after usual. During the 85 hours of the experiment, the following mountains of heat flux were observed: in the sample G-R, 1.15 mW/g.cement at 22 h; in the G-RSS, 0.98 mW/g.cement at ten h; in the G-MCSS-4, 0.87 mW/g.cement at 12 h; in the G-MCSS-16-CL, 0,28 mW/g.cement at 36h and in the G-MCA-16, 0,14mW/g.cement at 60h.

4. Conclusion

This preliminary study identifies the advantages of using microcapsules as an additive in cementitious matrices. In addition to the self-healing properties, the significant decrease in heat flow makes this material excellent for application in structures of large volumes of concrete, such as dams and large foundations, as this releases much heat from hydration and may cause retraction cracks. It is recommended to repeat the experiment by changing the concentration of microcapsules and lengthening the time in the calorimeter to evaluate a minimum of seven days. It would also add much knowledge to comparing the results by replacing the cement for other kinds, mentioned t in the norm, with or without additions.

Acknowledgements

This study is a part of a research project funded by Coordination of Improvement of Higher Education Personnel-Brazil (CAPES)-Funding Code 001. The authors acknowledge CAPES for their support and financial aid. Gratitude to Graduate Program in Industrial Engineering (PEI), Laboratory of Polymers and Bioprocesses, Mortar Technology Center (CETA), and Interdisciplinary Center for Energy and Environment (CIEnAm) for their support during her master's research. I also thank Acriplanos and ETEP Indústria Metalúrgica, who collaborated in the production of parts for equipment designed especially for this research.

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