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A study of early-age Ordinary Portland Cement Hydration according to Autocatalytic Reaction Model



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ABSTRACT

Early-age hydration of Ordinary Portland Cement was studied with semi-adiabatic calorimeter in the presence of limestone and calcium-silicate-hydrate (C-S-H) coated limestone. The calorimetric data was analyzed as an autocatalytic reaction. Early age hydration followed the principles of autocatalytic reaction and the rate controlling phase was the initially nucleated C-S-H. Addition of limestone did not increase it, whereas C-S-H coated limestone had a massive impact to the hydration reaction.

Key words: Early-age hydration, seeding, autocatalytic reaction, calorimeter.

1. INTRODUCTION

Attempts to reduce the CO₂ emissions of cement have increased the use of supplementary materials in blended cements. Their draw back is slow early age strength development. In order to enhance it, the rate controlling mechanisms need to be recognised. According to present understanding [1] the old concept of cement hydration's autocatalytic nature has reemerged [2]. In the present study the early age hydration Ordinary Portland Cement (OPC) was studied in paste with semi-adiabatic calorimeter and scanning electron microscope in the presence of various finely ground limestone fillers as well as fillers coated with calcium-silicate-hydrate (C-S-H). The calorimetric data was analyzed as an autocatalytic reaction (*Equations 1 and 2*) to distinguish reaction rate (k) and number of initially formed hydration nuclei ($[B_0]$). The latter are nuclei formed in supersaturated solution and precipitated through heterogeneous nucleation on surfaces [5]. The hydration heat was evaluated also to estimate the early-age and overall cement hydration degree.

2. MATERIALS AND METHODS

The cement used was CEM I 52,5 R, white cement from Aalborg. The limestone was jet-mill grounded to different finesses from Nordkalk's SB63 -calcite filler a commonly used limestone filler in Finland. Particle distributions were measured with a Beckman Coulter LS particle size analyzer (Figure 2). Calcium-silicate-hydrate (C-S-H) coated limestone was produced by vigorously mixing Na₂(SiO₂)_{3,3} and Ca(OH)₂ respectively to water in the presence of limestone. The amount of C-S-H was defined to produce a uniform layer with respect to the surface area of limestone. Extra water was evaporated from C-S-H coated limestone slurry by drying in 40°C. The uniform coverage of limestone with CSH was verified by JEOL Scanning Electron Microscope (Figure 2). Cement pastes were mixed with a Hobart mixer. The dry materials were first mixed for 1 min, tempered

water was added to during 30s period and the total mixing time was 5 minutes. Samples were placed into the calorimeter approximately 15 min after mixing. It was assumed that initial heat of dissolution was lost and heat observed originated from silicate reactions [3]. Heat capacities were calculated and the experiments conducted according to [4] with two parallel samples. Increased temperatures during semi-adiabatic calorimeter experiments were normalized to constant temperature with Arrhenius equation using the value of 33 kJ/mol for activation energy. The autocatalytic reaction model (Equation 2) was fitted to the normalized calorimeter curves using the Excel solver function. Assuming that observed hydration heat was proportional to the formation of C-S-H, $[B]$ represented the formed calcium-silicate-hydrate and $[B_0]$ the quantity of the initially formed C-S-H. $[A_0]$ was chosen arbitrarily as a value of 400 kJ. Fitting was done by letting both constants (number of initial C-S-H nuclei $[B_0]$ and reaction rate constant k) change freely until the point where the calorimeter curve and the autocatalytic model significantly deviated.

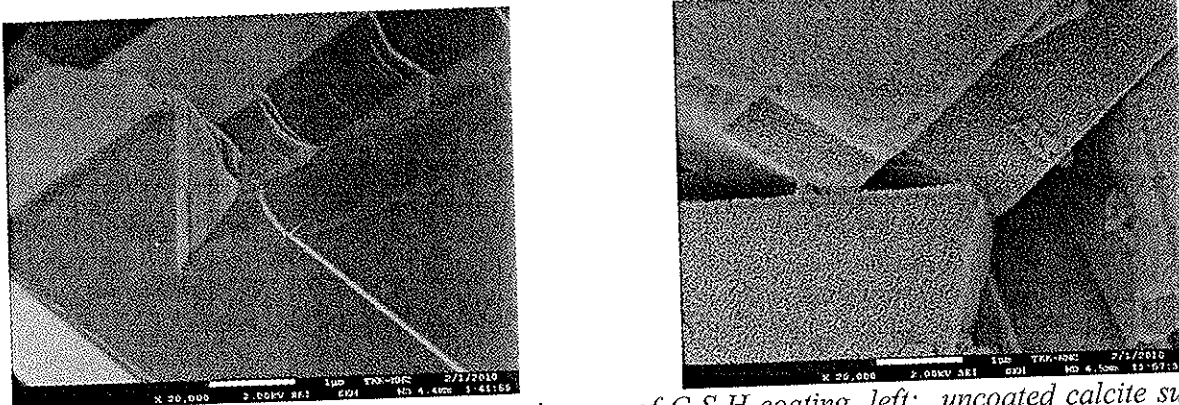


Figure 1. Scanning electron microscope images of C-S-H coating. left: uncoated calcite surface right: C-S-H coated calcite surface. (Vehmas, Kronl6f, Anoshkin).

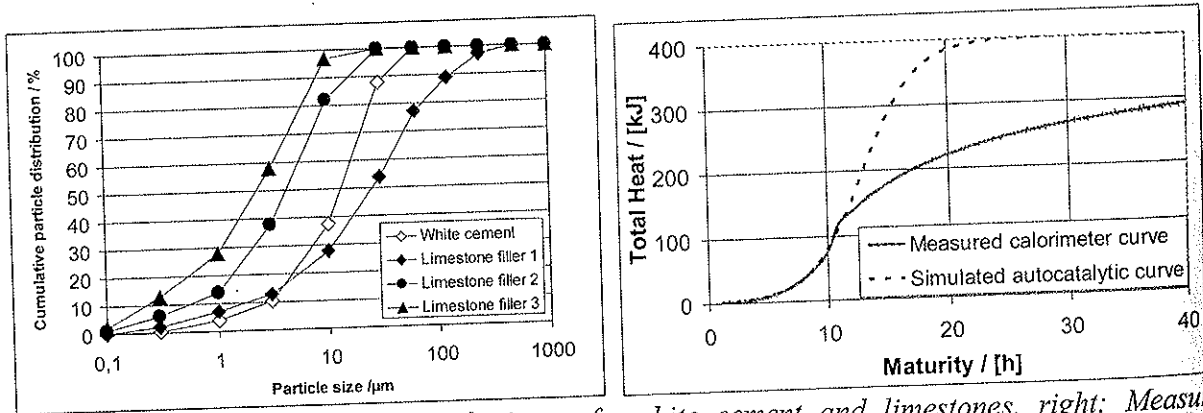
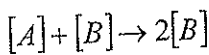


Figure 2. left: Particle size distributions of white cement and limestones. right: Measured calorimeter curve (grey, solid line) and simulated autocatalytic curve (black dashed).



$$[B] = \frac{[B_0] + [A_0]}{1 + \frac{[A_0]}{[B_0]} e^{-([A_0] - [B_0])kt}} - [B_0] \tag{2}$$

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3. RESULTS

The fitting revealed that number of initial C-S-H nuclei was clearly increased as water/cement - ratio (w/c) increased. The observed limestone filler's ability to enhance hydration did not significantly increase number of initial C-S-H nuclei for its effect was not dominating until a few hours after the time span discussed here. The effect of C-S-H coated limestone was remarkable. The number of initial C-S-H nuclei up to 4.5 fold compared to the effect of increased w/c.

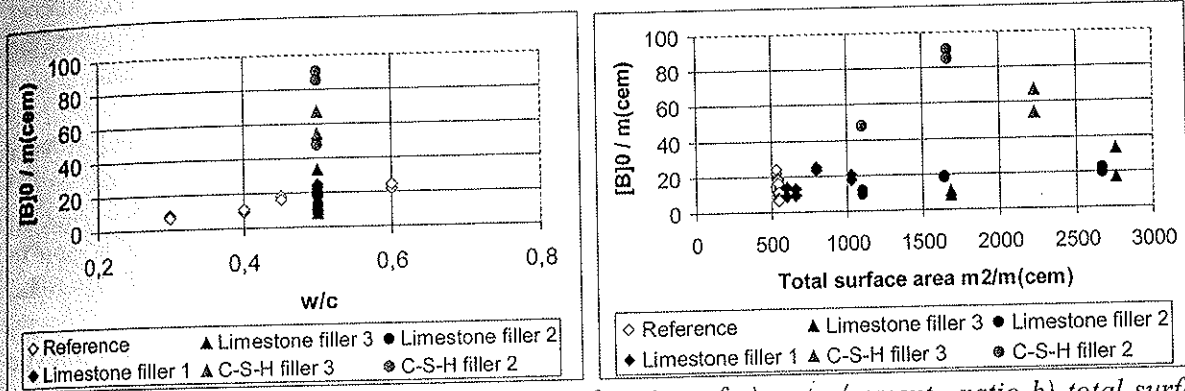


Figure 3. Modelled number of initial nuclei in function of a) water/cement -ratio b) total surface area of cement+ limestone filler divided by cement weight.

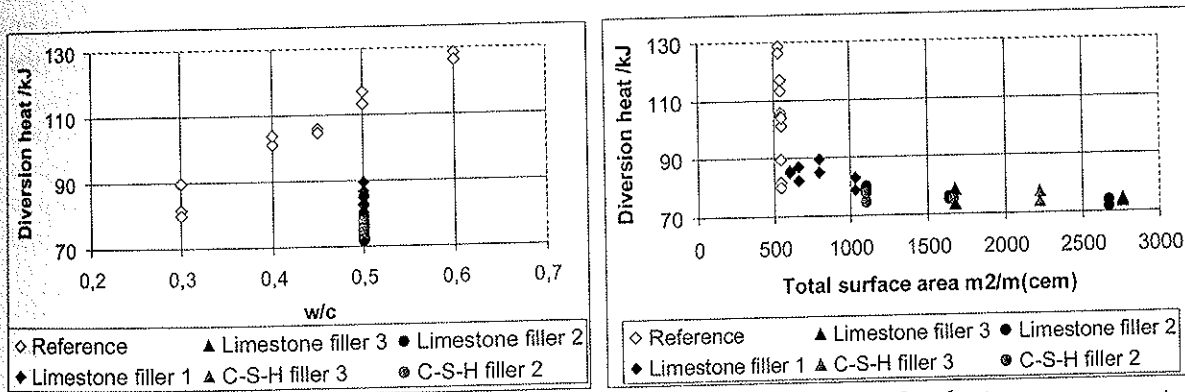


Figure 4. The point where modelled autocatalytic reaction and observed calorimeter curve started to differ in function of a) water/cement -ratio b) total surface area divided by cement weight.

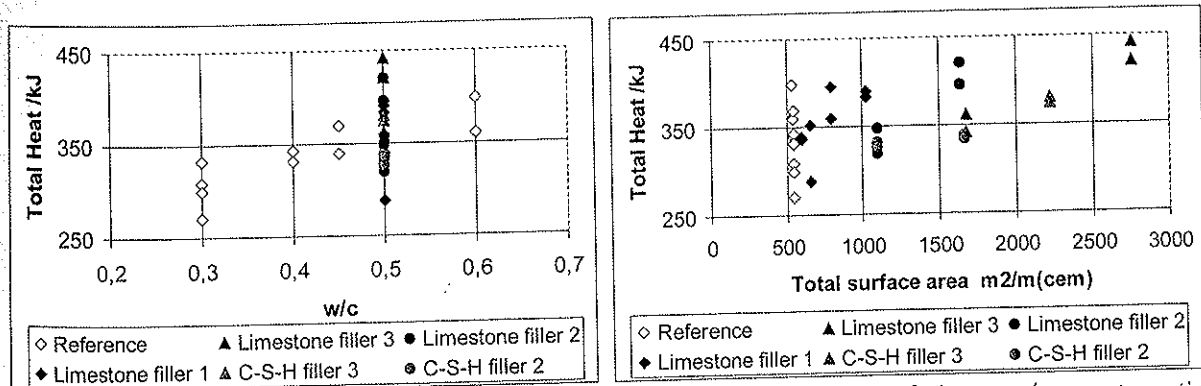


Figure 5. Total heat evolved during 100h observation time in function of a) water/cement -ratio b) total surface area divided by cement weight.

The point where the heat release rate begins to decrease equals to the point where autocatalytic model diverges from calorimeter data. The heat evolved at this point (diversion heat) increased as

w/c ratio increased. As limestone or C-S-H coated limestone was added, the diversion heat decreased nearly to a constant level. No difference between limestone and C-S-H coated limestone was detected. Total heat evolved in 100h observation time increased as the w/c ratio increased. Addition of limestone or C-S-H coated limestone increased total heat at higher dosages.

4. CONCLUSIONS AND DISCUSSION

Cement hydration followed the autocatalytic reaction principles within the first hours. The number of the initial nuclei increased as the w/c -ratio increased. This is in line with [5] stating that the number of initial C-S-H depends on amount of supersaturated silicon present in the solution.

Addition of limestone surface did not change the dominant mechanism. The shape of calorimeter curves indicated that the addition of limestone surface did not increase the number of the initial nuclei. The length of dormant period was still depended of number of initial C-S-H nuclei. However, the fact that the addition accelerated the reaction after the first hours give reason to postulate that limestone may enhance C-S-H nuclei production later during hydration process.

C-S-H coated limestone significantly accelerated the reaction and according to the autocatalytic reaction, increased the number of the initial C-S-H nuclei. It was concluded that the C-S-H coating served as initial C-S-H nuclei for the reaction. Regardless of the surface area of the C-S-H coated limestone introduced to the paste, the heat evolved at the point where calorimetric curve diverged from the model (diversion point) was observed to be relatively constant. This point has been anticipated to be the transition point of the reaction mode from the dissolution controlled into the diffusion controlled stage. The value rather decreased than increased as the total surface area increased (Figure 4) indicating that the amount of produced C-S-H needed to change the reaction mode was smaller the larger the surface area introduced to the paste. This observation contradicts with the basic concept of "diffusion barrier". The concept indicates that larger area would lead to thinner product layer per CSH produced and therefore to higher amount of C-S-H at the point of the mode change.

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REFERENCES

1. Jeffrey W. Bullard, Hamlin M. Jennings, Richard A. Livingston, Andre Nonat, George W. Scherer, Jeffrey S. Schweitzer, Karen L. Scrivener, Jeffrey J. Thomas, "Mechanism of Cement Hydration". *Cement and Concrete Research* In Press. Available online 29 October 2010.
2. Thomas J., Jennings H., Chen J., "Influence of Nucleation Seeding on the Hydration Mechanism of Tricalcium Silicate and Cement" *Journal of Physical Chemistry C*. Vol 113 2009 pp.4327-4334
3. Hesse C. Goetz-Neunhoeffler, Neubauer J., "A new approach in quantitative in-situ XRD of Cement pastes: Correlation of heat flow curves with early hydration reactions" *Cement and Concrete Research* Vol 41 2011 pp.123-128
4. RILEM TC 119-TCE: "Avoidance of thermal cracking in concrete at early-ages" *Materials and Structures* Vol. 300 1997 pp451-464
5. Garrault S., Nonat A., "Hydrated layer formation on Tricalcium and Dicalcium Silicate Surfaces: Experimental Study and numerical simulations" *Langmuir* vol 17 2001 pp. 8131-8138.