

## Synthesis and Hydration of Tricalcium Silicate

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### Abstract

During the last few years several computer models has been developed to simulate the evolution of cement microstructure during hydration. In the model,  *$\mu ic$* , that is been developed in our laboratory the evolution of the microstructure of cement and its main component, alite, is calculated based on the hydration of individual particles rather than the entire system. The study of the hydration kinetics plays a major role in the development of this modelling work. This paper reports the synthesis protocol and the characterization of pure tricalcium silicate and alite and their separation into discrete fractions of particle size distribution. The hydration of these fractions was studied by isothermal calorimetry and chemical shrinkage. Individual kinetic coefficients for incorporation into the model have been derived. It was shown that the hydration of any particle is not affected by psd of the hydrating powder and is independent from the hydration of its neighbours.

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## 1. Introduction

Over the past few decades several computer models have been developed to simulate the evolution of hydrating cement microstructure using various approaches [1,2,3,4,5]. The continuum approach, using discrete particles, rather than pixels, has been used in the model called **μic** (pronounced as Mike), developed in our laboratory. As opposed to calculating the hydration of the entire system, in this model the evolution of the microstructure is calculated based on the hydration of individual particles.

The Avrami equation [6], which relates to the reaction kinetics of processes involving nucleation and growth, has been shown to effectively emulate the early behaviour of cement [7,8,9,10]. The S-shape of the equation and the fact that the initial process of cement hydration can also be viewed as nucleation and growth have generally justified the use of this equation in modelling of early-age cement kinetics.

A modified form of the Avrami equation for the rate of reaction applicable to initial C<sub>3</sub>S reaction kinetics can be written as:

$$\alpha = 1 - e^{-kt^n} \quad \text{Eq. (1)}$$

Where  $\alpha$  is the degree of hydration,  $t$  the time and  $k$  and  $n$  are constants that depend on the material and the reaction mechanism.

A preliminary analysis of data from Scrivener [11] shows the rates of heat evolution of cement samples produced by fractionating the same cement to different particle sizes (Figure 1-a). The same curves normalised by the total surface area of the specimens, calculated by assuming mono-sized particles of radius equal to the geometric mean of the range, are shown in Figure 1-b. These graphs show that the heat flow and thus the rate of reaction are directly proportional to the total surface area of the particles. It is noticeable that the downturn in the curves occur earlier for the smaller particles, which can be attributed to the particles getting used up in the reaction. The fact that the reaction rate is proportional to the surface area is also supported by the fact that since the initial reaction is governed by the dissolution of material from the surface, higher surface areas would lead to a faster reaction. This same relationship between the rate of hydration and the specific surface area was also observed for the case of tricalcium silicate [12,13,14].

However, for the application of Avrami equation in the model, it is necessary that the reaction rates of individual particles, and not just that of the whole system, be known. To check and calibrate this equation, experiments were carried out on specimens with different particle size distributions. This involved measure of reaction rates of  $C_3S$  powders of different particle size distributions produced in our laboratory using different procedures such as Calorimetry, XRD and chemical shrinkage.

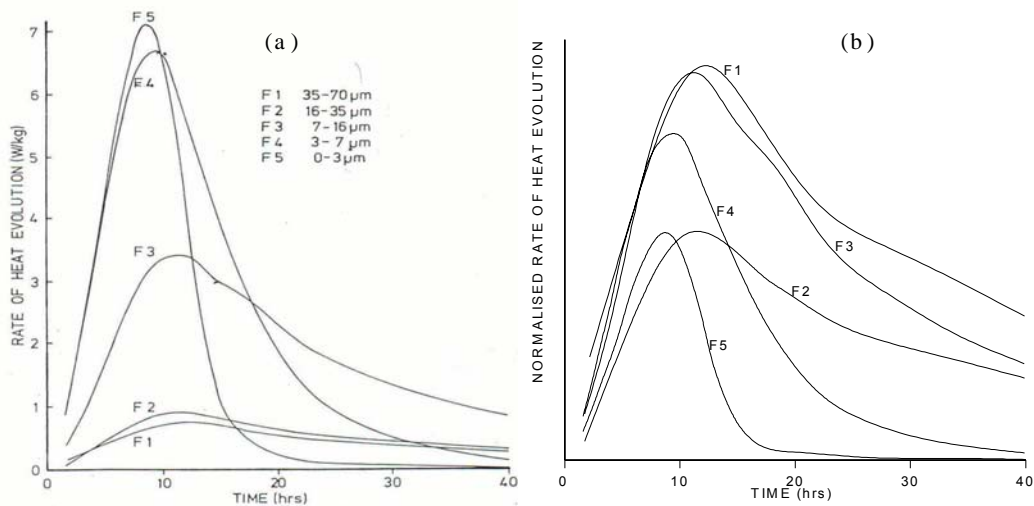


Figure 1: a) Rate of heat evolution and b) normalised relative to surface area for different particle sizes [11]

This paper reports the progresses made on the synthesis of alite and its separation in different particle size distributions. Hydration kinetic measurements by isothermal calorimetry and chemical shrinkage are presented. Finally, the first results obtained from the fit of the calorimetric curves of non-overlapping gradations against Avrami equation are discussed.

## **2. Synthesis and characterization of Tricalcium Silicate.**

Pure triclinic silicate (pure  $C_3S$ ), was prepared from a 1:3 stoichiometric mixture of high purity quartz powder and  $CaCO_3$  (both Merck). After homogenisation in water, the blends were dried at  $100^\circ C$  and then pressed into pellets with diameter of 3.5 cm. The pellets were burnt at  $1650^\circ C$  for 5 h and then cooled rapidly. This procedure was repeated until no free lime was detected by X-Ray diffraction (Panalytical). The  $C_3S$  crystals were broken down by 45 min mechanically grinding and 12 hours of ball milling.

Pure  $C_3S$  was identified by XRD as the polymorph Triclinic (TI) [14]. The particle size of this powder was investigated by a granulometry analysis technique (Mastersizer 2000, Malvern Instruments Inc.) and SEM on polished sections. It was evident the crystal size of the  $C_3S$  has a very narrow dispersion around 6  $\mu m$ , which is totally dissimilar to that of OPC. Another important fact to be noticed is that the crystals of  $C_3S$  grains fuse into agglomerates making it very difficult to grind. To break down these agglomerates 45 min of mechanical grinding followed by 12 hours of ball milling was needed.

A new synthesis protocol to get a bigger particle size was developed by adding Al and Mg ions. Alite was prepared by mixing calcium carbonate, high grade quartz, aluminum oxide and magnesium oxide. Several combinations have been tested (Table 1) to assess the influence of Al and Mg ions on particle growth, size and composition. The reason for adding Al and Mg to the blends lies in the nucleation and grain growth processes: small amounts aluminium ions increase the quantity of liquid phase, decrease the viscosity of the mix, allowing a better diffusion of chemical species and favoring the growth of larger grains as compared to pure  $C_3S$ . Mg ions improve the burnability of blend and favour the reduction of free lime [15,16,17]. The synthesis protocol is the same as for pure  $C_3S$  but at temperature of 1500°C.

Composition wt%	C1	C2	C3
$SiO_2$	23	25	25
$CaO$	74	72	73
$Al_2O_3$	2	1	0
$MgO$	1	2	2

Table 1: Components weigh % for alite synthesis

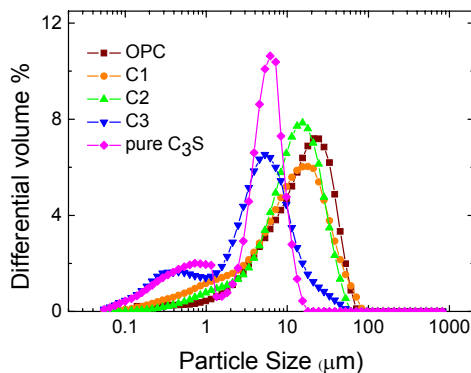


Figure 2: Psds of different wt % compositions of Mg and Al ions.

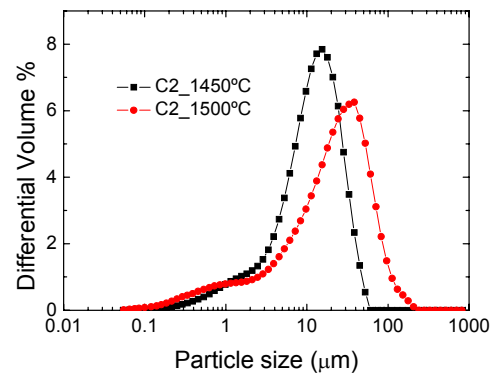


Figure 3: Effect of the burning temperature on the grain growth

Figure 2 shows the effect of the Al and Mg ions % on the grain growth. C1 and C2 compositions which contain Al ions present bigger particle size compared with C3. From these results is concluded that the Al ions plays the major role on the grain growth. Al ions coordinate themselves in the lattice and increase the quantity of liquid phase, allowing a better diffusion of the chemical species and favour the grain growth [15]. Despite the fact that aluminium has a major influence on the growth of the grains, the Mg ions helps to decrease the viscosity of the mix favouring the mass diffusion and decreasing the final  $C_3A$  content of the samples [17]. MgO is said to catalyze the dissolution reaction of  $C_3A$  in the liquid phase, which hinders  $C_3A$  formation and promotes the presence of  $Al^{3+}$  ions as interstitials in  $C_3S$  [16]. Moreover MgO helps reducing the CaO percentage in the liquid phase by improving the burnability of free lime [14]. No significant differences in particle size were found when the pellets were ground between the heating cycles.

The effect of the heating temperature is reported in the Figure 3. As expected, higher temperatures allow a better grain growth (better diffusion at higher temperatures).

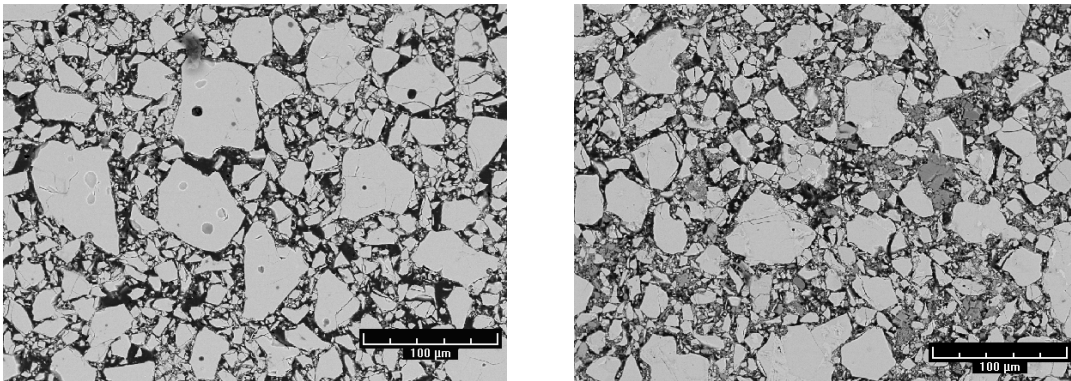


Figure 4: SEM images of synthesized Alite-C2 (left) and OPC (right)

Based on XRD characterization and laser granulometry, C2 was selected for its purity (the monoclinic MIII polymorph [14,18] was identified by XRD), grain morphology (Figure 4) and closest psd compared to OPC (Figure 2) for hydration kinetics study. C1 was not pure enough (crystallization of  $C_3A$ ) and C3 showed smaller crystallites

The narrow gradations needed for the study of hydration kinetics were obtained by mean of sieving (sieves of 50 and 25µm) for the coarser fractions and decantation in isopropanol for the smallest particles. The different gradations obtained are presented in the Figure 5.

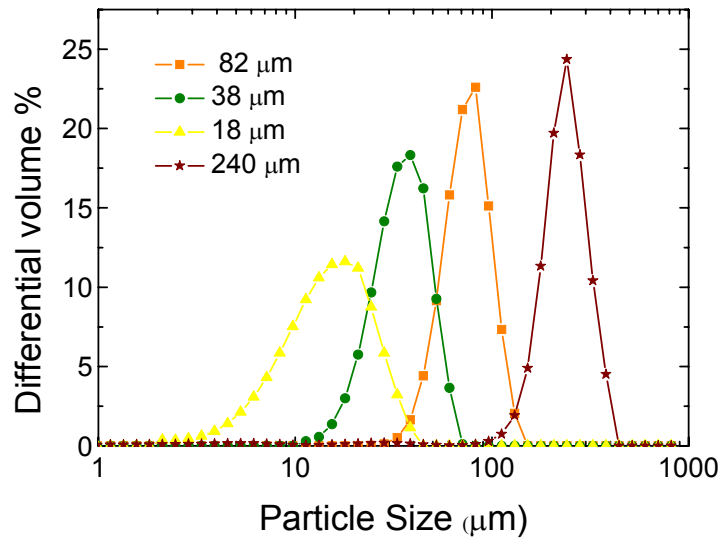


Figure 5: Psds used for kinetics study

### 3. Effect of particle size on hydration kinetics

The effect of alite particle size on the hydration kinetics was investigated in an isothermal heat flow calorimeter (TAM Air, Thermometric) at a temperature of  $20.0 \pm 0.1^\circ\text{C}$ . The different gradations were hydrated with a w/c ratio of 0.4 and the mix was carried out inside the calorimeter to allow monitoring the hydration from the very beginning when water was added to the sample.

The chemical shrinkage was followed by means of dilatometry following the protocol developed by Geiker [19]. This method involves the measurement of the decrease in the volume of the cement plus water by reading the water level in a water filled tube connected to the alite paste. In this experiment the evolution of water level in the pipettes was followed by recording photos every 10 minutes and then those photos were treated with image analysis software for reading the volume reduction. The powder gradations and the w/c ratio is the same as used for isothermal calorimetry experiments.

Isothermal calorimetry results (Figure 6 (left)) show higher heat evolution for gradations with finer particles. This can be explained by the fact that, since the smaller particles have a tendency to dissolve faster, the initial reaction rates are observed to be higher for these gradations. A similar trend can be observed in the results from chemical shrinkage (Figure 6 (right)), as these faster reaction rates manifest as higher shrinkage rates.

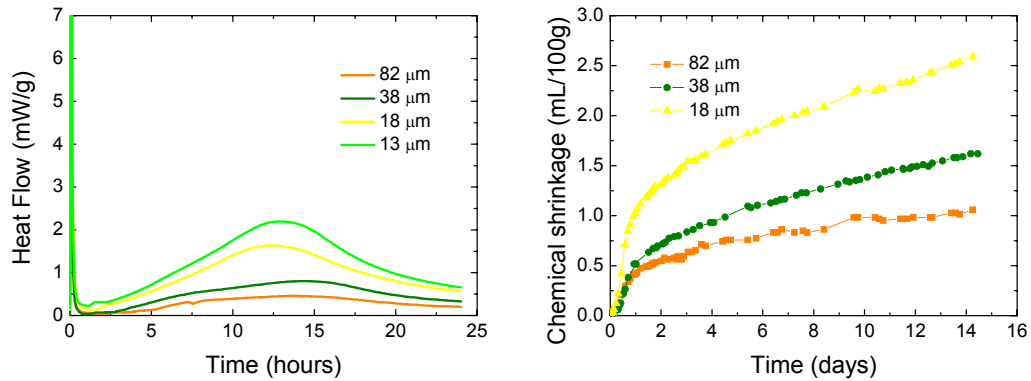


Figure 6: Isothermal Calorimetry curves (left) and Chemical Shrinkage (right) of hydrated psds of Alite.

The Isothermal Calorimetry results were fit against a generalized form of Avrami equation discussed earlier. Eq. (1) can be differentiated to:

$$\frac{d\alpha}{dt} = knt^{n-1}e^{-kt^n} \quad \text{Eq. (2)}$$

For small values of  $t$  and  $k$ , the exponential part of Eq (2) can be ignored. Further, an initial independent analysis of each curve showed that the value of  $n$  lies close to 2.0. With this assumption, the equation can be written as:

$$\frac{d\alpha}{dt} = 2kt \quad \text{Eq. (3)}$$

Eq. (3) can be used for simplified analysis to obtain estimates of  $k$ . Since this relation is linear, the linear part of heat-evolution curves (Figure 7) were extracted and fit against time. The obtained values of  $k$  are plotted against the calculated specific surface area of the respective powders in Figure 8. This specific surface was calculated by assuming a mixture of spherical particles of sizes in proportion to the obtained particle size distribution. The figure shows a predominantly linear variation of  $k$  with specific surface. Further, it was observed in the initial fitting attempts that the fit is not very sensitive to the value of  $n$  around 2.0. This could explain the discrepancy in values of  $n$ , ranging between 1.5 and 3.0, found in literature.

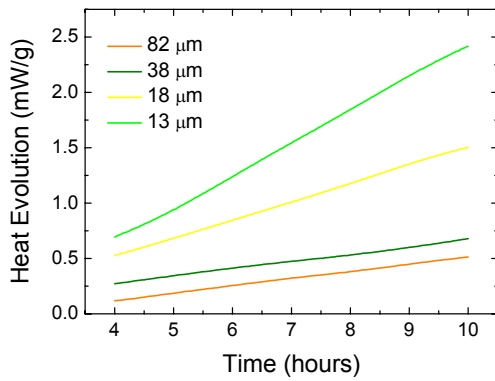


Figure 7: Isothermal Calorimetry curves of hydrating sieved fractions of Alite.

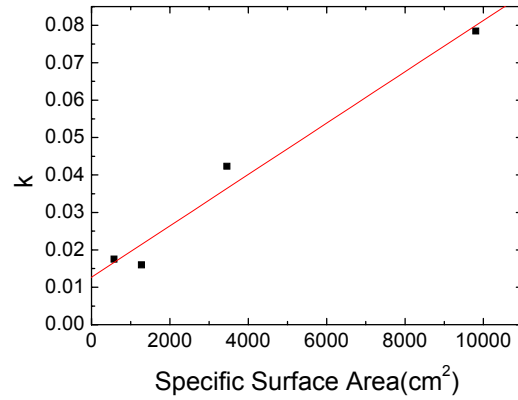


Figure 8: Rate constant against specific surface area for different fractions of Alite

In the next step, the calorimetric curves of two non-overlapping gradations of Alite were measured under isothermal conditions. Another third gradation was obtained by a 50-50 mix of these two powders. The heat evolution curves for these powders are shown in Figure 9. Figure 10 shows the comparison between the degrees of hydration for the mixed powders, plotted against the average of the observed degrees of reaction for the two non-overlapping gradations. A good linear agreement between the two values can be observed. Although further investigation is required, this result points towards the possibility of modelling the hydration of multi-sized systems as a linear addition of individual particle sizes.



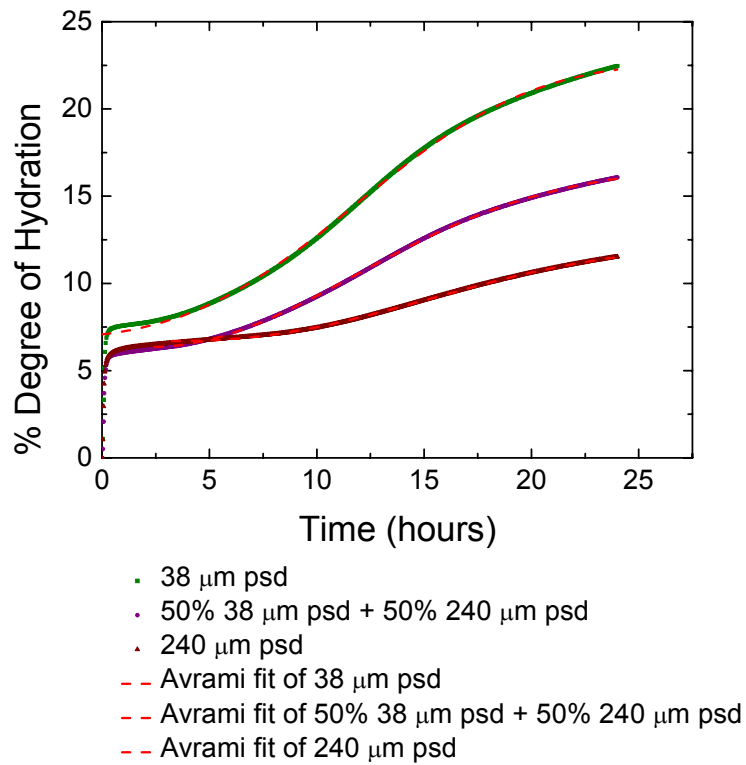


Figure 9: Avrami equation fit for non-overlapping psds

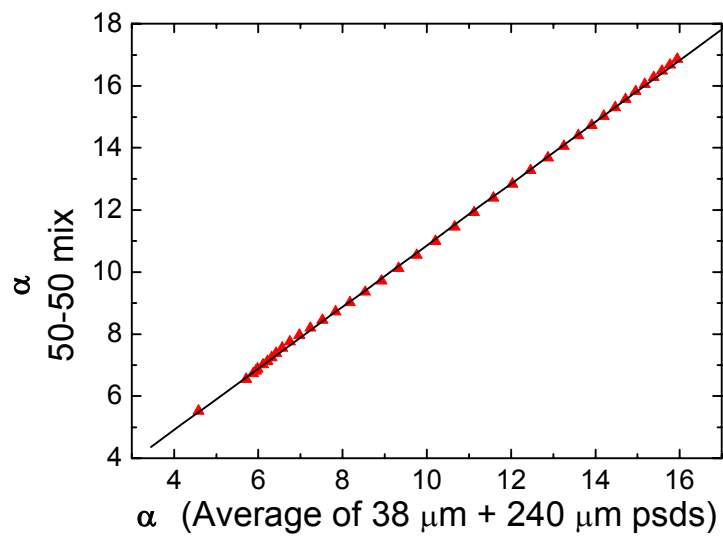


Figure 10: Plot of the degree of hydration for the average of two non-overlapping gradations against the degree of hydration of its 50-50 mixture

#### **4. Conclusions**

A protocol for alite synthesis has been developed assessing the effect of doping ions, like Al and Mg. Al ions plays the major role in the growth of the tricalcium silicate grains and Mg ions improve the burnability of the blend reducing the free lime content. The alite produced has been successfully divided into different gradations of particle size distributions by sieving and decantation methods. The hydration of this narrow psds has then been studied by isothermal calorimetry and chemical shrinkage. The observed rates of reactions were found to be higher for powders with higher specific surface. The heat evolution rates were fit against a modified form of Avrami equation and a predominantly linear relationship between the rate constant and the specific surface area was observed. Further, it was observed that the hydration of multi-sized system could be modeled as the linear addition of individual particle sizes.

#### **Acknowledgements**

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