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Study of C-S-H growth on C_3S surface during its early hydration

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ABSTRACT

A study to understand and quantify the growth mode of C-S-H during the hydration of tricalcium silicate grains is presented here based upon number of complementary approaches: study of C-S-H nucleation during the hydration of tricalcium silicate compared with experimental studies of homogeneous nucleation; experimental kinetics studies of C-S-H formation during tricalcium silicate hydration in dilute suspensions; direct observations of C-S-H growth by Atomic Force Microscopy; Simulation of curves obtained from experiments in dilute suspensions from a model based on AFM observations. With AFM the formation of CSH is observed by the agglomeration of identical elements 60x30x5 nm^3 in size on alite surface. This agglomeration takes place perpendicularly and parallel to the surface. Numerical simulation of the experimental curves of the degree of hydration versus time enabled us to quantify the variation of the growth rates parallel and perpendicular to the surface with lime concentration. It is shown that the growth rate of C-S-H only depends on the lime concentration in solution.

RÉSUMÉ

Une étude pour comprendre et mesurer le mode de croissance de C-S-H pendant l'hydration des grains de silicate tricalcique est présentée ici, basée sur un certain nombre d'approches complémentaires : l'étude de la nucléation de C-S-H pendant l'hydration du silicate tricalcique comparée aux études expérimentales de nucléation homogène ; études expérimentales de cinétique de formation de C-S-H pendant l'hydration du silicate tricalcique dans les suspensions diluées ; observations directes de croissance de C-S-H par microscopie de Force Atomique ; simulation des courbes obtenues à partir des expériences dans les suspensions diluées à partir d'un modèle basé sur des observations AFM. L'AFM permet d'observer la formation de CSH par l'agglomération d'éléments de tailles identiques de 60x30x5 nm^3 *sur la surface d'alite. Cette agglomération a lieu perpendiculairement et parallèlement à la surface. La simulation numérique des courbes expérimentales du degré d'hydration en fonction du temps nous a permis de mesurer la variation des taux de croissance parallèle et perpendiculaire à la surface avec la concentration en chaux. On montre que le taux de croissance le taux de C-S-H dépend seulement de la concentration en chaux en solution.*

1. INTRODUCTION

It is generally agreed that setting and hardening of Ordinary Portland Cement (OPC) are due to the formation of calcium silicate hydrate ($CaO-SiO_2-H_2O$ noted C-S-H) [1, 2] during its hydration. An understanding of the factors controlling its formation is very important, particularly during the early period corresponding to the transition from workability to setting, associated with rapid changes in kinetics. It is now generally recognised that the formation of C-S-H occurs by a dissolution-precipitation process [3-6], but the factors controlling the so-called dormant period and acceleration period are the subject of controversy [7-9]. The setting of cement takes place in two mechanical steps [10-12] which are coagulation of cement particles and rigidification. The first step results from attractive force between unhydrated particles and leads to the formation of agglomerates, the second is due to the strengthening of the agglomerates by the precipitation of C-S-H. Since the development of mechanical properties of the paste during setting mainly depends on the growth mode of C-S-H and its ability to develop contacts with and stick together the hydrating cement grains, experimental studies relating to the nucleation and growth of C-S-H during this early period are required. As Portland cement paste is an extremely complex system, it is preferable to use tricalcium silicate, which is the main component, as a model system. A study to understand and quantify the growth mode of C-S-H during the hydration of tricalcium silicate grains is presented

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here from different complementary approaches:

- Study of C-S-H nucleation during the hydration of tricalcium silicate compared with experimental studies of homogeneous nucleation.
- Experimental kinetics studies of C-S-H formation during tricalcium silicate hydration in dilute suspensions
- Direct observations of C-S-H growth by Atomic Force Microscopy
- Simulation of curves obtained from experiments in dilute suspensions from a model based on AFM observations.

2. NUCLEATION OF C-S-H [13]

When tricalcium silicate is suspended in water it dissolves releasing calcium and silicate ions. The typical variation of the silica concentration versus time is plotted in Fig. 1. The rise in concentration corresponds to pure dissolution. During this period, it is the rate of dissolution which governs aqueous silica concentration. The maximum value corresponds to the maximum supersaturation with respect to C-S-H which precipitates at this point. This precipitation leads to the decrease in concentration. It is important to note that the initial C-S-H precipitation occurs in the first few minutes. After the peak of concentration, dissolution and precipitation rates both govern aqueous silica concentration.

The nucleation was investigated in order to understand how it proceeds. First, the homogeneous nucleation of C-S-H was studied from different solutions, supersaturated with respect to C-S-H, obtained by mixing stable solutions of lime and silica with more concentrated lime solution. The degree of supersaturation with respect to C-S-H is given by the activity product of the constituents of the C-S-H phase:

$$\beta = \frac{K_{supersaturation}}{K_{solubility}}, \qquad (1)$$

where $K_{supersaturation}$ is the activity product of the supersaturated solution and $K_{solubility}$ is the solubility product.

The time before nucleation (measured by following the electrical conductivity of the solution) was determined for various levels of supersaturation (Fig. 2). The experimental results show that for β greater than 26, nucleation occurs spontaneously. For values of β less than 10 the time for nucleation is very long.

For Ca_3SiO_5 hydration in various lime solutions, the C-S-H precipitation always occurs between 1 and 5 minutes after introduction of the Ca_3SiO_5 to the solution (Fig. 3). For lime concentrations higher than 8 mmol/L, the C-S-H nucleation occurs instantaneously at degrees of supersaturation ($\beta < 10$) for which homogeneous nucleation time was more than 100 minutes.

These experimental results clearly indicate that during the hydration of tricalcium silicate in lime solutions the nucleation is heterogeneous and takes place on anhydrous silicate grains.

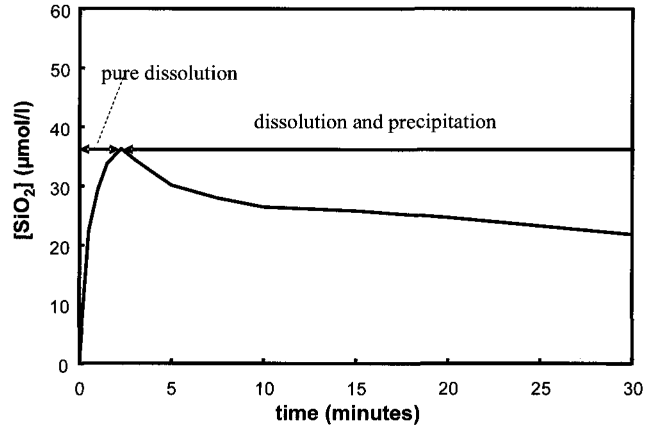

Fig. 1 - Variation of the silica concentration against time during Ca_3SiO_5 hydration in saturated lime solution.

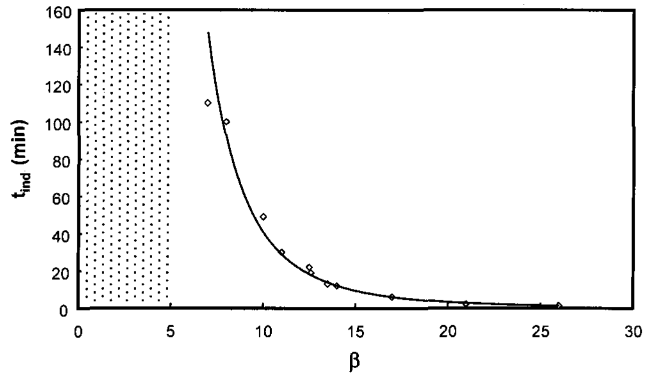

Fig. 2 - Variation of induction time needed to have homogeneous nucleation versus degree of supersaturation.

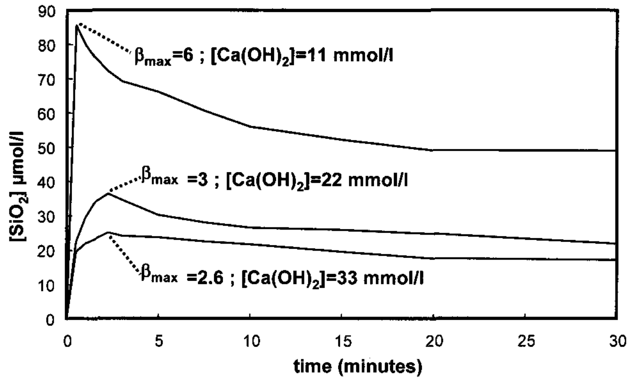

Fig. 3 - Variation of the silica concentration against time during Ca_3SiO_5 in various lime concentration, l/s=50.

3. C-S-H GROWTH DURING Ca_3SiO_5 HYDRATION IN DILUTE SUSPENSION

In order to control all the parameters, these experiments were performed in dilute suspensions, it having been well established that there is a perfect continuity of hydration process from paste to more dilute suspensions [14]. Moreover, as the lime concentration varies during hydration, due to the difference in stoichiometry between tricalcium silicate (Ca/Si=3) and C-S-H (Ca/Si<2), an experimental system has been developed, which allows the lime concentration in dilute suspension to be kept constant [17]. The lime concentration is monitored by measuring the electrical conductivity which is proportional to the lime concentration. When it increases, a volume of pure water is added whereas the same volume of solution is sucked up through a filter to maintain the water/cement ratio constant. The percentage of reaction is calculated from the number of calcium ions taken from the liquid phase. Each experiment is then representative of what happens at a given instant during paste hydration where lime concentration varies.

The degree of tricalcium silicate hydration versus time follows a sigmoid law characterised by the duration of the initial period when degree of reaction remains small (Fig. 4) and the degree of reaction at which the rate of reaction decelerates.

The kinetics of hydration varies with the lime concentration in solution (Fig. 4):

- the lower the lime concentration, the shorter the initial period;
- the lower the lime concentration, the lower the degree of reaction corresponding to the onset of the deceleration period.

These variations can be attributed to the influence of the number of C-S-H nuclei and their growth mode which both depend on lime concentration.

By preliminary hydration in different lime solutions of different concentrations it is possible to vary the quantity of C-S-H nuclei and study the influence of this parameter. Samples were pre-hydrated for 30 min in two different lime solutions. The relative quantities of C-S-H nuclei are deduced from the $[SiO_2] = f(t)$ curves (Fig. 5). The quantity of C-S-H initially nucleating (noted $n_{C\text{-}S\text{-}H}$) per the quantity of tricalcium silicate used in experiments (20g in experiments presented on Fig. 5) depends on the difference in silicate concentration ($\Delta[SiO_2]$ in Fig. 5) between the maximum supersaturation with respect to C-S-H and the supersaturation at which growth becomes faster than nucleation and can be expressed by the relationship:

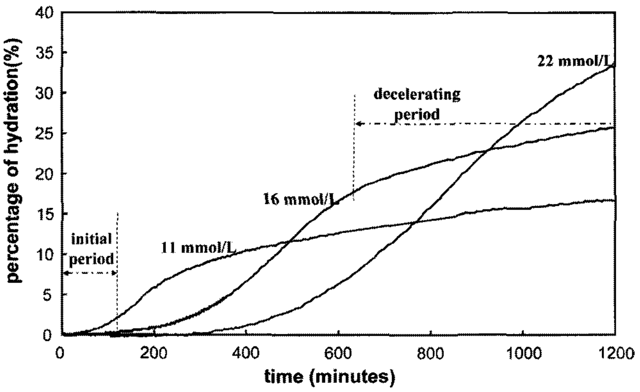

Fig. 4 - Variation with lime concentration of the percentage of hydration against time during the hydration of Ca_3SiO_5 grains, l/s=50. The characteristic periods are indicated for the curve obtained at 16 mmol/L.

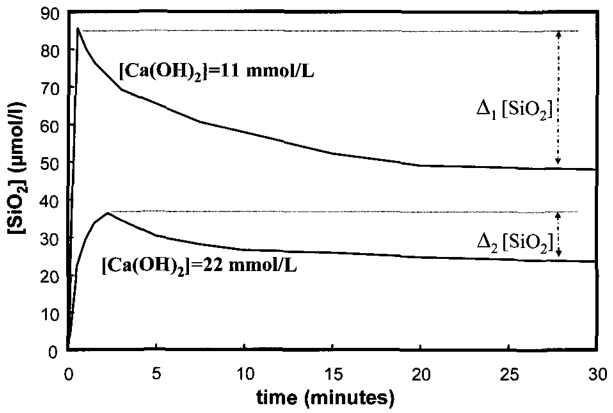

Fig. 5 - Variation of the silica concentration against time during Ca_3SiO_5 hydration in two different lime solutions (20g in 1000 ml of solution).

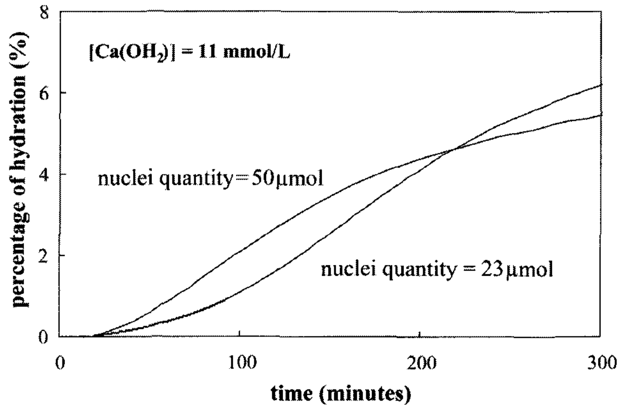

Fig. 6 - Variation of the percentage of hydration against time during hydration of Ca_3SiO_5 grains wearing different quantities of C-S-H nuclei.

$$n_{C\text{-}S\text{-}H}=\frac{\Delta[SiO_2]}{(x/3)-1}V \qquad (2)$$

where V is the volume of solution and x the stoichiometric ratio Ca/Si of the C-S-H (the used values are respectively 1.3 and 1.8 for pre-hydration at 11 and 22 mmol/L).

This calculated quantity of C-S-H is proportional to the number of C-S-H nuclei since it has been shown in previous studies that the size of nuclei does not vary so much in the lime concentration range studied here [13][1].

In the experiments presented here, there are 23 µmol of C-S-H precipitated for pre-hydration in saturated lime solution and 50 µmol for pre-hydration at 11 mmol/L.

The two pre-hydrated samples were then further hydrated in the lime solutions of the same concentration to elucidate the role played by the different initial quantities of nuclei (Fig. 6). This indicates that the duration of the initial period is associated with the quantity of C-S-H nuclei formed, which decreases as the lime concentration increases.

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[1] *AFM does not enable to observe nuclei, because AFM prevents C-S-H nucleation.*

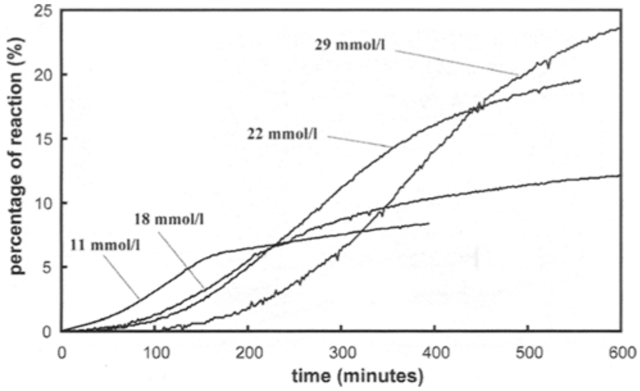

Fig. 7 - Variation with lime concentration of the percentage of hydration against time during the hydration of Ca_3SiO_5 grains wearing the same quantity of C-S-H nuclei.

Several samples pre-hydrated in the *same* lime solutions ($[Ca(OH)_2]$=11mmol/L), *i.e.* having the same quantity of C-S-H nuclei, were then further hydrated in *different* lime solutions (Fig. 7). This shows that the lime concentration also controls the growth mode of the C-S-H. Two growth modes have been distinguished from AFM and SEM observations, growth parallel to the surface of the tricalcium silicate grain and growth perpendicular to the surface [15]. The C-S-H nuclei grow on the anhydrous silicate surface until to form a diffusion layer around tricalcium silicate grains (it has been shown than after nucleation, it would have less than 15% of silicate surface covered by C-S-H [13]). At low lime concentrations the slowing down of the rate of reaction, corresponding to coverage of the Ca_3SiO_5 particles by C-S-H occurs earlier, so it has been deduced that the growth of C-S-H parallel to the surface is faster in this case. At high lime concentrations, the C-S-H seems to faster grow perpendicular to the surface, as the degree of reaction before coverage of the surface is greater.

Observed by SEM of tricalcium silicate grains hydrated in lime solution of different concentrations support these conclusions (Fig. 8). In the image of Ca_3SiO_5 grains hydrated at low lime concentration, the growth of C-S-H seems to be mainly parallel to the surface. The image of Ca_3SiO_5 grains hydrated at high lime concentration at the same degree of reaction shows that the growth is more perpendicular to the surface; more surfaces remain uncovered by C-S-H.

Despite the good agreement between SEM observations and experimental kinetics studies, some limitations exist with SEM: the C-S-H growth is not observed in situ and the appearance of the sample may be affected by the high vacuum and the conductive coating. To investigate the growth of C-S-H in situ, direct observations of its formation by Atomic Force Microscopy has been carried out.

4. DIRECT OBSERVATIONS OF C-S-H GROWTH BY AFM

In the Atomic Force Microscope, the surface of the sample is scanned line by line with a tip located at the end of a cantilever. The repulsive force between the tip and the sample is measured, based on the deflection of the cantilever. The spatial variation of the tip height recorded during scanning is converted into an image [16]. The contrast in the resulting image is related to the spatial variation of the tip height. The colour-scale used is presented at the right of each image.

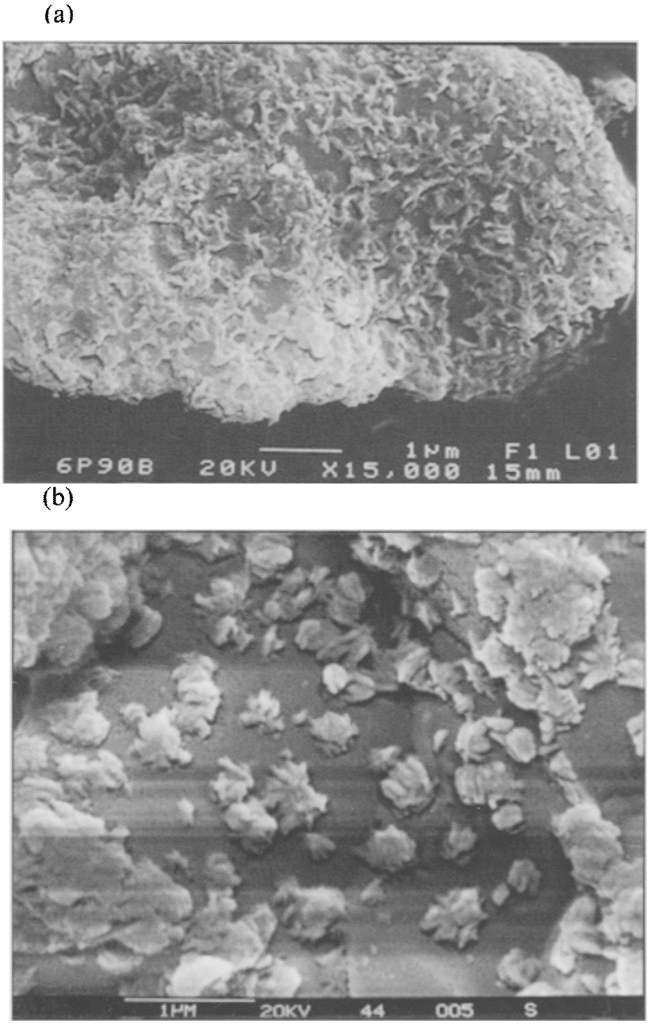

Fig. 8 - Morphologies of C-S-H on the surface of tricalcium silicate grains hydrated at low lime concentration (a) and at high lime concentration (b). In both image the degree of hydration is the same.

Contrary to the SEM, model system must be used as samples in the Atomic Force Microscope. A flat surface is needed to obtain good images. For the experiments described here, sintered pellets of tricalcium silicate (alite) were polished with alumina powder and absolute alcohol. Fig. 9 presents a scan of the initial surface, the low surface roughness is clearly indicated by the homogeneity of colour, the final roughness was about 10 nm in 25 μm^2.

The development of C-S-H on the surface was observed in situ by scanning the surface wetted by a drop of a lime saturated solution (in a wet cell). As soon as the surface is wetted, it begins to dissolve. It is difficult to image the process at the beginning but the aspect surface can be seen after 10 minutes (Fig. 10) where preferential sites of dissolution appear.

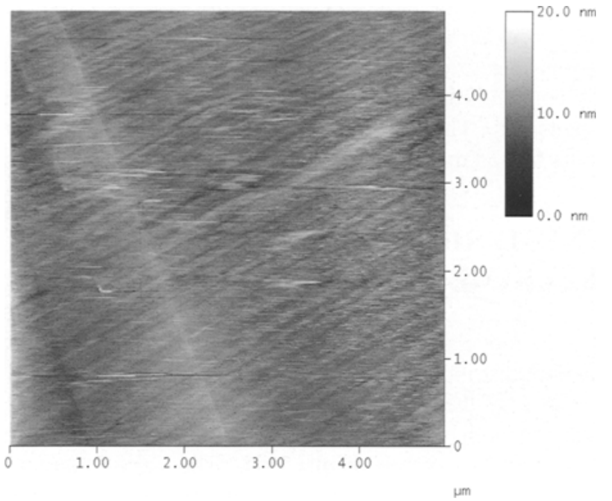

Fig. 9 - Initial alite surface observed in air in the AFM.

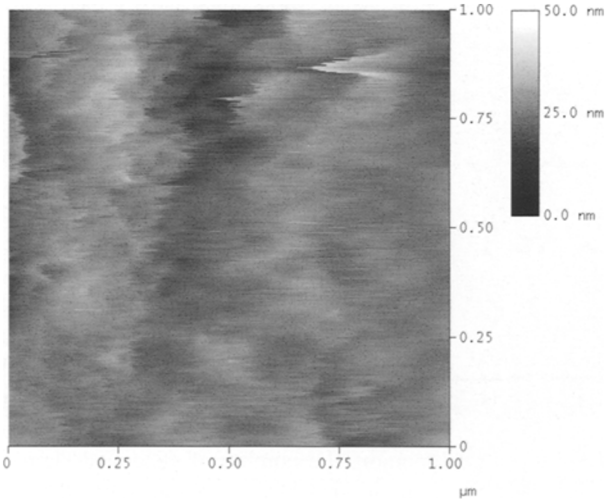

Fig. 10 - Alite surface after 10 minutes of hydration observed in situ with AFM.

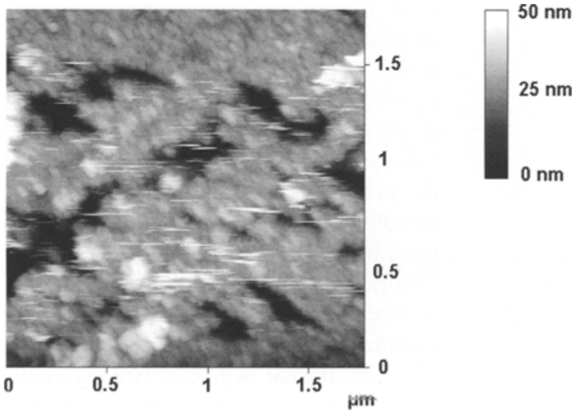

Fig. 11 - Alite surface after 4 hours of hydration observed in situ with AFM.

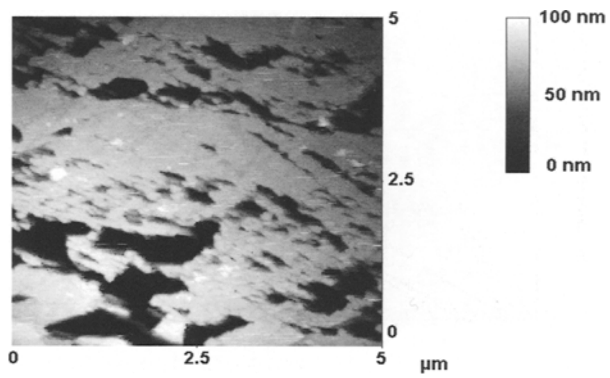

Fig. 12 - Alite surface after 5 hours of hydration observed in situ with AFM.

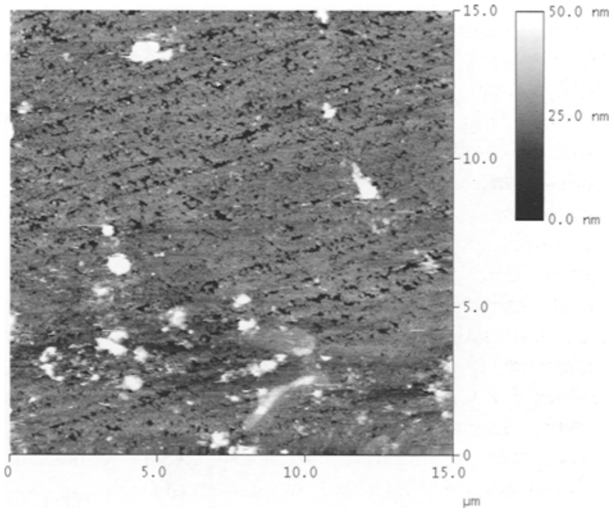

Fig. 13 - Alite surface after 7 hours of hydration observed in situ with AFM.

Fig. 11 presents a typical image obtained after 4 hours of hydration. The covering of the surface by C-S-H is observed by small elements typically 60 x 30 x 5 nm in size, their most developed faces being parallel to the surface. The resulting porosity appears clearly as the dark zones (Figs. 11, 12 and 13). All the experiments carried out indicated that these elements are always arranged side by side in the same manner and well aligned while the surface is not completely covered. The orientated arrangement of the aggregation is confirmed by the linear organisation of the residual porosity particularly well visible in Fig. 13.

It can be noted that the C-S-H assemblage is very dense and flat from the beginning of the C-S-H precipitation up to the point where the alite surface is virtually covered. Growth occurs in the residual porosity of the uncovered surface which reduces with time. When the porosity is filled up the reaction becomes limited by diffusion. During this last step, the morphology of the C-S-H becomes quite different, it is less dense and is more porous (Fig. 14).

AFM also allows the parallel and perpendicular rates of growth to be quantified. As the strong interaction between the alite surface and the AFM tip prevents C-S-H nucleation on the alite surface it has been possible to use this phenomenon to get an experimental quantification of the growth rates. Fig. 15a shows an image (15x15 µm) scanned after a long scanning time (1 hour) at a small scale (1.5x1.5 µm). The square

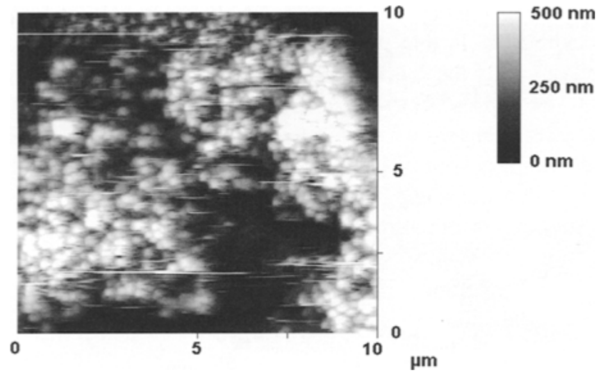

Fig. 14 - Alite surface after 20 hours of hydration observed in situ with AFM.

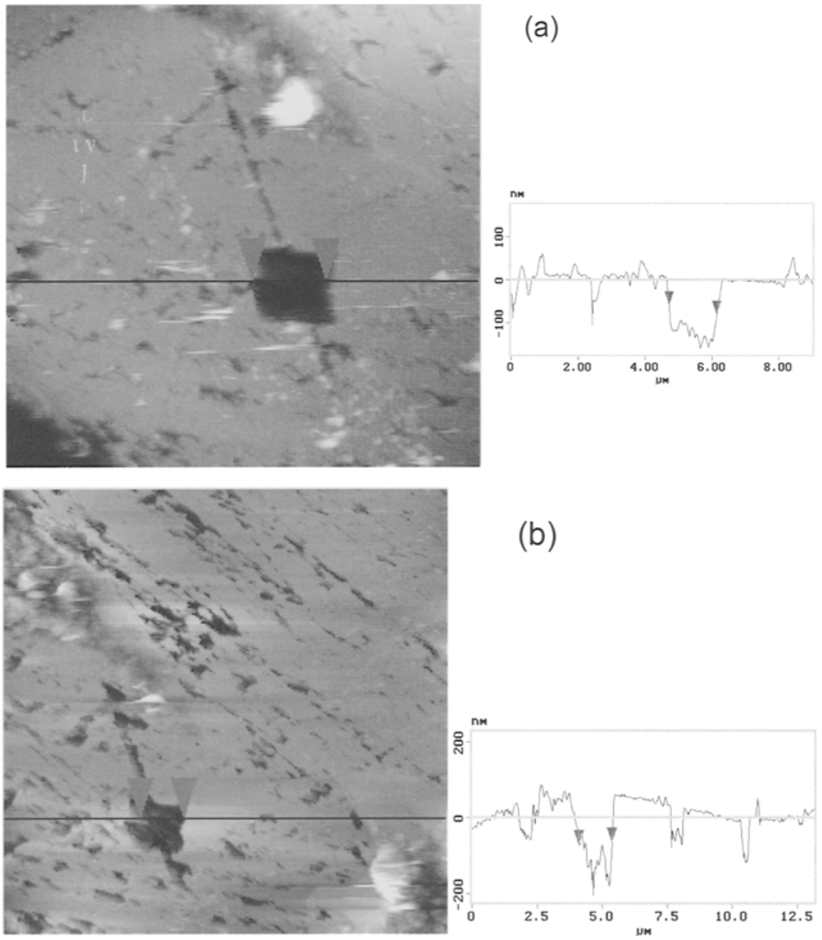

Fig. 15 - Alite surface in saturated lime solution with unhydrated square at two different times. (The profile presents the evolution of the roughness of the studied surface at the horizontal straight line on the image. So it is then possible to have the dimensions of the unhydrated square at the two different times.)

scanned during this long period, in which no growth has taken place is evident, around it normal C-S-H growth occurred. It is then possible to measure the thickness of the C-S-H layer. The same area was scanned less than 2 hours later, with no scanning between the two observations. The partial filling in of the scanning square allow the rate of parallel growth to be estimated at 4.10^{-11} m/s and the perpendicular rate, $1.8\ 10^{-11}$ m/s, is calculated from the change of C-S-H layer thickness.

Because of the experimental set up it is not possible to maintain different lime concentrations with AFM. So it is not possible to quantify the variation of growth rates with lime concentration observed from the experiments in dilute suspensions. This was done by simulating the experimental results from a model based on the AFM observations.

5. NUMERICAL SIMULATIONS OF EXPERIMENTAL CURVES [17]

In the model, the heterogeneous nucleation is described by a random distribution of particles on the surface. The growth is simulated by the aggregation of identical nuclei around it in directions both parallel to the calcium silicate surface and perpendicular to it. The Ca_3SiO_5 surface is represented by matrix of cells whose elements are either 0 or 1. When a C-S-H nucleus occupies a cell it is assigned a value of 1, while unoccupied cells (free surface) are represented by 0. The parallel growth is obtained by successive convolution of the "surface matrix" by a "growth matrix". To account for the actual quasi-spherical symmetry of calcium silicate grains, when a growing cluster reaches one of the matrix sides, the growth continues on the opposite side (periodic boundary conditions).

The number of generated elements per element at each iteration (I) is equal to the dimension of the growth matrix. The perpendicular growth is obtained by superposing (kI) layers identical to those formed by parallel growth. At each iteration, the number of generated elements is multiplied by k (multiplication factor). It is only possible to simulate with the model the part of the experimental curves corresponding to the growth process which is not limited by diffusion, that is, before the complete coverage of the calcium silicate grains by C-S-H. To fit the experimental curves, it is necessary to determine the parameters of the model: the number of initial nuclei (randomly generated matrix), the parallel growth rate (dimension of the convolution matrix), and the perpendicular growth rate (the value of the multiplication factor).

The number of generated elements obtained in the simulation is connected to the experimental degree of reaction and the number of iterations to time. There is only one relationship for each type of experiments.

Fig. 16 shows experimental and simulated curves corresponding to hydration of tricalcium silicate grains with different quantities of C-S-H nuclei but hydrated in the same lime solution. For the simulation the same convolution matrix and multiplication factor have been used, only the number of nuclei is varied. The relative number of nuclei in the two simulations is the same as the relative quantities of C-S-H precipitated as nuclei during pre-hydration of the samples. One can notice that the good agreement between the simulated and experimental curves.

Fig. 17 corresponds to the hydration of Ca_3SiO_5 grains with the same quantity of C-S-H nuclei in various lime concentrations. In this case the simulated curves are obtained modifying only the growth rates. The dimension of the growth matrix decreases from (60x5) to (3x3), the value of the parameter k increases from 3 to 6 when lime concentration varies from 11 mmol/L to 29 mmol/L. The ratio obtained between parallel and perpendicular growth rate against lime concentration is represented in Fig. 18.

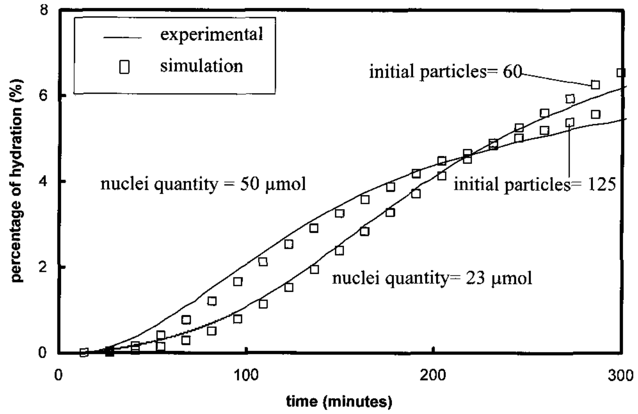

Fig. 16 - Variation of the percentage of hydration obtained experimentally and by simulation during the hydration in the same lime solution (11 mmol/L) of Ca_3SiO_5 with different quantities of C-S-H nuclei.

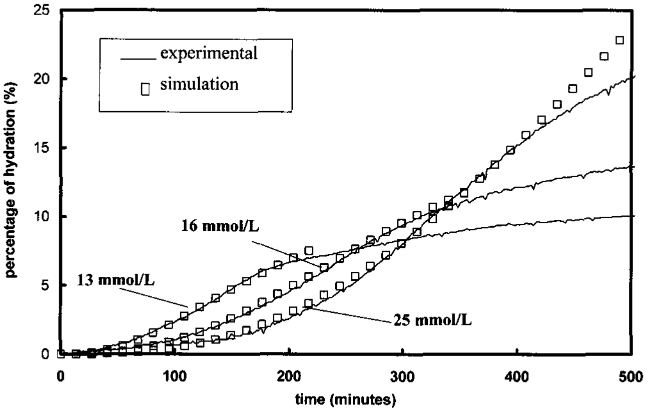

Fig. 17 - Variation of the percentage of hydration obtained experimentally and by simulation during the hydration in different lime solutions of Ca_3SiO_5 wearing the same quantities of C-S-H nuclei.

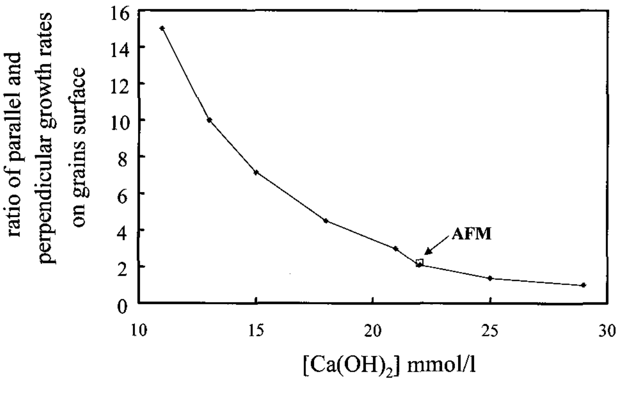

Fig. 18 - Variation against lime concentration of the ratio between parallel and perpendicular growth rates used for simulations.

The value obtained by atomic force microscopy is reported on the same graph. There is a good agreement between experimental value and simulated one.

This model has been validated in many cases. The influences of calcium chloride (commonly used as set accelerators for Portland cement), sodium chloride and potassium oxide (usually present in Portland cement), all known as hydration accelerators, have been explained and quantified in terms of growth and nuclei number changes by the same numerical simulations [18]. Moreover, the experimental curves of the evolution of the degree of reaction obtained during the hydration of dicalcium silicate grains in different lime solutions could also be simulated using the same rates of parallel and perpendicular growth determined to simulate tricalcium silicate hydration curves in the same lime solution [17]. This signifies that the rate of hydration of calcium silicates depends only on the growth of C-S-H, and is not influenced by the nature of the surface on which it grows.

6. CONCLUSIONS

With AFM the formation of C-S-H is observed by the agglomeration of identical elements 60x30x5 nm^3 in size on alite surface. This agglomeration takes place perpendicularly and parallel to the surface. Numerical simulation of the experimental curves of the degree of hydration versus time enabled us to quantify the variation of the growth rates parallel and perpendicular to the surface with lime concentration. It is shown that the rate of growth rate of C-S-H only depends on the lime concentration in solution.

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