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Interactions between chemical evolution (hydration) and physical evolution (setting) in the case of tricalcium silicate*

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This paper describes recent experimental results concerning investigation of the parameters which determine, on the one hand, the kinetics of hydration of tricalcium silicate and the thermodynamic, morphological and structural characteristics of C–S–H and, on the other hand, the evolution of the particle interactions at the origin of setting. It is shown that, in both cases, lime concentration in solution is the most important parameter. As a consequence, the chemical evolution of the system, which controls the lime concentration in solution, determines the nature of particle interactions and the physical evolution of the suspension or paste. In return, the contacts between particles, resulting from the coagulation of the suspension, seem to have a role in the kinetics of the chemical reaction.

1. INTRODUCTION

Hydration, setting and hardening are key words in cement and concrete science. Although these terms are all related to the main properties of hydraulic binders, that is to say the ability to get a hard material by mixing powders with water (and eventually aggregates), they involve very different processes with very different mechanisms. Hydration is a chemical process which, from the anhydrous material through several chemical reactions, leads to the formation of hydrates. This complex process has thermodynamic, kinetic and structural features which depend on both chemical and physical parameters. Setting is a definite time event which corresponds to the transition of the paste from soft (pourable, the material is ductile), to hard (no longer pourable, the material is fragile). Hardening is certainly a less ambiguous term: it involves increase in the strength of the material. This process depends also on several physicochemical parameters, such as degree of hydration, water to cement ratio, and curing conditions. One might reasonably think that the elementary acts involved during the hardening process are the same as those leading to setting. The purpose of this paper is to examine the interactions that may exist between these simultaneous processes, which together contribute to build up the complex materials that are cement paste and concrete.

A good idea of what are the contributions of chemical processes in the building up of cement pastes and concrete is given by simulating the development of microstructure from a dissolution–precipitation process by computational techniques such as those developed at NIST [1]. Such a method is very useful for predicting the properties of the material, but it is based only on an idea of randomness, it is not able to account for kinetics, and it does not let us determine which parameters determine the evolution of the system.

Thus in our approach, which is not an alternative but a complementary experimental way towards a better understanding of the phenomena involved in hydration and setting processes, we focused our attention on the elementary acts of the chemical and physical evolution of a system of particles that hydrate. Taking into account that the true material, Portland cement, is at least as complex as the processes involved after its mixing with water, we studied a reasonable simpler model system: tricalcium silicate.

It is not the purpose here to give detailed experimental results but only to illustrate through the main results the spirit of the work. Considering the fact that both chemical and mechanical properties change the most during the earlier part of the temporal evolution of the solid–liquid system, we studied the period following the mixing to the setting of the paste.

The problem may be summarized very simply by the following main questions.

> What are the features of hydration, i.e., the chemical reactions, the nature of the products, and the parameters determining thermodynamics, kinetics, and their structural and microstructual properties?
>
> What are the processes involved in setting and the determining parameters?
>
> What are the interactions between hydration and setting?

2. CHEMICAL AND MECHANICAL EVOLUTION OF A NORMAL C_3S PASTE

Fig. 1 shows the evolution versus time of (a) the percentage of hydration, i.e. the chemical evolution of the solid phases, (b) the lime concentration in solution, i.e., the chemical evolution of the liquid phase, and

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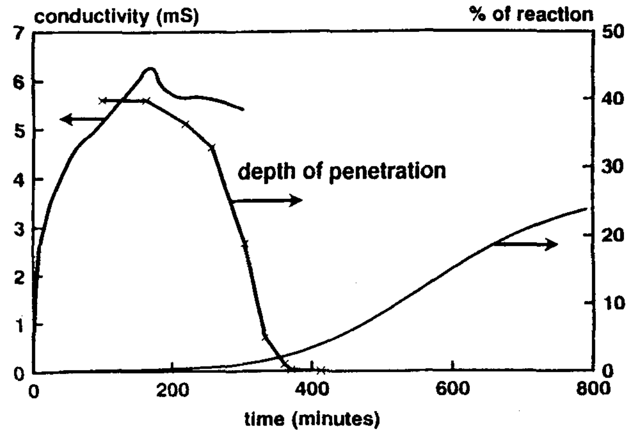


Fig. 1 Evolution with time of the percentage of hydration, the electrical conductivity of the pore solution, and the depth of penetration of the Vicat needle, in the case of a C_3S paste in pure water ($w/c = 0.5$, $T = 25°C$).

(c) the depth of penetration of the Vicat needle, i.e., the mechanical evolution of the system. Based on this figure, two important remarks can be made. First, setting, which corresponds to the time at which the Vicat needle no longer pentrates the paste, occurs only when less than 5% of C_3S has hydrated; the set paste is a continuously connected network of very partially hydrated C_3S particles. Second, the lime concentration in the pore solution evolves significantly during the period between the mixing and setting. Thus, the lime concentration may be an important parameter controlling both hydration and setting processes.

In order to investigate, on scientific bases, hydration and setting phenomena, we develop experimental procedures allowing control of the ionic concentrations in a better way than in paste, based on conductimetric, calorimetric and granulometric measurements on more or less diluted suspensions of particles ($0.5 < w/c < 300$) [2–5].

3. PARAMETERS CONTROLLING THE HYDRATION OF C_3S

An extensive conductimetric and calorimetric study of the hydration of C_3S with $5000 < w/c < 0.5$ allows us to demonstrate perfect continuity of phenomena from the paste to more and more diluted suspensions [2, 6, 7]. Hydration proceeds through three successive reactions becoming gradually simultaneous [8]:

the dissolution of C_3S providing calcium, silicate and hydroxide ions in solution;

as soon as the supersaturation maximum with respect to C–S–H is reached, it precipitates from silicate ions and a part of the calcium and hydroxide ions, C/S of C–S–H depends on the lime concentration in solution; and

as soon as the lime concentration reaches its supersaturation maximum with respect to portlandite, it precipitates.

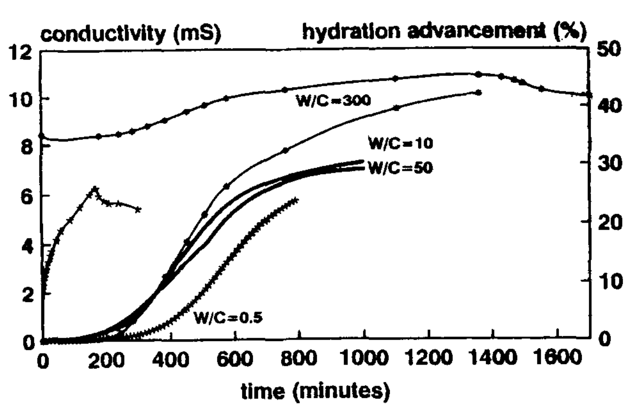


Fig. 2 Evolution with time of the percentage of hydration in the case of hydration in saturated lime solution with different C_3S ratios.

The rate and enthalpy of each reaction have been experimentally determined.

In the case of paste, the volume of solution is very small, so the increase in the lime concentration is very rapid, and portlandite begins to precipitate early. The more diluted the suspension is (higher the volume of solution per g C_3S), the later portlandite precipitates for the same rate of reaction without preventing C–S–H precipitation. So when C_3S is hydrated in pure water, the lime concentration in solution and the water to cement ratio are not independent variables, and portlandite precipitation appears to be a side reaction.

3.1 Kinetics of C_3S hydration

From the kinetics point of view, portlandite precipitation seems not to be a determining process. This result is illustrated in Fig. 2 showing the advancement of hydration versus time for different liquid to cement ratios. In these cases, C_3S was mixed with saturated lime solutions. The kinetics of the reaction does not depend very much on the water to cement ratio, while portlandite precipitation occurs at a very different time, very early in paste and very late, after the deceleration period, in diluted suspensions. It is even possible to hydrate C_3S completely without any portlandite precipitation. The water to cement ratio is then no longer, by itself, a determining parameter.

If C_3S is hydrated by keeping the lime concentration constant in solution at various values, the kinetics change very much [9]. Fig. 3 shows the advancement of hydration of C_3S when the lime concentration in solution is kept at different values in the range 10–36 mmol kg^{-1}. All these kinetic curves have a sigmoid shape, and it is possible to distinguish an induction period, or C–S–H nucleation period, and a C–S–H growth period, which may be divided into an accelerated period, a decelerated period and a period with a slow and quasi-constant rate.

The main changes concern the duration of the nucleation period and the percentage of reaction at the end of the decelerated period, when hydrates completely

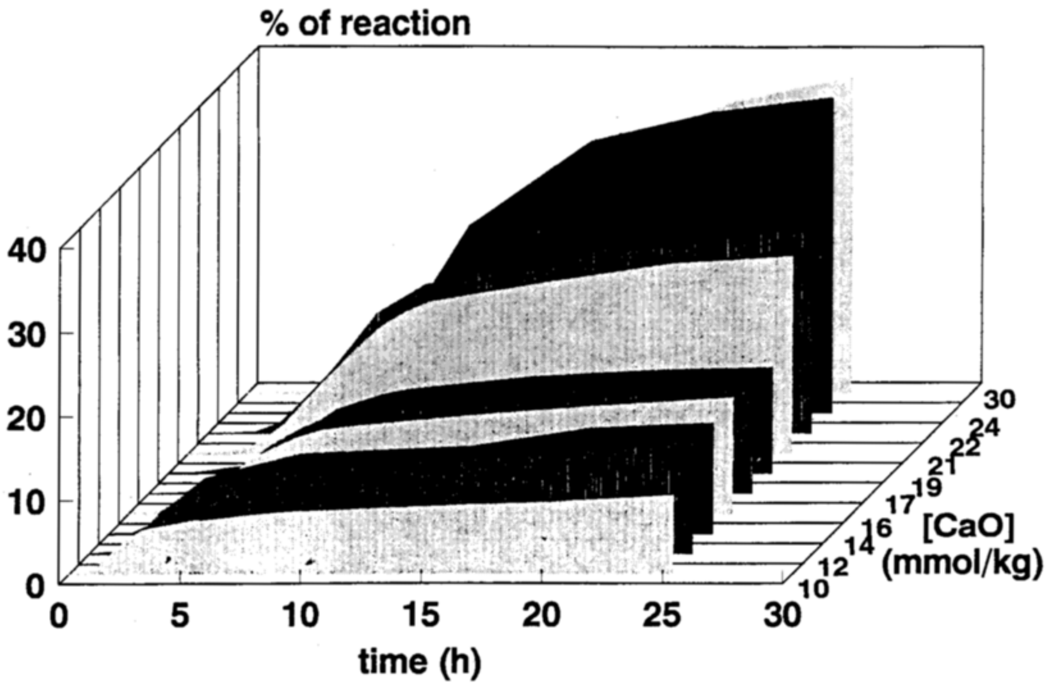
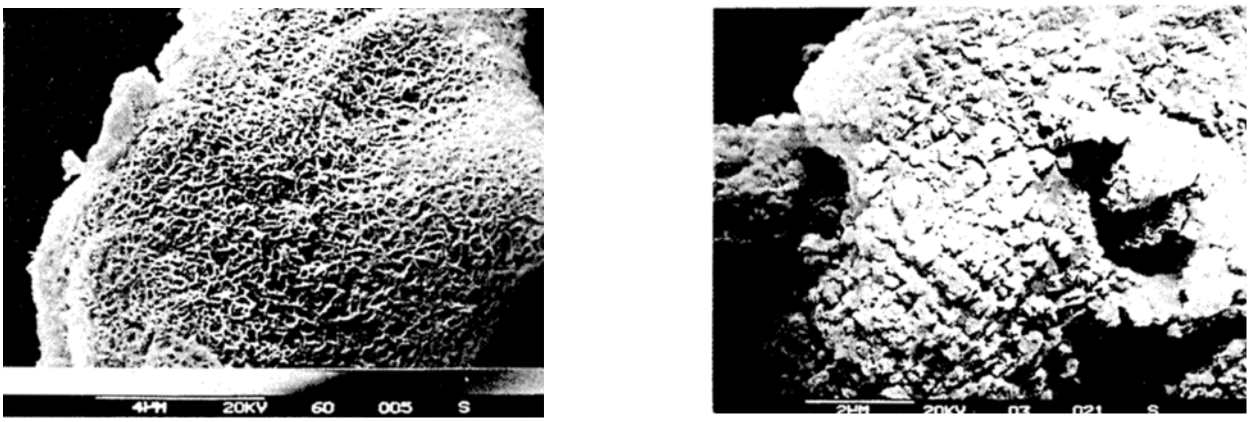


Fig. 3 Evolution with time of the percentage of hydration when the lime concentration in solution is kept constant at different values.



(a)

(b)

Fig. 4 Micrographs of the surface of partially hydrated C_3S: (a) low lime concentration, and (b) high lime concentration.

cover the surface of anhydrous grains. The nucleation period is very short (a few minutes) at low lime concentrations, and becomes longer and longer as the lime concentration increases. This is the same for the percentage of reaction at the end of the decelerated period, which increases with a dramatic discontinuity near 20 mmol lime per litre of solution.

3.1.1 *The induction period*

The duration of the nucleation period depends essentially on the number of nuclei of C–S–H that are precipitated from the solution in its state of maximum supersaturation with respect to C–S–H. The lower the lime concentration, the greater is the number of nuclei and, as a consequence, the shorter is the nucleation period [10].

3.1.2 *The accelerated and decelerated periods*

These periods correspond to the sigmoid part of the advancement curve. The rate of hydration during them depends little on lime concentration, but the percentages of hydration corresponding to the inflection point and the end of the decelerated period are influenced drastically by it: these percentages are very low if the lime concentration is below 20 mmol l^{-1} and are about double when the lime concentration is above 22 mmol l^{-1}. This difference is due to a different growing mode of C–S–H on the surface (Fig. 4). At low lime concentrations, C–S–H seems to grow parallel to the C_3S surface from numerous nucleation sites: the surface is then rapidly covered by a small quantity of hydrates. By contrast, at high lime concentrations, nuclei are few on the surface and C–S–H seems to grow more perpendicular to the

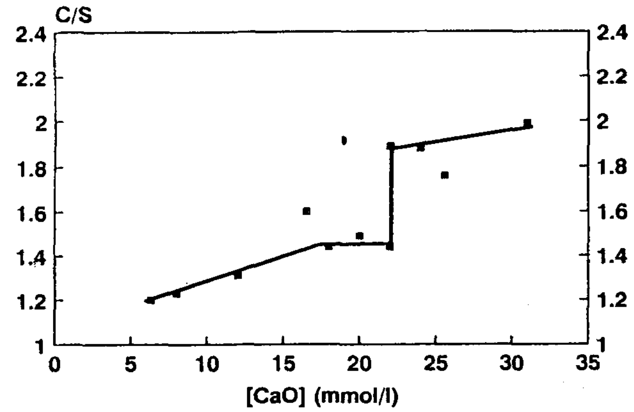


Fig. 5 Evolution of the calcium to silicon ratio of C–S–H obtained by complete C_3S hydration, with the value of the lime concentration in solution.

surface: a greater quantity is needed to cover the surface and it slows the reaction.

3.1.3 *The quasi-content rate period*

The rate does not seem to depend much on the lime concentration during this period. However, our experiments are very short with respect to the duration of this period, which is the longest one. The reaction rate is limited by diffusion of reactants (ions and water molecules) through the C–S–H layer, so the permeability of the C–S–H layer has to be the main parameter determining the kinetics of attaining complete hydration of the C_3S. Further work is needed to establish the evolution of the permeability of the C–S–H layer with lime concentration.

3.2 Stoichiometry and structure of C–S–H

The evolution of the stoichiometry of C–S–H versus the lime concentration expressed as the calcium to silicon ratio (C/S) is plotted in Fig. 5. C/S increases continuously between 1.2 and 1.5 when the lime concentration increases from 6 mmol l^{-1} to about 20 mmol l^{-1}; it shows also a discontinuity near 22 mmol l^{-1} and varies between 1.8 and 2 for lime concentrations between 22 mmol l^{-1} and 35 mmol l^{-1}. This change of stoichiometry is associated with a change of silicate chain length [9, 11]. Fig. 6 gives a schematic representation of the structure of C–S–H. It is constituted by calcium layers and parallel silicate chain layers. The silicate chains are dimers and pentamers, with 2 pentamers for one dimer when $C/S = 1.2$. The increase in calcium to silicon ratio is due to the elimination of bridging tetrahedra between dimers, as suggested first by Taylor [12]: 3 dimers for 2 pentamers when $C/S = 1.5$. When lime concentration is up to 20 mmol l^{-1}, the replacement of bridging tetrahedra by 2 hydroxyl groups occurs: one pentamer for five dimers when $C/S \doteq 1.8$. This process seems to be associated with a weak change in the crystalline structure. So silicate chains become shorter when the lime concentration increases.

4. PARAMETERS CONTROLLING THE SETTING OF C_3S

Setting results from the transformation of a dense suspension of more or less dispersed particles in a mechanically irreversible network of connected particles. An understanding of setting depends on knowledge of the processes involved in that transformation and the parameters that determine the mechanism. With the ability to control hydration in dilute suspensions, we used a granulometric method to study the evolution of the particle suspensions, some of which were subjected to dispersive sonication by ultrasonic waves for 30 s [4, 5].

4.1 The coagulation and rigidification processes

Fig. 7 shows the case of a suspension of C_3S in a lime saturated solution ($[CaO] = 22$ mmol l^{-1}, $w/c = 300$); it represents the evolution of the percentage of the coarser (Fig. 7a, $D < 15$ µm) and finer particles (Fig. 7b, $D < 5$ µm) in suspension. The duration of the nucleation period is about 60 min, and throughout there is practically no formation of hydrates. During this time, before initial dispersion by ultrasonic waves, the particles are aggregated.

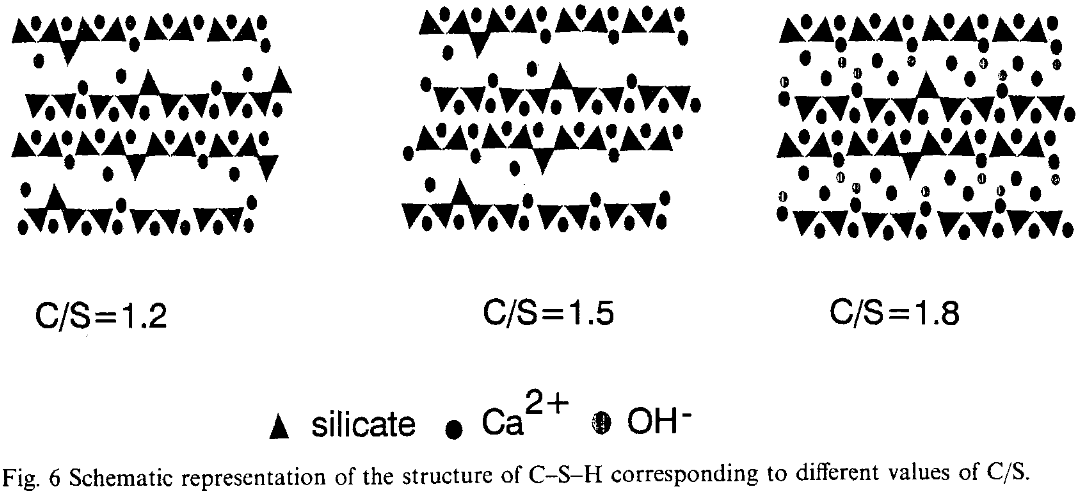
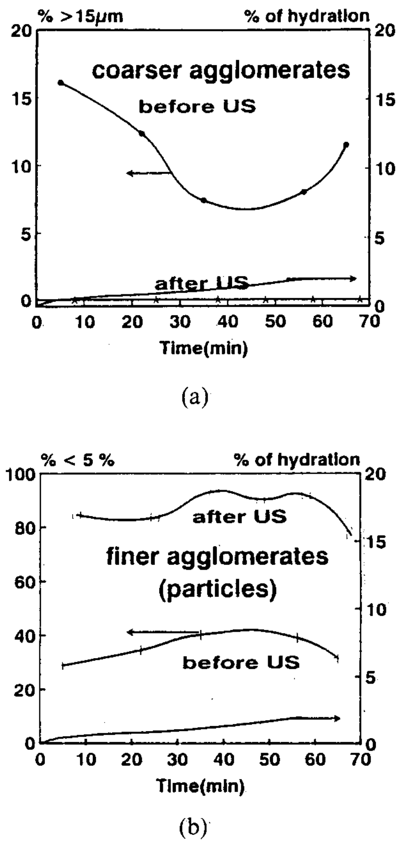


Fig. 6 Schematic representation of the structure of C–S–H corresponding to different values of C/S.



(a)

(b)

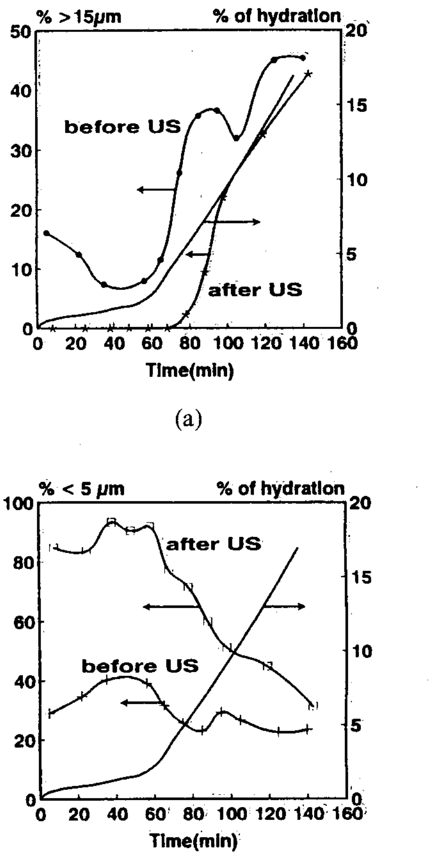
Fig. 7 Evolution during the nucleation period of the percentage of coarser (a) and finer (b) particles of the suspension, before and after 30 s sonication.

They are distributed as 16% coarser particles and 30% finer. Sonication disperses the particles since the population becomes 90% finer and 0% coarser particles. About 10 min after sonication, the population becomes virtually as before, showing the mechanical reversibility of the interparticular bonds. Further sonication destroys the aggregate structure and again disperses the suspension, which again coagulates when sonication is removed: this is the coagulation phenomenon in the sense of colloid science. Fig. 8 shows that, after the nucleation period, as soon as C–S–H formation accelerates the sonication destroys the structure less and less: C–S–H formed at the particle contacts rigidifies them.

So, setting proceeds through two fundamental steps: 1, coagulation at the origin of the essential contacts between particles; and 2, rigidification by hydrates of the contact points between anhydrous particles.

4.2 Parameters determining the coagulation process

Coagulation is due to attractive forces between particles. These forces may result from interaction of various origins: van der Waals forces, chemical interactions, electrostatic forces or solvation forces [13]. It is not clear what are the main interactions responsible for coagulation, but the ionic constitution of the surrounding solution plays an important role.



(a)

(b)

Fig. 8 Evolution during the acceleration of hydrate formation of the percentage of the coarser (a) and finer (b) particles of the suspension, before and after 30 s sonication.

In the present case, particles are reactive, their dissolution provides calcium, silicate and hydroxide ions. The respective concentrations of these ions are not independent, they are fixed by the solubility equilibrium of C–S–H

$$\text{C–S–H} \rightleftharpoons x\text{Ca}^{2+} + y\text{H}_2\text{SiO}_4^{2-} + z\text{OH}^-$$

$$K_s = [\text{Ca}^{2+}]^x[\text{H}_2\text{SiO}_4^{2-}]^y[\text{OH}^-]^z$$

So, for example, an increase in the calcium concentration decreases the silicate concentration, and vice versa. By controlling these concentrations in solution, we have demonstrated the evolution of the coagulation process. Fig. 9 shows D_{50}, which is the average diameter of the particle distribution (characteristic dimension of the aggregate before sonication), versus calcium concentration, and indicates that coagulation is most effective in the range 2–100 mmol l^{-1}. During C_3S hydration under normal conditions, the calcium concentration is such that coagulation always occurs.

4.3 Parameters determining the rigidification process

Rigidification occurs as soon as hydrates rigidify the contacts between particles. It is revealed in diluted suspensions by the time at which the characteristic

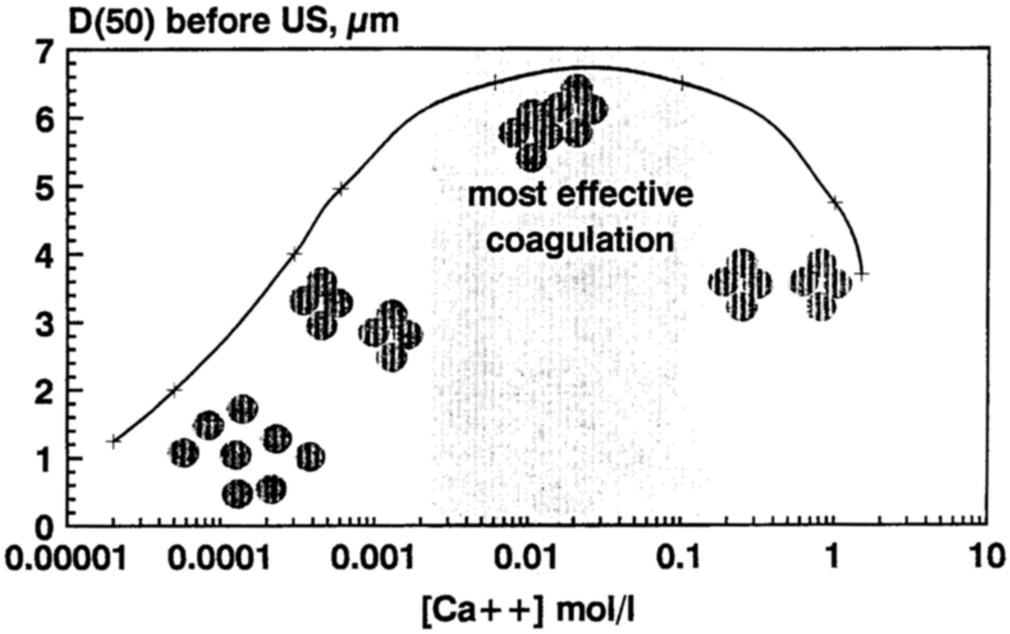


Fig. 9 Evolution with calcium concentration in solution of the average diameter (D_{50}) of particle aggregates in suspension before sonication.

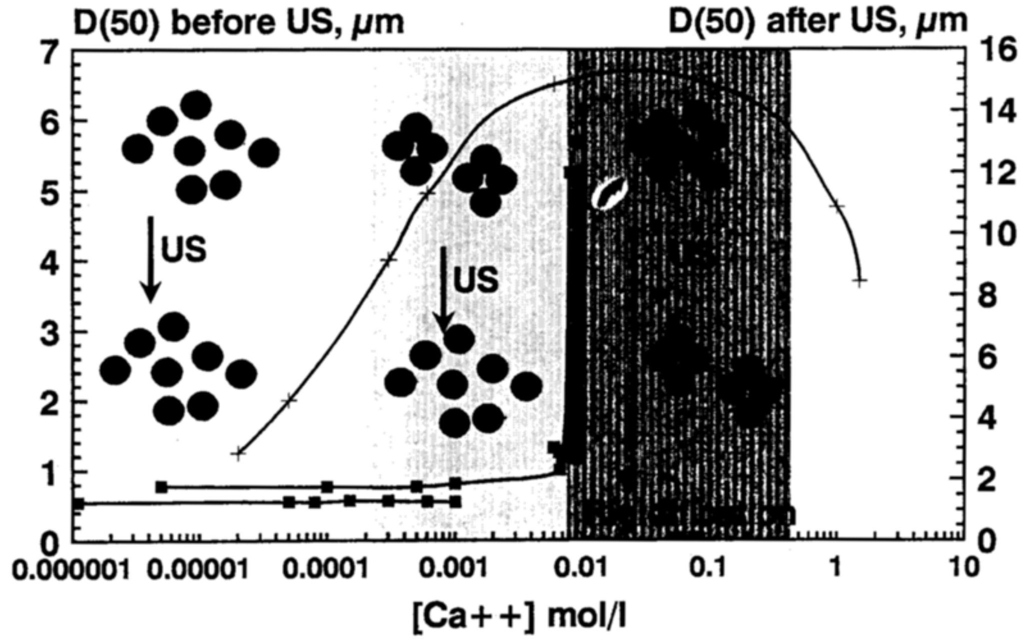


Fig. 10 Evolution with calcium concentration in solution of the average diameter (D_{50}) of particle aggregates in suspension after sonication in the case of C_3S hydration in a solution more or less initially concentrated in calcium or silicate ions.

dimension of aggregates after sonication increases. A systematic study of rigidification in suspensions, having initial calcium and silicate concentrations in the ranges 0–22 mmol l^{-1} and 20–0 mmol l^{-1}, respectively, shows that rigidification occurs as soon as the calcium concentration reaches about 10 mmol l^{-1}, whatever the percentage of precipitated hydrates. This is illustrated in Fig. 10 where the evolution of the average diameter of the coagulates is plotted against the lime concentration in solution. Below 0.1 mmol l^{-1} Ca^{2+}, rigidification cannot occur, because the particles are always dispersed. Between 0.01 mmol l^{-1} and 100 mmol l^{-1}, particles coagulate, but they become rigid only when the lime concentration in solution is greater than 10 mmol l^{-1}. In fact, this threshold value corresponds to the concentration at which the solubility of C–S–H in solution becomes very low (Fig. 11); only in such conditions does C–S–H precipitate on the surface of anhydrous grains where it is able to bridge particles. In the case where the calcium concentration cannot reach this threshold value at

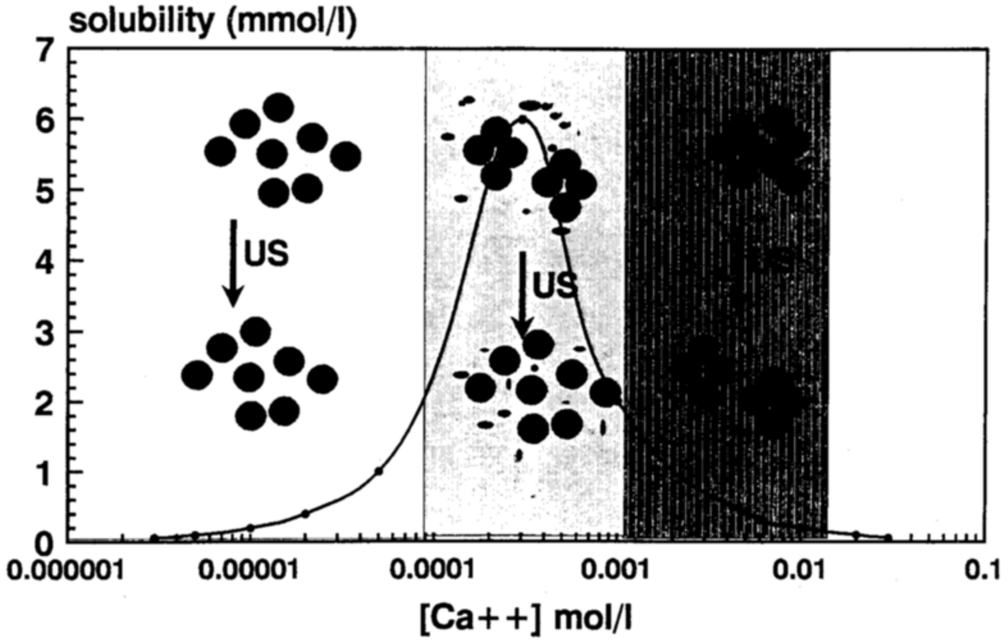


Fig. 11 Evolution with calcium concentration in solution of the solubility of C–S–H. Rigidification occurs only when solubility is low.

complete hydration of C_3S, rigidification never occurs. This clearly shows that hydration alone is not sufficient for setting.

5. INTERACTION BETWEEN CHEMICAL AND PHYSICAL PROCESSES

It is now clearly established that both coagulation and rigidification processes depend on calcium and silicate concentrations in solution. In the present case, this is determined by the chemistry of the $CaO-SiO_2-H_2O$ system. The hydration of C_3S, in terms of chemical reaction does control the particle interactions leading to coagulation and rigidification.

On the other hand, in the case of suspensions or pastes in concentrated lime solutions in which the solubility of C–S–H is very low, rigidification occurs at very weak percentages of reaction, suggesting that contact zones are preferential sites for nucleation of C–S–H. Other experimental facts agree with this hypothesis and even suggest that contacts act as nuclei.

1. By decreasing the *w/c* ratio of pastes mixed with saturated lime water, the induction period is shortened while the number of initial nuclei is reduced; only the number of contacts between particles is increased.

2. The effect of fine mineral powders (fillers) also lends support (Fig. 12) [14]. By replacing part of the C_3S grains by the same weight of smaller limestone particles, hydration begins more rapidly: the smaller are the particles, the greater is the number of contacts. By contrast, using minerals which do not coagulate with cement grains as silica or alumina, tends to prevent contacts between cement grains and increases the nucleation period.

3. The effect of addition of superplasticizer on the hydration and coagulation–rigidification process of C_3S also seems to agree with this hypothesis [15]: Fig. 13 shows the evolution of a C_3S suspension in a saturated lime solution ($w/c = 300$) with and without melment. Without melment, the conductivity of the solution and the average diameter of the particle aggregates rapidly increase, due to hydrate formation and rigidification, respectively. With 5% melment, there is a very long induction period. The particles are completely dispersed, and thus contacts between particles are suppressed. Hydrate formation, as indicated by the increase in the conductivity of the solution, begins as soon as the particles are in contact again.

6. CONCLUSIONS

A systematic study of the effects of lime concentrations on C_3S hydration leads us to conclude that lime concentration is certainly the most important parameter determining the thermodynamic, kinetic, morphological and structural features of C–S–H formation, whatever the *w/c* ratio. So all processes which will tend to change the lime concentration in solution, such as a lime consuming process (leaching, carbonation, reaction with silica fume or reactive aggregates, . . . ,) or the displacement of the solubility equilibrium of portlandite (increase of temperature, addition of calcium salts or alkalis . . .) might change the characteristics of C–S–H formation. Lime concentration in solution also determines both the particle interactions and the solubility of hydrates which control the coagulation–rigidification processes at the origin of setting. On the other hand, contacts between particles resulting from particle interactions seem to act as preferential sites for C–S–H nucleation. Their increase in number has the same result

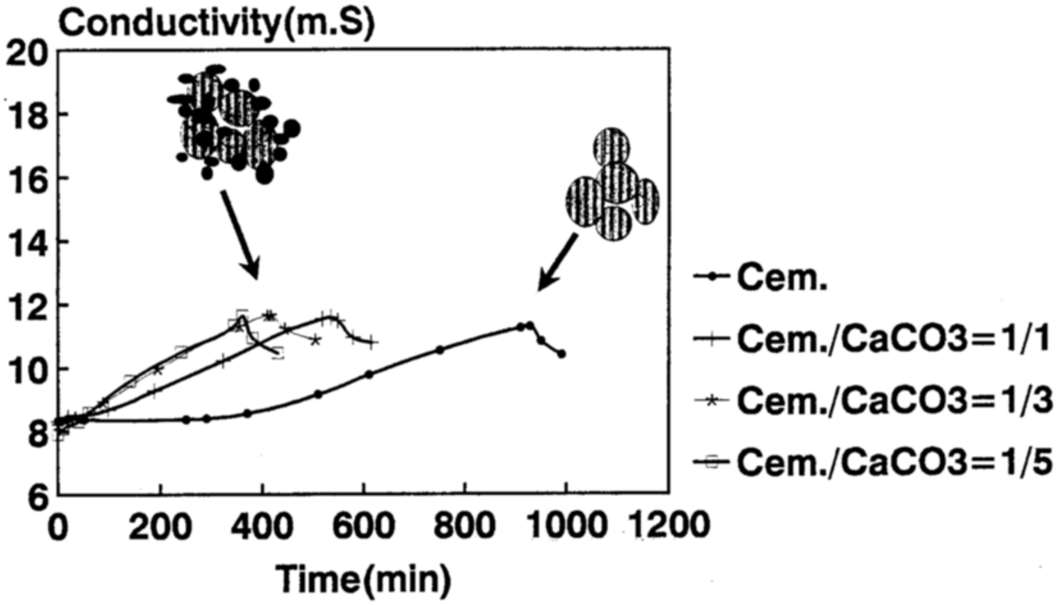


Fig. 12 Influence of limestone filler addition on the duration of the induction period as indicated by the length of the conductivity plateau.

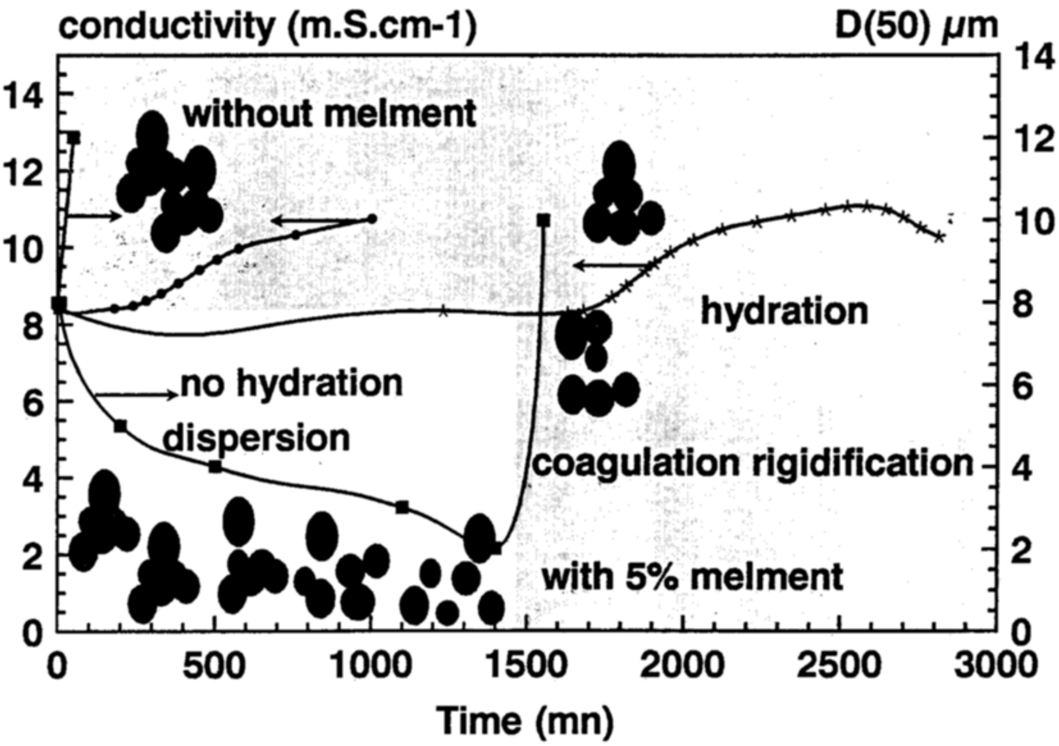


Fig. 13 Effect of melment superplasticizer addition on the duration of the induction period. The dispersion of the particles which suppresses the contacts between them seems to be at the origin of the lengthening of the induction period.

as the increase in C–S–H nuclei, viz., the shortening of the induction period.

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RESUME

Interactions entre l'évolution chimique (hydratation) et l'évolution physique (prise) dans le cas du silicate tricalcique

Cet article décrit les résultats expérimentaux récents concernant la recherche des paramètres déterminant, d'une part, la cinétique d'hydration du silicate tricalcique et les caractéristiques thermodynamiques, morphologiques et structurales du C–S–H produit, et d'autre part, l'évolution des interactions interparticulières à l'origine de la prise. On montre que, dans tous les cas, c'est la concentration en ions calcium en solution (ou en équivalent hydroxyde de calcium) qui est le paramètre déterminant. De ce fait, l'évolution chimique du système, qui fixe la concentration en calcium en solution, détermine la nature des interactions particulières et l'évolution physique de la suspension ou de la pâte. En retour, le nombre de contacts entre les particules résultant de la coagulation de la suspension, apparaissent avoir un rôle sur la cinétique de la réaction chimique. Cet article est une adaption de la conférence présentée à l'occasion de la remise de la Médaille Robert L'Hermite, lors de la 47*ème Réunion du Conseil Général de la RILEM à Haïfa, le* 13 *Octobre* 1933.