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STUDIES ON MECHANISM AND PHYSICO-CHEMICAL PARAMETERS AT THE ORIGIN OF THE CEMENT SETTING.
I. THE FUNDAMENTAL PROCESSES INVOLVED DURING THE CEMENT SETTING

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ABSTRACT

The mechanical evolution and the structure of the cement paste have been analysed in relation with the chemical evolution of the system. The setting process can be described as following two fundamental steps : the coagulation of cement grains during the first minutes following the mixing, and the rigidification of the coagulated structure which arises simultaneously with the acceleration of the hydrates formation. During the coagulation step, the structure formed is proved to be mechanically reversible. The rigidification of the coagulated structure is provided by the hydrates formation in the contact zone. The increase of the paste cohesion at this stage is proportional to the quantity of precipitated hydrates, the structure thus rigidified becoming mechanically irreversible.

Introduction

Setting is a process of transformation from an initial state, a scattered concentrated suspension, to a final state, a connected and strengthened system of particles. This transformation in the practice of cement and concrete, is obtained during chemical reactions between anhydrous cement particles and water producing hydrates : i.e. cement hydration.

It is generally considered that thee is a simple direct relation of cause and effect between hydration and setting. Indeed, by accelerating hydration through raising the temperature or using an accelerating admixture, the setting time can be shortened and the early strength can be increased. However, some other experimental facts indicate that there exists no direct relation between hydration and setting. For example, the setting and the initial strength growth of cement paste depend greatly on initial W/C ratios whereas the hydration advancement or the second exothermic hydration peak (as determined by calorimetry) are very little modified (1). A second example is given by the effect of an addition of afwillite particles which accelerate the C_3S hydration, but the strength growth was not increased in the same order of magnitude (2). A similar behaviour has also been observed with the seeding by synthetic C-S-H or partially hydrated C_3S (3). Finally, in a third example mentioned by Le Chatelier (4), by precipitating calcium sulphate dissolved in an alcoholic solution, one obtained a deposit of small gypsum crystals, presenting an entanglement as perfect as one may wish to have, possessing however no cohesion.

All these experimental facts clearly show that hydration, in term of hydrates formation, is not a simple and direct cause for setting, other parameters or conditions must be brought in and identified, so as to full understand the setting mechanism and the processes of appearing the initial cohesion of the paste. In other words, this amounts to elucidate some basic questions such as follows :

- what are fundamental processes at the origin of a cohesive structure formation and strength growth ? How can they be characterised and what they depend on ?

- what is the real role of hydration products? How they fit together and lead to a cohesive structure? What is the nature of interaction forces responsible for such a strengthened system cohesion ?

These questions have not yet got clear answers in spite of continuing scientifical and practical interest. The literature survey reveals that there is a disproportion between the few studies on cement setting as compared to the numerous studies on cement hydration.

Stemming from his general theory of coagulation in suspension of a finely divided solid dispersed in a liquid, Rebinder and co-workers (5,6) put forward as early as 1950's a mechanism of setting and hardening processes. According to them, the cement paste solidification is considered to consist of three distinct but overlapping stages : a dispersion or "colloïdisation" of cement particles, followed by the formation of a coagulated thixotropic structure from the dispersion of unhydrated cement components and hydration products, and the formation of a crystallisation structure from a supersaturated solution. However, the physico-chemical mechanisms of formation of the crystalline structure were unknown. Shchukin and co-workers (7,8) studied the formation of crystallisation contacts by bridging gypsum crystals by a new phase nucleating from a supersaturated solution (7). Their experimental work confirmed Rebinder's theory of setting mechanism and underscored two kinds of forces linking the crystals at the contact point. The first one is in the order of magnitude of Van der Waals forces, corresponding to the emergence of a coagulation contact. The second one is in the order of magnitude of crystalline bonds which results from the subsequent bridging of the crystals by a new phase nucleating and growing near the contact zone from highly supersaturated solution (termed bridging contact).

According to these theoretical and experimental studies, one may think that the appearance and the development of concrete mechanical strength would also result from these two kinds of inter particles forces; the first ones intervene in the coagulation phenomenon, the forming structure being mechanically reversible; the second ones make rigid the coagulated structure by means of the bridging contacts, the final structure becoming mechanically irreversible. The viscosity studies on the cement paste by Hattori and Izumi (9) seem to be in line with this approach. They concluded that the first increase in viscosity is due to the coagulation forces, and the second increase due to the resisting effect of cement hydration.

The present study is a contribution to the understanding of the cement setting phenomena using the concepts of coagulation and rigidification by the bridging hydrates developed by Shchukin (8). The investigations have been carried out on the real system of cement paste and also on cement suspensions by means of analysing comparatively the chemical evolution (i.e. hydrates formation, ionic concentration), the physical evolution (i.e. agglomeration of particles in suspension) and the mechanical evolution (i.e. cement paste shear strength).

In the first part of this paper, the experimental evidence of two fundamental steps of the paste shear strength growth, corresponding to coagulation and rigidification respectively was demonstrated by using a mechanical reversibility/irreversibility criterion. The existence of two types of contact interactions between the cement grains in course of hydration, corresponding respectively to the coagulation contacts and the bridging contacts was also demonstrated by measuring changes in particles agglomeration in diluted suspensions, using an adapted granulometric method.

Experimental

Materials

It is generally recognised that normal set in the Portland cement is the consequence of the formation of C-S-H resulting from C_3S hydration (10,11). In order to avoid problems and artefacts due to multicomponents system and to minimise chemical entities and reactions, simpler cements like pure alite would be better to use. However, the great quantities required for mechanical measurements often obliged us to use less pure materials. So, we chose a silica-rich Portland cement for the investigations (offered by Ciments Lafarge), refered to as SRPC. The chemical and mineralogical composition are given in the Table 1.

TABLE 1

Chemical and Mineralogical Composition of SRPC (%)

CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	K_2O	Na_2O
66.5	24.54	3.0	2.6	2.1	0.8	0.2	0.1

C_3S	C_2S	C_3A	C_4AF	$C\bar{S}$	CaO_{free}
63.7	18.3	3.8	7.0	3.6	1.2

Experimental methods

Cement pastes:

The cement pastes were prepared with distilled water by a mechanical mixing using a Kenwood mixer at 250W input power during 2 minutes. The chemical evolution of cement hydration system implies continuous chemical changes in the solid phases as well as in the interstitial solution. The progress of cement hydration was determined by isothermal microcalorimetry (12) using a high sensitive microcalorimeter (0.3μW) through measuring the heat evolution rate either in a cement paste or in a very diluted suspension. The evolution of the interstitial solution was followed by the electrical conductivity, measured directly by a conductimeter.

A shearing method was used to monitor the evolution of mechanical properties of cement paste during setting. The yield shear (cohesion forces) was measured by applying a torque on a four fins moving body immersed in the paste following a procedure deriving of the one advocated by Legrand (14). The measuring range is between 0 and 0.12 MPa. The effect of a mechanical treatment on the reversibility of bonds created during setting was studied by submitting the paste to successive mixings under the same conditions as above.

Cement diluted suspensions :

For studying the time dependent changes of contact interactions between the particles in cement suspension, a particle size analyser CAPA-500/700 HORIBA was employed to follow the evolution of the particle size distribution. The cement suspension to be studied was prepared in a cell thermostated at 25°C with a W/C ratio equal to 300 for satisfying the conditions of use of the analyser. During the granulometric experiments the suspension was subjected continuously to a gentle mechanical stirring (to avoid sedimentation of solid) and periodically to an ultrasonic activation (during 30 seconds, power : 300W) using a VC 500 Sonics & Materials Inc. disintegrator. It is assumed that the ultrasonic treatment will break up "weak" contacts between particles ($<10^{-2}$ dyne), but not "strong" ones ($>10^{-1}$ dyne).

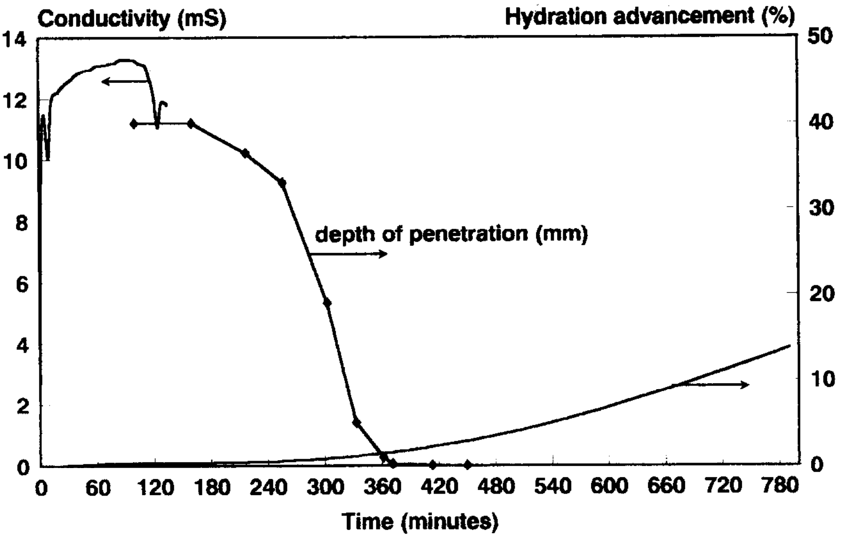

FIG. 1.
Chemical and mechanical evolutions versus time of SRPC paste (W/C=0.35) represented respectively by the electrical conductivity of the pore solution, the advancement of the hydration and the depth of penetration of the Vicat needle .

Results and Discussion

Characterisation of initial structure formation during setting of the cement paste

The mechanical evolution of SRPC paste is evaluated by the shear strength (MPa), while the chemical evolution is represented here by the advancement of cement hydration (%) determined from the heat flow following a procedure describe elsewhere (154).

The percentage of reaction for a paste of W/C=0.35 is given in Fig.1 with the electrical conductivity of the pore solution and the depth of penetration of the Vicat needle. The shear strength for the same paste was measured during the early stage of hydration (Fig.2). The comparison lead to distinguish the paste mechanical behaviour before and during the acceleration period of hydrates formation.

The earliest increase in cohesion appears when there is practically no hydrates formed (Fig.3), whereas the interstitial solution become rapidly an electrolytic solution as shown by the conductivity curve on Fig.1, because of the protonation-dissolution process of the surface of cement grains. In the case of pure alite, the lime concentration reaches rapidly 6 mmol/l after 1 min, and then continuously increases until 36 mmol/l after 120 min, with pH value as high as 12.6 (154).
The second increase in cohesion, which is more important, ranging between 0.01 and 0.1 MPa, corresponds to the acceleration of the hydrates formation (Fig.2). According to the Vicat test, this stage coincides with the setting of the paste (Fig.1). Moreover, as shown in Fig.4, the paste strength

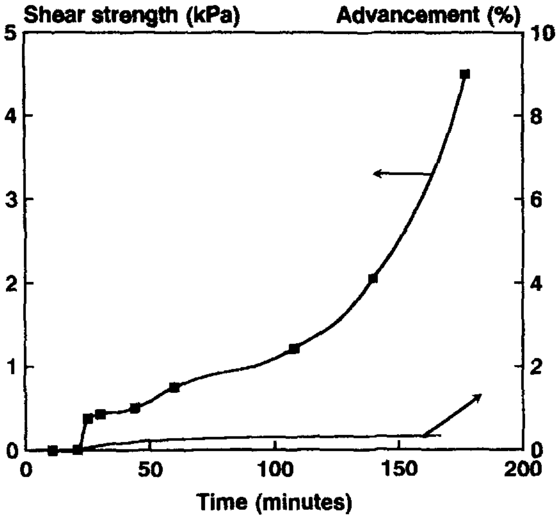

FIG. 2.
Evolution of the degree of hydration and the initial shear strength versus time of SRPC paste (W/C=0.35). The paste showes an initial shear strength even if hydration is only beginning.

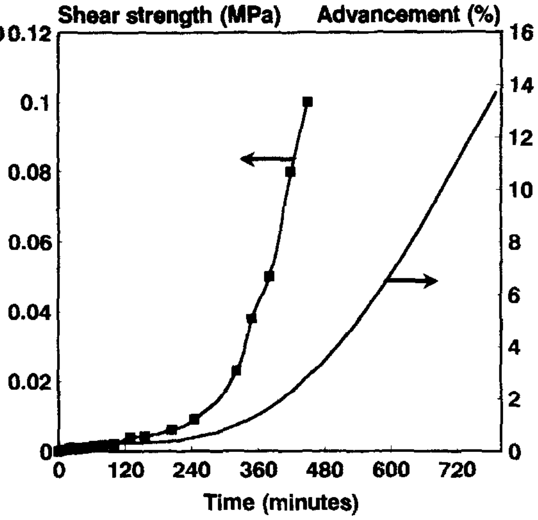

FIG. 3.
Evolutions of the shear strength and the degree of hydration versus time of SRPC paste (W/C=0.35) during the first 3 hours. The rapid growth of the shear strength coincid with the hydration acceleration.

in this second stage is proportional to the quantity of hydrates formed for a given W/C ratio. For a given percentage of precipitated hydrates, the smaller the W/C ratio, the more rigid the paste. It is noticeable that at the end of setting, the hydrates are very few, less than 2 and 4% at W/C = 0.3 and 0.5 respectively, so they have to precipitate near the contact zone for strengthening the cement grains network (165).

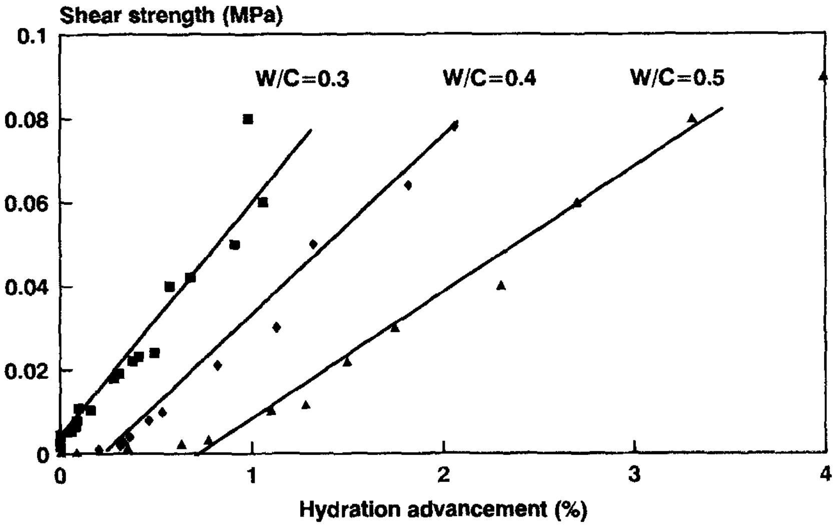

FIG. 4.
Evolutions of the shear strength growth versus degree of hydration of SRPC pastes with different W/C ratios.

In order to characterise the "structure" formed at these two stages, experiments of successive mixings of the SRPC paste in the same condition of initial mixing were carried out during 5 minutes at the end of each hour , and the shear strength was measured again after each mixing. The results are shown in Fig.5. During the first stage (between 0 and 4 hours), the mechanical treatment (i.e. mixing) of the paste destroyed the "structure" but the later is rebuilt afterwards in such a way that the shear strength evolution is identical, proving that the bonds involved, like bond due to Van der Waals forces, are mechanically reversible bonds. According to Shchukin's concept, this first stage corresponds to the formation of a coagulation structure, named coagulation stage. During the second stage (after 4 hours hydration), the degree of irreversibility increases as the cement hydration progresses, meaning that increases the number of non destroyed bonds or contacts by such a mechanical treatment (mixing), like chemical bonds. According to Shchukin's concept, this stage (named "agglutination stage" by the author) corresponds to the strengthening of the coagulated structure due to the formation of hydrates bridging the grains near their contact zones; we call it rigidification stage. The same experiment was also carried out in the paste of SRPC mixed with a supersaturated lime solution (30 mmol/l). In this case, the cement hydration reaction was retarded, thereby delaying the rigidification stage, and allowing well visualise the coagulation stage (see Figure 6).

Evidence of two types of contact interactions between particles responsible for the coagulation and rigidification phenomena

granulometric measurements :

In order to further clarify the fundamental processes of coagulation and rigidification during cement setting (or initial structure formation), we investigated the time dependent changes of contact interactions between particles. For this purpose, a granulometric method was adapted to follow the particles size evolution in the diluted suspension. If there exist the contact interactions between

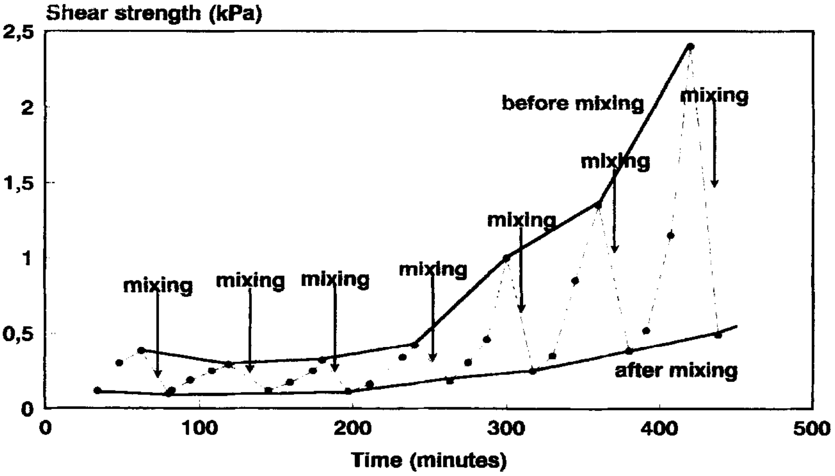

FIG. 5.

Effect of successive remixings in the same conditions of initial mixing on the shear strength evolution versus time of SRPC paste mixed in pure water (W/C=0.35). During the four first hours, a five minutes mixing is able to detroyed the structure, the shear stength is the same as initialy, which is rebuilt after mixing. After four hours, with a same mixing it is no more possible to recover the initial value of the shear stength, it is irreversibily increasing, showing the rigidification of particle contacts by hydrates.

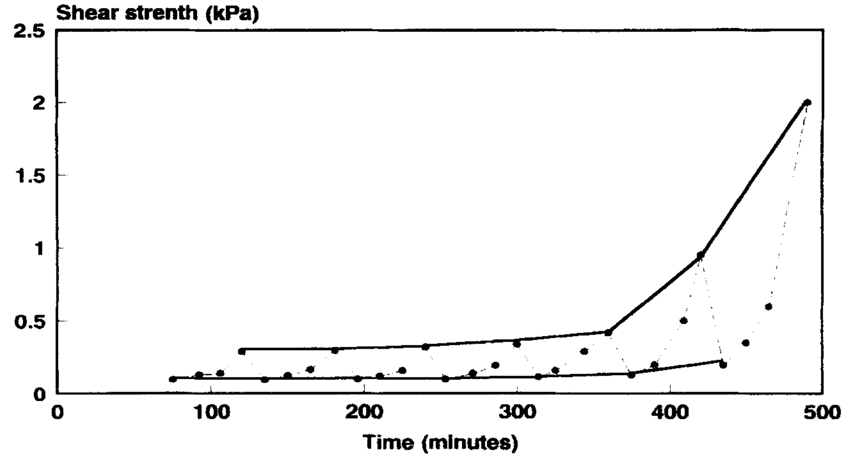

FIG. 6.
Effect of successive re mixing on the shear strength evolution versus time of SRPC paste mixed in initially supersaturated lime solution (W/C=0.35). The time during which the contacts between particles are mechanically reversible is growing longer due to the lengthening of the nucleation period.

particles, the agglomeration would take place. Agglomerates of several particles are registered as a single particle of a larger size. If the particles contact interactions are "weak", e.g. the coagulation contacts, then an ultrasonic treatment would break them up, producing a dispersing effect. Otherwise, if the contact interactions are "strong", such an ultrasonic treatment would be not able to break up the agglomerates. The method we used is similar to the one employed by Odler et al. (176)but with some modifications. Suspensions are less diluted (W/C=300 in place of 1000) and suspensions are

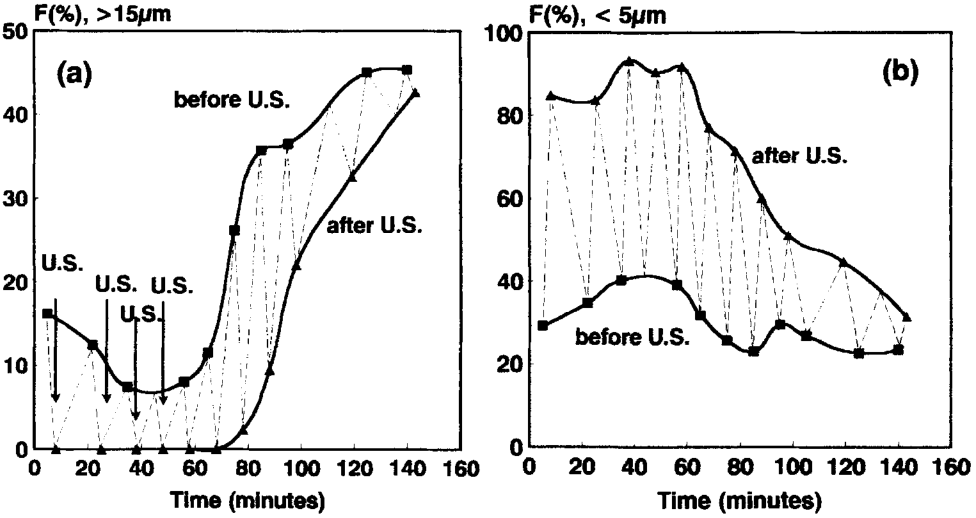

FIG. 7.
Evolution versus time of the finer (a) and the coarser (b) granulometric classes population of SRPC suspension mixed in initially saturated lime solution (W/C=300) which is periodically subjected to the ultrasonic treatment (U.S.).

made with lime solutions. Indeed, in a diluted suspension in pure water, the kinetics of cement hydration from beginning is fast and the percentage of hydrates formed is important (15,18). In order to simulate the particles contact interactions involved in the cement paste in which the pore solution rapidly becomes supersaturated with respect to portlandite, the diluted suspension should be prepared in lime saturated or supersaturated solutions. In such suspensions, the hydrates formation is retarded, and the chemical evolutions both in the solid phase and in the interstitial solution are similar to that of the cement paste (154).

The granulometric analyses were carried out on the SRPC suspensions (W/C=300, cement grains sieved to ≤ 40 μm) prepared in saturated lime solutions (22 mmol/l). The curves in Fig.7 show the evolution of the percentage of the coarser (a) and finer (b) particles in suspension, alternatively and periodically measured before and just after subjected to 30 seconds of ultrasonic treatment. Simultaneously, the electrical conductivity of the suspensions was followed and showed in the Fig.8 with the median diameter obtained after sonification. From these experiments, some interesting results emerge.

(i) According to the reversibility criterion, the coagulation stage and the rigidification stage can be clearly distinguished from the granulometric curves. The gap between the two kinetic curves respectively before and just after the ultrasonic treatment expresses the coagulation phenomenon, and their evolution with time reveals wether rigidification is occuring. During the coagulation stage, the ultrasonic treatment disperses the particles agglomerates, since the finer particles population increases to the detriment of the coarser ones. About 10 minutes after stopping the sonification, the population reverts to its original state, the particles agglomeration reappears, showing the mechanical reversibility of inter particles contacts (bonds). During the rigidification stage, the same ultrasonic treatment becomes less and less dispersive : the finer population continuously decreases as the

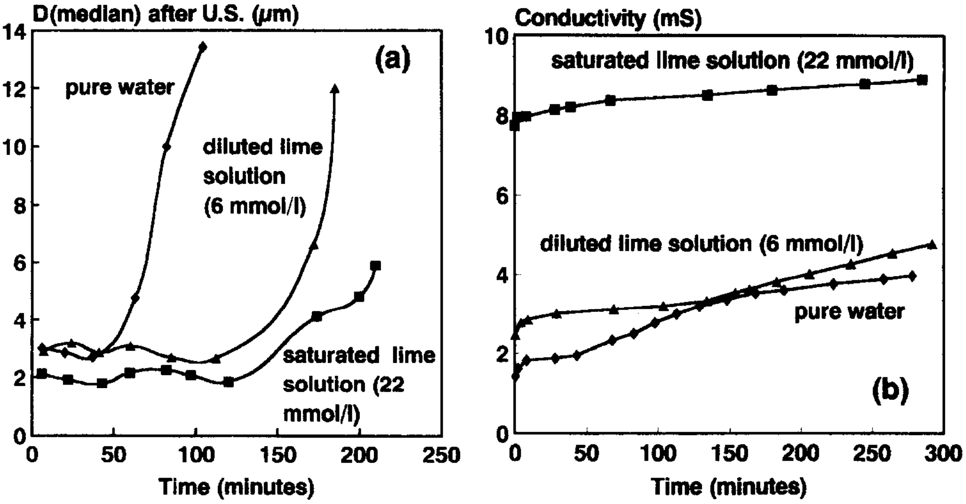

FIG. 8.

Evolution versus time of the median diameter measured after being periodically subjected to the ultrasonic treatment (U.S.)(a) and the electrical conductivity of the solution (b) in the case of SRPC suspensions initially mixed with pure water, 6 and 22 mmol/l lime solutions (W/C=300). The increase of the median diameter after U.S. due to the agglomerates rigidification coincids with the begining of the reincrease of electrical conductivity due to the acceleration of the hydrates formation.

coarser one increases, and the median diameter of the particles increases, showing the irreversibility of contact interaction between particles due to the hydrates bridging effect.

(ii) The agglomération of SRPC suspensions with the same W/C in different solutions, pure water and lime solutions,[CaO]= 0, 6 and 22 mmol/l respectively, are given Fig. 8. It can be noticed that the beginning of the rigidification stage coincides with the re-increase of the electrical conductivity (FIG. 8 (a) and (b)).The transition from the coagulation stage to the rigidification is retarded as the initial lime concentration in the suspension is increased (Fig.8 (a)). This is because the hydrates formation is retarded due to the decrease of the number of initial nuclei (154). On the other hand, in a very diluted water suspension, during the initial hydration the hydrates formation of which the rate is very high, is proceeding through nucleation/growth within the bulk solution, whereas after the re-increase in electrical conductivity (corresponding to the re-increase of lime concentration in the solution), the hydrates formation is proceeding as heterogeneous nucleation/growth on the surfaces of the anhydrous grains because the solubility of C-S-H is reduced. In the case of the lime-saturated suspension, the hydrates formed at the very beginning are very few and localised on the cement grains surfaces. These results lead us to conclude that during the cement setting, only the hydrates formed on the surfaces of anhydrous grains that become the bridging elements at their contact zones, making the coagulated structure rigid.

Sedimentation measurements :

It is also possible to point out coagulation phenomena in less diluted suspension by means of sedimentation measurements. Indeed a stable suspension, i.e. perfectly dispersed, slowly sediments, leading to a small settling volume. On the contrary, an unstable suspension i.e. in which particles agglomerate, rapidly sediments to give a large settling volume. So, we have carried out sedimentation measurements on less diluted SRPC suspensions (W/C=20). 5 grams of cement was put into 100 cm^3 of saturated lime solution (22 mmol/l). The suspension was mechanically stirred during 2 minutes before being introduced in a test tube (100 ml graduated cylinder). The settling volume was measured after 15 minutes of rest. A new cycle is conducted every 2 min of stirring and after 15 min of rest the settling volume is measured again. For the sake of comparison, the sedimentation measurements were also carried out using alcohol as liquid phase which is a good dispersing medium for cement. The figure 9 reports the results of the test which shows the evolution of the settling volume versus time. In the alcohol suspension, the sedimentation volume is small, the liquid above in the test tube is very cloudy. Both facts indicate that neither coagulation nor rigidification manifest between cement particles, as it is also demonstrated by the granulometric method. In the lime water

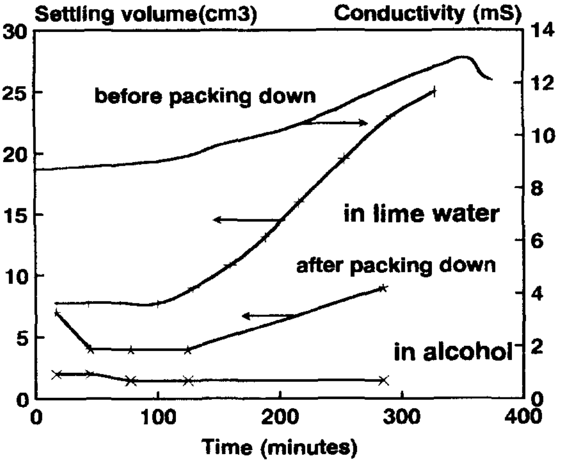

FIG 9.
Evolutions versus time of the electrical conductivity and of the settling volumes before and after packing down by a vibration treatment of the suspensions (W/C=20) in initially lime saturated solution. The settling volume of the same suspension in pure alcohol is also given for comparison. The coincidence between rigidification and hydration acceleration is also observed.

suspension, the settling volume from the beginning of the experiment is larger as compared to that in the alcohol suspension, and the liquid above in the test tube is very clear. These facts indicate that there are attractive inter particle forces between the cement particles leading to the formation of agglomerates. Such coagulated structure can be established again after each mechanical dispersion occurring during the stirring. After 100 minutes, the cement hydration is accelerated (as indicated by the conductivity curve in Figure 9), the settling volume increases progressively. The nature of the particles interactions in the sediment may also be clarified by submitting it to a mechanical treatment such a vibration using a vibration table (50 Hz frequency, 1 mm amplitude). During the first 100 minutes, the settling volume can be reduced to such as 2 cm by the vibration treatment showing the reversibility of contact interactions between particles, e.g. coagulation contacts. After 100 minutes, the settling volume can be less and less reduced by the same vibration treatment, showing the irreversibility of contact interactions between particles, due to the hydrates bridging effect. Also in this case, the hydrates which formed near the contact zones make rigid the inter particles contacts, thus increasing the dimension of agglomerates.

Conclusion

In this paper, the initial mechanical evolution of the cement paste and the contact interactions between particles in the cement suspension have been studied in relation with the chemical evolution of the system. In so doing, the hydration-setting relationship is more precisely established, and the role of the hydrates during the initial structure formation and the setting is more precisely identified.

The structure formation and the setting process of the cement paste can be characterised as two fundamental processes : coagulation and rigidification.
After the cement and water are mixed, whatever the W/C ratio ranging from 0.3 to 300, a weak and thixotropic coagulation network is formed which is proved to be mechanically reversible. The continuity of behavior from paste to diluted suspensions shows that contrary to the ideas of Schukin and al.(19), coagulation contacts between particles do not result from an internal stress in the paste, but from attractive particle interactions existing in paste and very diluted suspensions as well, they are due to the electrolytic nature of the pore solution and are at the origin of what Powers defined as the flocculated structure of cement paste (20). Setting is due to the rigidification of the connex network of coagulated cement grains and not to the bridging of disperse particles by hydrates .
The rigidification of the coagulated structure is provided by formation of hydrates near the contact zones, it can then occurs with only a weak hydration percentage. The rigidified structure becomes mechanically more and more irreversible, and the increase of paste strength at this stage is proportional to the quantity of precipitated hydrates. Forces at the origin of cohesion between particles are not yet perfectly known but the rigidification phenomenon which leads to the cement paste setting is also effective in very diluted suspension. In such conditions, the very great excess of water dismisses the role of drying in the cohesion between particles as it has been suggested (21).

The conditions and the influencing physico-chemical parameters on the cement setting can be identified from the studies of the coagulation and rigidification processes. The granulometric method used in this study proved to be a simple and efficient method for simulating the cement setting process, by studying the contact interactions (agglomeration) between the particles in diluted suspensions. The coagulation and the rigidification processes can be identified from the two kinetic granulometric curves. The fact that the diluted suspension can be adapted to the cement setting studies allows us to manage the parameters acting on the contact interactions by modification of either the surface of the grains or the surrounding interstitial solution. The studies on physico-chemical parameters determining the coagulation and the rigidification processes will be reported in the second and the third part of this work.

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