Pergamon

Cement and Concrete Research, Vol. 26, No. 3, pp. 491-500, 1996
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0008-8846/96 $15.00 + .00

PII S0008-8846(96)00005-1

STUDIES ON MECHANISM AND PHYSICO-CHEMICAL PARAMETERS AT THE ORIGIN OF THE CEMENT SETTING

II. PHYSICO-CHEMICAL PARAMETERS DETERMINING THE COAGULATION PROCESS

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(Refereed)
(Received March 7, 1995; in final form November 27, 1995)

ABSTRACT

The physico-chemical parameters determining the coagulation of cements grains previously identified as the first fundamental process of cement setting have been investigated in diluted suspensions using an adapted granulometric method. The analysis of the influence of the ionic concentration in solution on the coagulation reveals that calcium concentration is the parameter which determines the particle interactions. There exists a minimum critical concentration of calcium ions in solution which is required to occur the coagulation of cement particles and a dispersive effect appears for very high concentrations. The results are discussed in relation with DLVO theory and specific interactions.

Introduction

In the first part of this paper (1), it was shown that the cement setting processes through two fundamental stages. The first one, the coagulation of cement grains, is at the origin of the essential contacts between particles and leads to the formation of a mechanically reversible connected network. During the second one, what we call rigidification, hydrates precipitating near the contact zone strengthen the structure resulting from coagulation leading to a mechanically irreversible network of particles. It was also demonstrated that two fundamental processes responsible for setting in paste can be studied in diluted suspensions as well (W/C = 20 and 300). The fact that setting can be studied with a wide variation of W/C ratio opens the possibility to evaluate the physico-chemical parameters determining the cement setting behaviour.

In this second part, we focuse on the first stage of setting, i.e. the coagulation process, which implies the emergence of coagulation contacts between the solid particles in a dispersed solid-liquid system. Taking into account the fact that the suspension is reactive and that the solution becomes readily an electrolytic one with quite high ionic strength, we investigate especially by the previously defined method (1), the effect of the variation of the ionic constitution of the solution on the establishment of such coagulation contacts from a dispersed cement particles system. The material used in this study is a calcium silicate based cement leading to Ca^{++}, OH^-,

TABLE 1

Chemical and Mineralogical Compositions 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	CS	CaO_{free}
63.7	18.3	3.8	7.0	3.6	1.2

$H_2SiO_4^{--}$ ions in solution. Experiments were conducted in order to change their respective concentrations. A mechanism of coagulation in the cement-water binding system is proposed.

Experimental

A silica-rich Portland cement was used for the investigations (supplied by Ciment Larfarge), referred to as SRPC. The chemical and mineralogical compositions are given in the Table 1.

To determine the effect on the coagulation of non-aqueous liquid and the role of the ionic concentration in the aqueous ionic solutions, diluted suspensions were prepared in pure ethanol as liquid phase, in pure water and lime solutions, in sodium metasilicate solutions and in calcium chloride solutions. The calcium concentration in the pore solution is fixed by the solubility of the portlandite in the absence of extra silicate ions, and ranges from a few mmol/l to 36 mmol/l depending on the pH value. The addition of silicate ions lead to very low calcium concentrations and the addition of calcium chloride leads to calcium concentration higher than 36 mmol/l.

The chemical evolution of the suspensions was followed by recording the heat evolution of cement hydration, using an isothermal micro calorimeter especially adapted to study diluted and stirred suspensions (2,3) and by measuring simultaneously or independently the electrical conductivity. Some analyses of calcium and silicate ions in solution during the course of the experiments have been made by atomic absorption spectrometry.

A granulometric method was adapted as described in detail in part I of this paper (1), to follow the particles agglomeration through measuring the particle size distribution in suspension (W/C = 300, cement grains sieved to < 20 μm) before and after submitting it to an ultrasonic treatment. According to the reversibility criterion, the coagulation stage can be clearly identified from the granulometric curves as shown on Fig. 1. During the coagulation stage, particles agglomerate giving a large population of apparent coarser particles (agglomerates) and respectively a small population of finer particles; an ultrasonic treatment of such a coagulated suspension destroys the agglomerates and thus the population of the finer particles increases and the population of the coarser decreases (or the equivalent mean diameter decreases).

Results

Suspensions of Cement Dispersed in Pure Alcohol. The granulometric curves obtained in the diluted alcohol suspension of SRP cement are presented in Figure 2. They show that after an

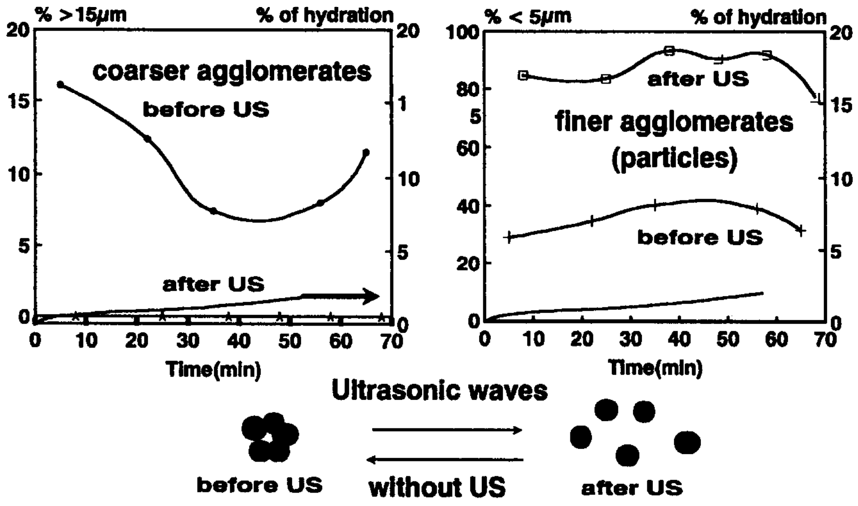

FIG. 1.

Coagulation-dispersion process studied by granulometric measurement associated with an ultrasonic treatment.

initial dispersion of the solid particles by the ultrasonic treatment, the particles were disagglomerated and not agglomerated again in the sequel. The same results were also obtained in the C_3S suspension (4). It is evident that no coagulation contacts manifest between solid particles in this non aqueous solution. The micro calorimetric and conductivity measurements reveal that no

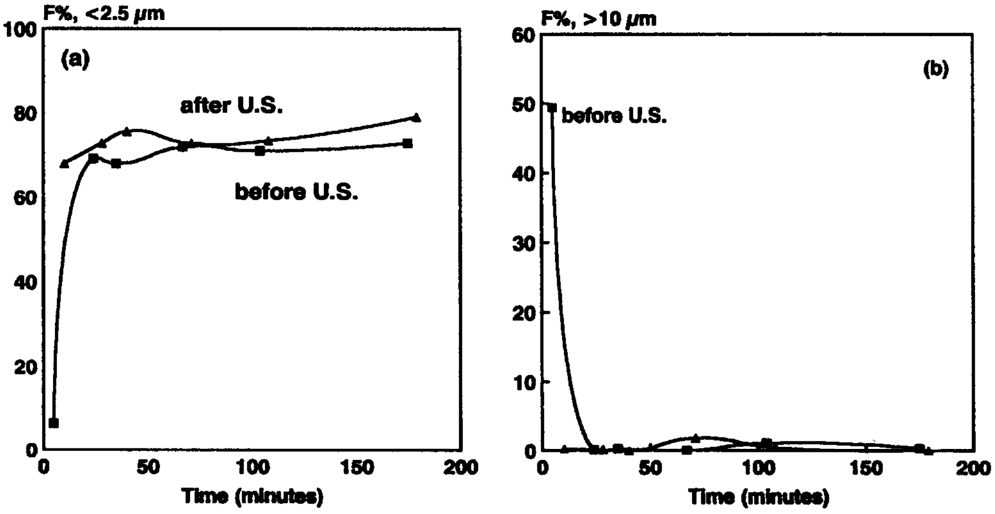

FIG. 2.

Granulometric curves obtained in diluted alcohol suspension (w/c = 300) of SRPC subjected periodically to sonication: evolution of the percentage of (a) the finer particles (< 2.5μm) and (b) the coarser (> 10 μm).

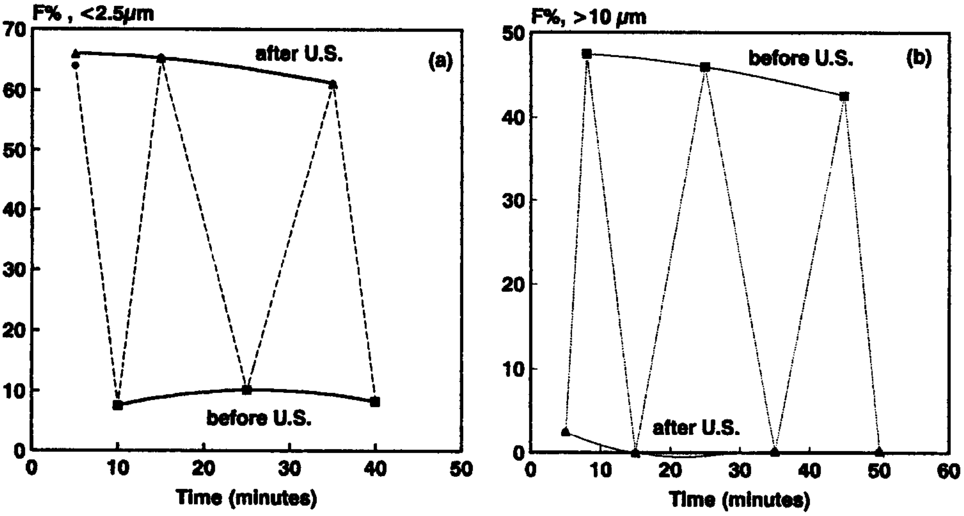

FIG. 3.

Evolution versus time of the finer (a) and the coarser (b) granulometric classes population of a SRPC ($\phi < 20$ μm) suspension mixed in water (W/C = 300) which is periodically subjected to an ultrasonic treatment.

dissolution and hydration reactions occur in such a system. It seems thus that an aqueous ionic solution should be used in the cement binding system to induce the coagulation contacts.

Suspensions of Cement Dispersed in Pure Water and in Lime Solutions. The curves of the figure 3 and 4 show the populations evolution versus time, of the granulometric classes ranged between 0–2.5 μm and > 10 μm before and after the ultrasonic treatment, in pure water and in a saturated lime solution respectively. After the anhydrous cement was mixed in pure water (Fig. 3) or in saturated lime solution (Fig. 4), the cement particles are in a coagulated state, since the particles are agglomerated before sonication and dispersed by sonication then agglomerated again showing the mechanical reversibility of the inter particular bonds. In these cases, the mean diameters of the apparent particles (agglomerates) before and after coagulation are 2 and 6 μm respectively. In these conditions during the experiments, the silicate concentration in solution is very low, less than 1 mmol/l, the lime concentration varies between few mmol/l and 22 mmol/l.

Suspensions of Cement Diluted in Sodium Metasilicate Solutions. A method to lower calcium concentration in solution is to increase silica concentration, according to the equilibrium solubility limits of CaO and SiO_2 determined in studies of the system $CaO\text{-}SiO_2\text{-}H_2O$ (4). For this purpose, sodium metasilicate solutions $Na_2SiO_3.5H_2O$ were used. The curves of Fig. 5 were obtained in diluted suspensions made with sodium metasilicate solutions of different concentrations, 5, 10, 20 and 30 mmol/l respectively. The gap between the median diameters of particles or agglomerates before and after the ultrasonic treatment decreases as the concentration of sodium metasilicate solution of suspension increases, which implies that the

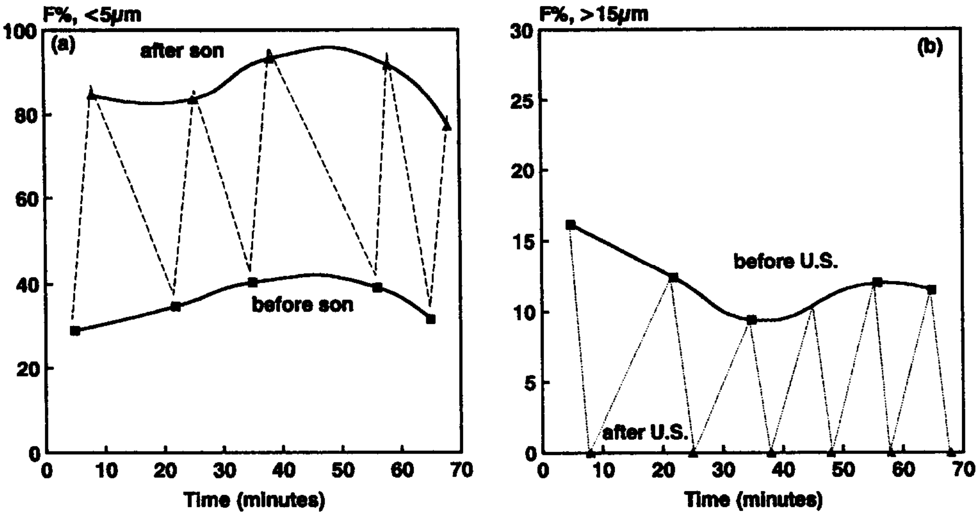

FIG. 4.
Evolution versus time of the finer (a) and the coarser (b) granulometric classes population of a SRPC ($\phi < 20$ μm) suspension mixed in a saturated lime solution (W/C = 300) which is periodically subjected to an ultrasonic treatment.

coagulation contacts between the cement particles are less and less important; the suspension becomes completely dispersed when the initial silicate concentration reaches 30 mmol/l.

The calcium and silica concentrations left in the filtrate of above suspensions were measured by atomic absorption spectrometry. The Table 2 gives the results of dosage after 90 min and 210 min of hydration in the diluted suspensions (W/C = 300). From these data, it can be seen that calcium and silica concentrations do not vary very much during the experiments and that low calcium concentrations in solution are actually associated with high concentrations of silica.

Suspensions of Cement Dispersed in Calcium Chloride Solutions. Calcium chloride solutions were used to reach initial calcium concentrations greater than the super solubility of portlandite. Experiments were performed on suspensions in calcium chloride solutions with calcium concentrations reaching 1.5 mol/l. The curves on Fig 6 show that the coagulation of particles is more difficult when the $CaCl_2$ concentration is high since the equivalent mean diameter of agglomerates before sonication is smaller than in low concentration solutions. It seems that this effect is due to calcium ions and not to chloride ions. Indeed, the same experiment made in a 2 mol/l NaCl solution lead to an initial equivalent mean diameter greater than in a 1 mol/l $CaCl_2$ solution (see Fig. 7).

Discussion

Influence of the Chemical Medium on the Coagulation Process. Experiments in pure alcohol prove that the coagulation cannot occur without ionic species in solution and/or hydrates provided by the hydration of cement. In pure water, the coagulation quickly occurs; with the

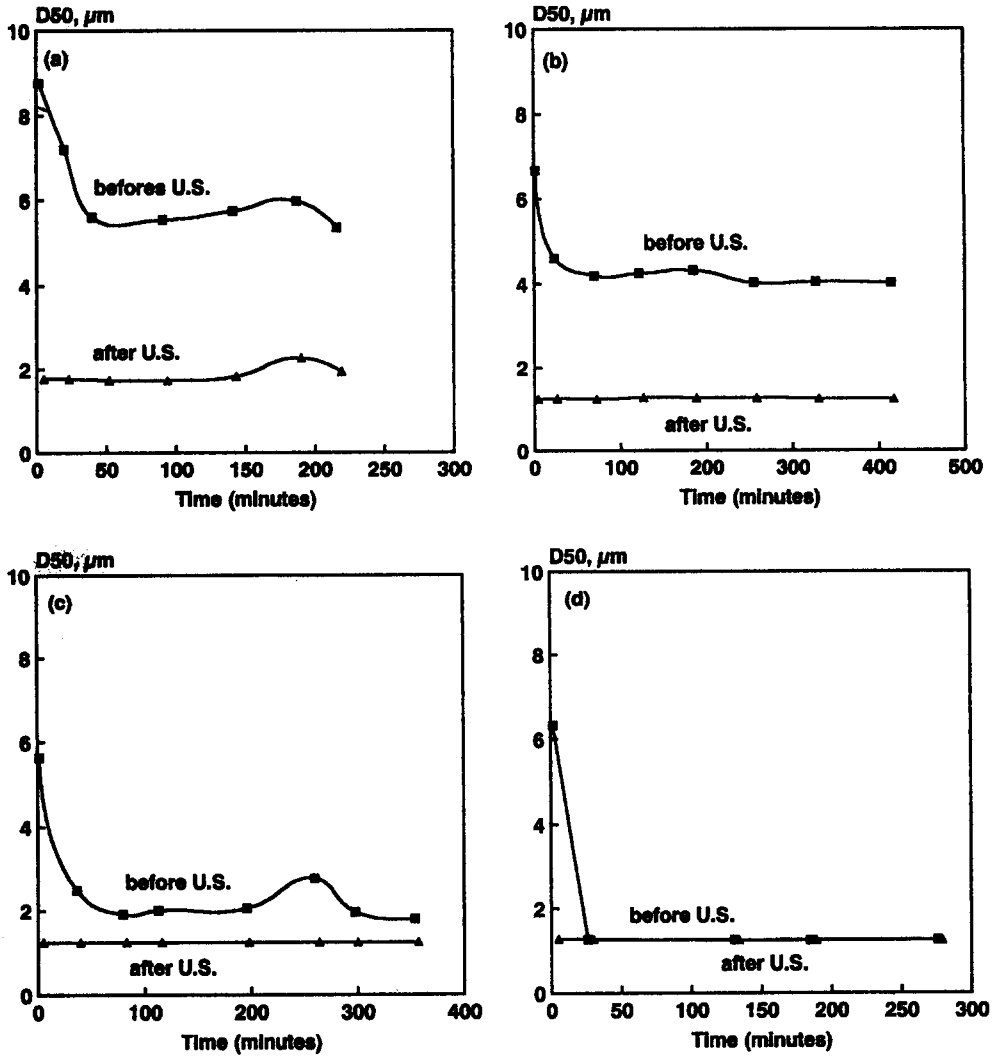

FIG. 5.

Evolution versus time of the median diameter of SRPC ($\phi < 20$ μm) suspensions mixed in 5 (a), 10 (b), 20 (c) and 30 (d) mmol/l $Na_2SiO_3.5H_2O$ solutions (W/C = 300) which are periodically subjected to an ultrasonic treatment.

water to cement ratio used in our experiments (W/C = 300), the calcium concentration rapidly rises and goes up 6 mmol/l and the degree of hydration reaches more than 20% in the first minutes. For a calcium concentration in the same order of magnitude, in a saturated lime solution (22 mmol/l), the coagulation also occurs while there are practically no C-S-H (< 0.1%) formed before one to two hours (5). In the other hand, in the silicate solutions in which calcium concentration is very low, assuming that the diminution of silica concentration (Table 2) is the consequence of the precipitation of C-S-H (with C/S = 1), the percentage of precipitated C-S-H

TABLE 2

Si and Ca Concentrations for Solutions Filtered from Suspensions Made with 4 Different Concentrations of Sodium Metasilicate Solution, W/C = 300

	[Si] mmol/l	[Ca] mmol/l
Sample 1		
0 min	4.7	/
90 min	3.78	0.58
210 min	2.35	0.64
Sample 2		
0 min	9.85	/
90 min	9.40	0.30
210 min	9.32	0.23
Sample 3		
0 min	18.96	/
90 min	18.07	0.056
210 min	17.88	0.038
Sample 4		
0 min	28.95	/
90 min	28.20	0.016
210 min	28.15	0.020

reaches about 3% without coagulation of particles. Thus we conclude that hydrates formation is not a necessary condition for the emergence of coagulation. So, one can think that change in ionic concentration, mainly [Ca^{2+}], in the surrounding solution may play a determining role in appearance of the coagulation process.

We have plotted on Fig. 8, the value of the median particle diameter (D_{50})of the agglomerates after the first coagulation, versus the initial calcium concentration in solution. The curve shows a bell shape pointing out the importance of the calcium ions in the coagulation process. Coagulation only occurs if a sufficient calcium concentration in solution is reached (> 0.1 mmol/l), and tends to be less effective if the calcium concentration is greater than 100 mmol/l. However, it should be noted that the low calcium concentrations as well as the high ones are only obtained by addition of extra ions, sodium silicates and chlorides respectively. Althougt we have checked that the chloride do not have a dispersive effect,we are not sure that silicate ions by themselves might not have an effect.

Mechanisms of Coagulation. From the above results, it is reasonable to think that the coagulation process of cement particles is mainly determined by calcium ions, and it seems that there exists a minimum critical concentration of calcium ions in solution which is required to occur the coagulation of cement particles.

Several possible mechanisms may be considered (6). The first one relies on the DLVO theory. In such systems, an electric double layer is developed near the surface of solids in contact with electrolytic solution and the stability of the suspension depends on the combination of long-range repulsive forces caused by the overlap of double layers and the short-range attractive van der Waals forces. Coagulation occurs as soon as attractive forces are greater than electrostatic repulsive forces. According to DLVO theory, the latter are the lowest when the zeta

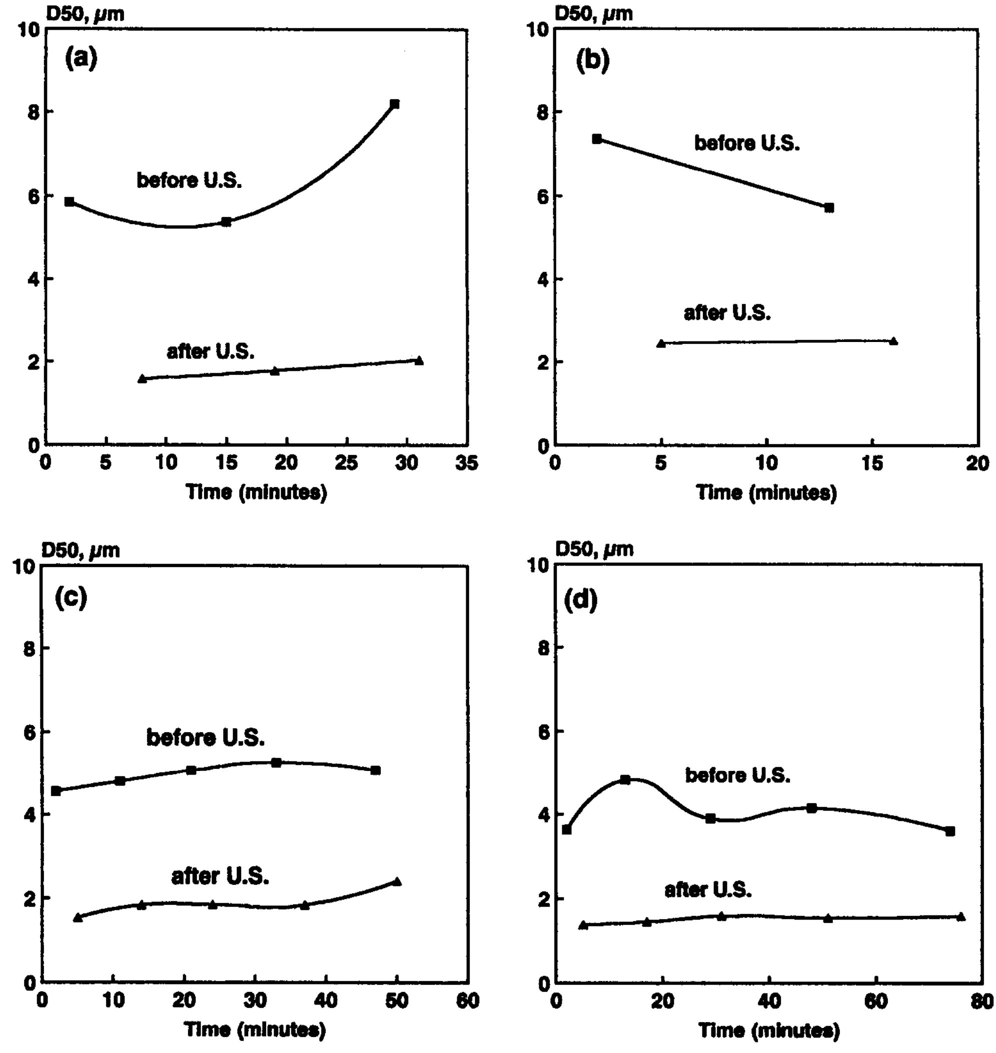

FIG. 6.

Evolution versus time of the median diameter of SRPC (Ø < 20 μm) suspensions mixed in 20 (a), 100 (b), 1000 (c) and 1500 (d) mmol/l $CaCl_2$ solutions (W/C = 300) which are periodically subjected to an ultrasonic treatment.

potential is equal to 0 and it is generally considered that coagulation may occur when -25 mV $\leq \zeta \leq +25$ mV. The dependence of the coagulation phenomenon with the calcium concentration seems to be in agreement with such a mechanism. The protonation-dissolution process of hydration of C_3S leads to a surface negatively charged and calcium and OH^- ions in solution (6); zeta potential likely depends on calcium concentration in solution. This is supported by experiments due to Stein on unreactive anhydrous and hydrated calcium silicates (7) for which the zero potential is found for a calcium concentration ranging from 1 to 4 mmol/l, values which are not far from those obtained by Tan and Roy from cement particles hydrated in water-organic

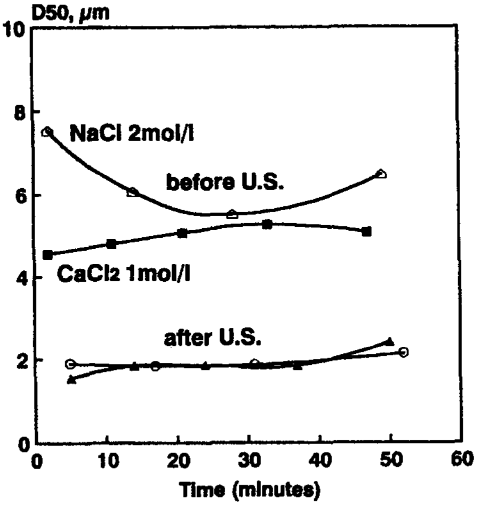

FIG. 7.
Evolution versus time of the median diameter of SRPC (Ø < 20 μm) suspensions mixed in solutions with a same 2 mol/l chloride concentration, 2 mol/l NaCl and 1 mol/l $CaCl_2$, which are periodically subjected to an ultrasonic treatment.

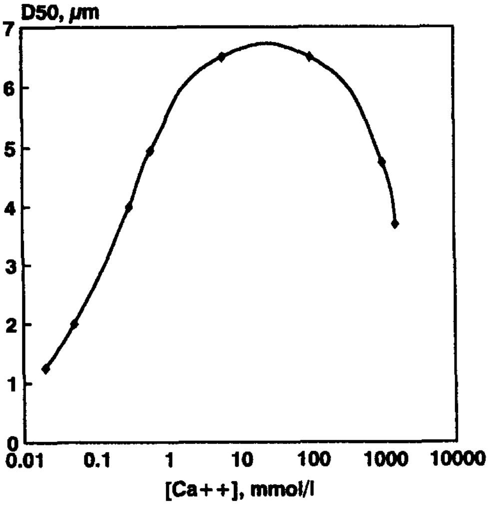

FIG. 8.
Variation of the median diameter of the agglomerates after coagulation versus the initial calcium concentration in solution.

mixtures (8). However, one should bring in mind the dynamic character of cement interfaces by repeating sequences of the superficial hydroxylation and dissolution (9): the interface is always out of thermodynamic equilibrium and the ionic strength in solution changes during hydration (10) and is rather high. This is a limitation of the DLVO theory.

The second possible mechanism involves the calcium ability to bridge particles as it has been proposed for the coagulation of colloidal silica (11) and aqueous TiO_2 suspensions (12). In this case, coagulation may occur for calcium concentrations below the value required by DLVO theory for an ionic strength effect and charge screening and different from the zero potential. Coagulation could result from electrostatic interactions between $SiOCa^+$ sites of one particle due to the chemical binding of calcium ion to negative surface sites (13), and SiO^- sites of another particle.

In the third mechanism, attractive forces would be due to hydration forces. At small separation between surfaces, below few molecular diameters, the discrete molecular nature of the solvent cannot be ignored and the short distance intermolecular pair potential can be quite different from that expected from continuum theories (13). The short range hydration forces between smooth rigid surfaces is always oscillatory due to the ordered layering of water molecules bound to hydrated surface groups. They can exceed the van der Waals force at separation below a few molecular diameters. Hydration forces are generally repulsive solvation forces but they can be attractive at short separation distance. In a suspension of hydrating cement grains it can be believed that there is a stratification of calcium hydrated ions near these surfaces at the origin of short-range attractive forces between particles.

Conclusion

By using the granulometric method, the physico-chemical parameters susceptible to influence the coagulation process were analysed in suspensions. It is shown that the coagulation of cement particles in the cement binding system is mainly determined by calcium ions. A minimum critical concentration of calcium ions in solution seems to be required to coagulate cement particles. In the case of cement paste, the coagulation conditions seem to be rapidly obtained. The increase from 0 to 6 mmol/l of the Ca^{++} concentration in the interstitial solution during the first minutes following the mixing should go beyond the minimum critical value. Different mechanisms of coagulation are proposed. In order to identify particle interactions responsible for coagulation, investigations on the electokinetic properties of the hydrating suspensions and the interaction forces between particle surfaces are in progress, they will be reported in a forthcoming paper.

Acknowledgments

The authors wish to thank the "Association Technique de l'Industrie des Liants Hydrauliques" and the "Conseil Régional de Bourgogne" for the financial support.

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