
Chemistry of Colloidal Silicates and Cements [and Discussion]

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Chemistry of colloidal silicates and cements

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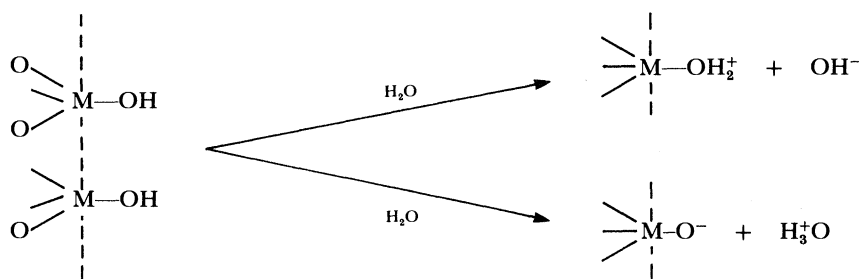
During the hydration of cement, colloidal particles are formed in the aqueous environment between the aggregate units. Their subsequent behaviour depends on the chemical nature of the particles and the additives present in the system. A review is given of the properties of colloidal particles likely to be present in the cement paste and the manner in which their properties are likely to influence the ultimate behaviour of the material.

1. INTRODUCTION

In the hydration of cement, reactions at interfaces must play a major role in determining the subsequent chemistry that occurs and ultimately the strength of the composite material formed. Moreover, the reactions that occur lead to the formation of colloidal particles and these also play an important part in the setting and ageing process (Taylor 1966; Double *et al.* 1978). Although the systems involved are complex, it is of considerable interest to examine this subject from a fundamental viewpoint to see whether this approach can provide guidance in the interpretation of existing phenomena and suggest how modifications might be made to produce materials with new properties. In this paper some of the salient points of the colloidal chemistry of inorganic materials are summarized and suggestions are made as to their applicability to cement hydration.

2. BEHAVIOUR OF OXIDE SURFACES

It is a general property of most oxide surfaces, if not all, that on contact with water, hydrolysis occurs leading to the formation of surface hydroxyl groups. The latter can then react with water to form either negatively or positively charged surface groups. This can be represented schematically in the following way:



Since at the surface there are many charged groups per unit area it acquires an electrostatic potential, ψ_0 , relative to the bulk solution (earth). To maintain the condition of electro-neutrality, the charge on the surface has to be compensated by an equal and opposite charge in the solution phase. Thus, ions of opposite charge to the interfacial charge (counter-ions) are attracted towards the surface (positively adsorbed), while ions of opposite charge to the surface (co-ions) are repelled (negatively adsorbed). The distribution of ions in this region close to the

surface, the so-called diffuse electrical double layer, is given by the Boltzmann equation (Verwey & Overbeek 1948). On the basis of this simple model, for a planar interface with $\psi_0 < 25$ mV, the potential in the solution phase at a distance x from the surface is given by

$$\psi_x = \psi_0 \exp(-\kappa x).$$

The parameter κ is directly related to the electrolyte concentration in the bulk phase by the relation

$$\kappa^2 = 2n_0 v^2 e^2 / \epsilon_r \epsilon_0 k T,$$

with n_0 = the number of ions of each kind per unit volume of the bulk phase, v = the magnitude of the valency of the ions, assuming a symmetrical electrolyte, ϵ_r = the relative permittivity of the solution phase and ϵ_0 that of free space; k = the Boltzmann constant and T = absolute temperature.

The quantity, κ , which has dimensions of reciprocal length, is important in that it moderates the fall off of potential with distance from the surface, i.e. when $x = 1/\kappa$, then $\psi_x = \psi_0/e$. Hence at low electrolyte concentrations, for example 10^{-5} mol dm $^{-3}$, 1:1 electrolyte, $1/\kappa \approx 100$ nm and at 0.1 mol dm $^{-3}$, $1/\kappa \approx 1$ nm. The effect of the electric field from the particle extends to a distance of the order of $2/\kappa$, so that in 10^{-5} mol dm $^{-3}$ electrolyte the fields of two particles overlap when their surfaces are separated by a distance of the order of 400 nm, a long range interaction; whereas in 0.1 mol dm $^{-3}$ electrolyte the range of the interaction is two orders of magnitude smaller.

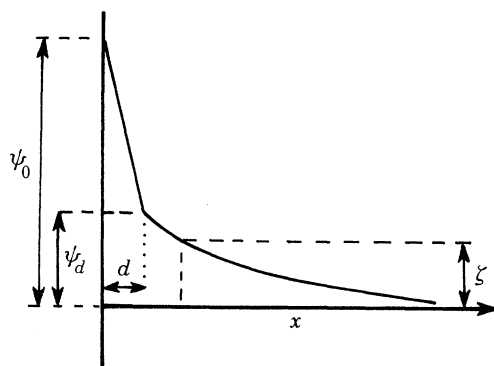


FIGURE 1. Schematic illustration of the electrical double layer.

A more sophisticated model of the electrical double layer includes the possibility of some counter-ions adsorbing in a layer adjacent to the charged surface and at a distance d from it, to form the so-called Stern layer (Stern 1924; Verwey & Overbeek 1948). The potential distribution on this basis is given in figure 1. There is now a linear drop between the surface and the inner layer followed by an exponential decrease with distance into the solution phase. The potential ψ_d is not easy to determine, but a quantity closely approaching it in magnitude, the zeta-potential, ζ , can be measured by electrokinetic experiments (Kruyt 1952). One of the simplest methods is to determine the electrophoretic mobility, u , by observing the movement of a particle, microscopically or ultramicroscopically, in an electric field (Hunter 1981). Then u is related to ζ by the expression (Wiersema *et al.* 1966)

$$u = (\epsilon_r \epsilon_0 \zeta / \eta) f(\kappa a, \zeta),$$

where η = the viscosity of the medium and $f(\kappa a, \zeta)$ is a numerical factor, which can be obtained from the literature (Ottewill & Shaw 1972; O'Brien & White 1978).

Some results obtained from silica and alumina particles as a function of pH in 10^{-3} mol dm $^{-3}$ sodium chloride solution are shown in figure 2 (Ottewill & Holloway 1975). These show clearly that the charge at the surface of a silica particle is negative over a wide pH range and becomes increasingly negative as the pH is increased, i.e. it behaves as an acidic oxide. Alumina particles, however, are positively charged at pH values below *ca.* 9.0, and negative above this; alumina behaves as a basic oxide.

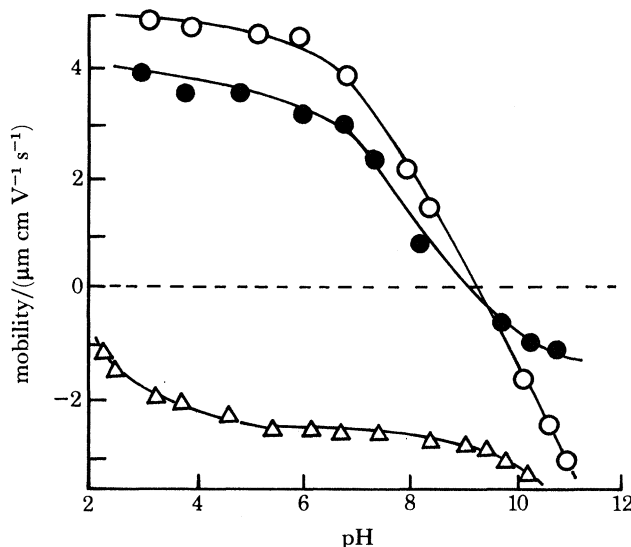


FIGURE 2. Mobility against pH. Key: Δ , silica in 10^{-3} mol dm $^{-3}$ sodium chloride solution; \circ , alumina in 10^{-3} mol dm $^{-3}$ sodium chloride solution; \bullet , alumina in 10^{-1} mol dm $^{-3}$ sodium chloride solution.

Figure 2 also shows the effect of electrolyte concentration on the electrophoretic mobility of alumina. Increasing the concentration of sodium chloride decreases the electrophoretic mobility, and hence the magnitude of ζ , by compression of the electrical double layer.

3. EQUILIBRIA BETWEEN SURFACE AND SOLUTION

In examining the properties of a surface, particularly oxides as a function of pH, it is important to consider also the solution species that are likely to be in equilibrium with the surface. For many systems, stability constants are available (Martell & Sillen 1964) and hence solubility diagrams can be constructed. Examples of these are shown in figures 3 and 4 for three of the possible components of cement paste, silica as quartz (Stumm & Morgan 1970, pp. 395, 396), alumina (Gayer *et al.* 1958) and calcium hydroxide (Stumm & Morgan 1970, pp. 168, 169). From these diagrams it is clear that silica in the pH range of interest in cement pastes, 12.5–12.7 (Birchall *et al.* 1978), is appreciably soluble and that its solubility increases rapidly with pH above pH 10.0. Several silicate species also exist in solution and in addition the possible presence of polymeric species cannot be excluded since the rate of attainment of equilibrium in these systems is often slow (Iler 1979). Alumina particles are soluble in both acid and alkaline environments and it should be noted that the minimum solubility occurs at a pH of *ca.* 7.5, quite close to the isoelectric point (see figure 2). In fact, a close correlation exists between the

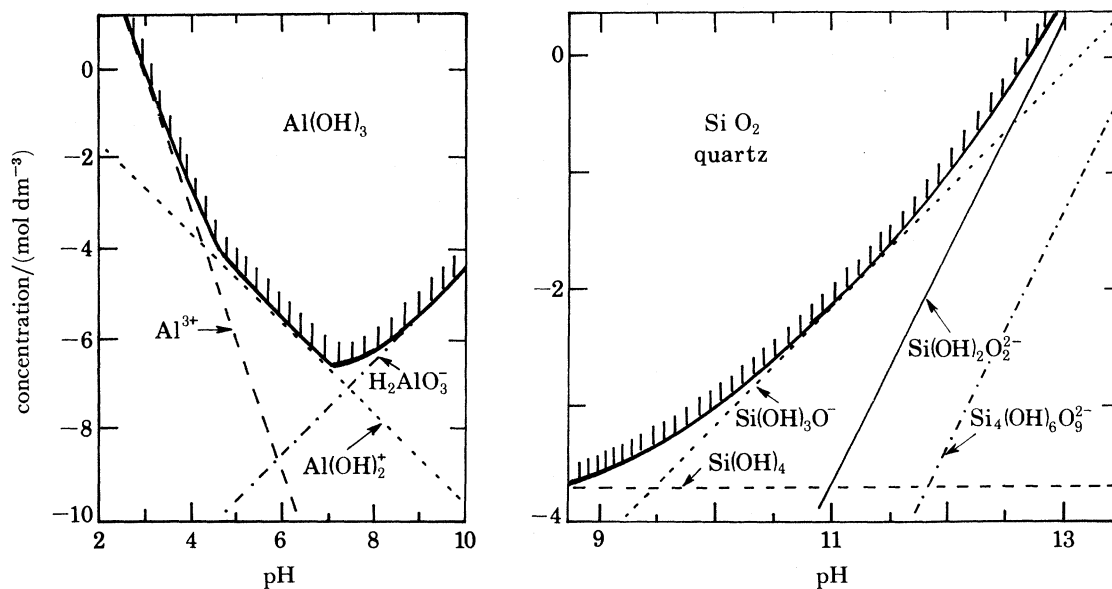


FIGURE 3. Solubility diagrams for alumina and quartz. (Logarithmic ordinate.)

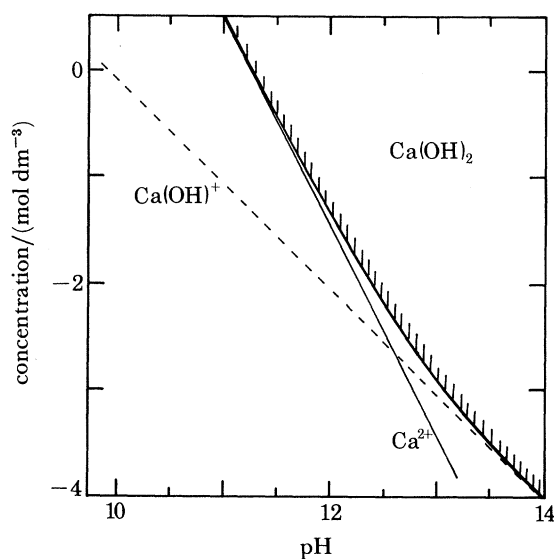


FIGURE 4. Solubility diagram for calcium hydroxide. (Logarithmic ordinate.)

solid solution equilibrium and the surface properties (Parks 1965; Stumm & Morgan 1970, pp. 474–493). The diagram for calcium hydroxide is an interesting one in that it shows, contrary to silica, a decreasing solubility as the pH increases and the presence of both Ca^{2+} and $\text{Ca}(\text{OH})^+$ in the region of interest.

4. ION EXCHANGE AT SURFACES

The simplest possible form of ion exchange is that between ions in the diffuse electrical double layer and the solution phase. If the ions have the same valency this occurs in direct proportion to their concentrations in the bulk phase. Exchange of a 2+ ion for a 1+ ion, however, is

always in favour of the higher valent counter-ion because of the larger electrostatic factor, and hence is also dependent on the electrostatic potential (Kruyt 1952). Such exchange processes are non-specific in the chemical sense and are seldom found in practice.

To introduce specific effects, ion-exchange processes in the inner part of the double layer must be considered, and a chemical free energy of interaction with the surface introduced, in addition to the electrostatic term. The interaction of the adsorbed ion with the surface varies from simple electrostatic attraction to chemical bonding. In some cases the chemical reaction can be sufficiently extensive that metathesis occurs and the surface becomes coated with a layer of a new chemical compound.

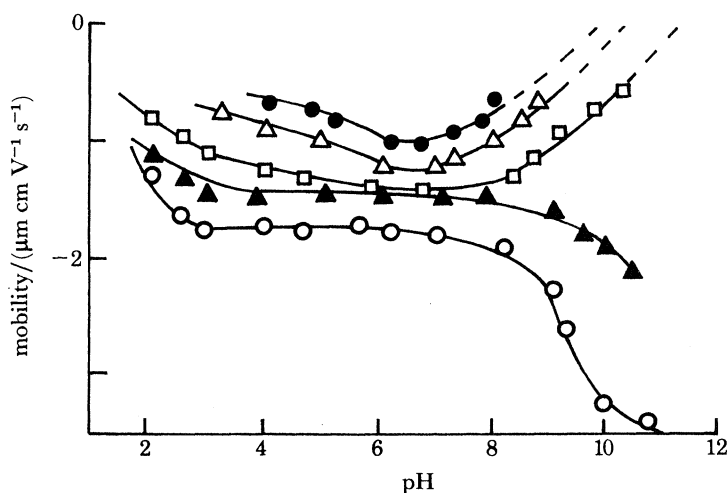
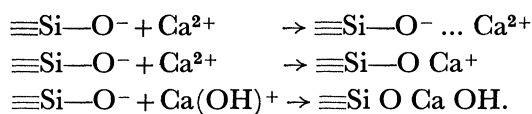
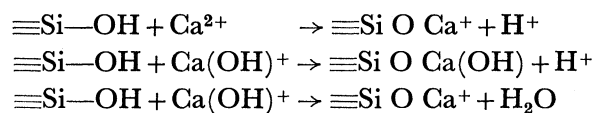


FIGURE 5. Mobility against pH for silica particles in various concentrations (mol dm⁻³) of calcium chloride: ○, 10⁻⁴; ▲, 10⁻³; □, 10⁻²; △, 5 × 10⁻²; ●, 10⁻¹.

To demonstrate this effect we can examine the influence of calcium chloride on silica particles as a function of pH by using the electrokinetic results shown in figure 5. At low concentrations of calcium, 10⁻⁴ mol dm⁻³, there is little effect and the behaviour is very close to that of silica (Ottewill & Holloway 1975). At 10⁻² mol dm⁻³ calcium chloride, little effect other than double layer compression is observable below pH 7. Above this pH, however, the behaviour changes and the mobility starts to decrease rapidly. At about pH 10 (see figure 6) the system coagulates, i.e. it forms compact clumps. However, at a slightly higher pH flocculation occurs and a loose fluffy texture is observed. Increasing the calcium concentration still further enhances the effect above pH 7 and it appears that at 10⁻¹ mol dm⁻³ extrapolation to pH 10 would give charge reversal of the surface, but coagulation made measurements in this region unreliable. Clearly, a reaction has occurred between calcium ions and the surface. The most likely reactions are:



Alternatively, reaction could also occur with remaining unionised hydroxyl groups



The fact that the net charge on the particles is reduced and that Ca^{2+} is the dominant ion in solution probably favours the first three equations although it is recognized that hydroxylated ions have a high affinity for surfaces (Matijević 1977) and could hydrogen-bond to surface hydroxyls. Although the electrokinetic technique does not in itself elucidate the actual reaction, it does provide direct evidence that a reaction has occurred. That some ion exchange at the surface can also occur, is demonstrated by the results given in figure 6. Addition of sodium chloride causes an increase in the magnitude of the negative mobility, which suggests the displacement of calcium ions by sodium ions.

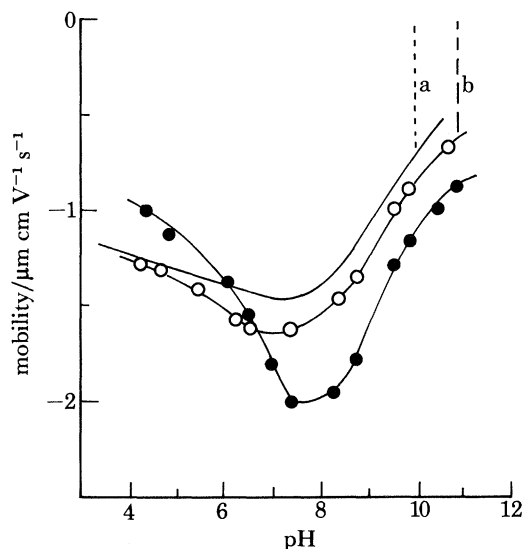


FIGURE 6. Mobility against pH for silica particles in the presence of 10^{-2} mol dm^{-3} calcium chloride: —, sodium chloride absent; \circ , 10^{-2} mol dm^{-3} sodium chloride; \bullet , 10^{-1} mol dm^{-3} sodium chloride; a, coagulation, and b, flocculation.

5. THE STABILITY OF COLLOIDAL DISPERSIONS

The basis of current theories of colloid stability is to consider the interaction between two particles in terms of the electrostatic repulsion, V_r , and the van der Waals attraction, V_a , as a function of the distance of surface separation, h , as illustrated in figure 7. For two spherical particles of identical radius, a , V_r is given by the equation

$$V_r = 2\pi\epsilon_r\epsilon_0 a\psi_a^2 \ln [1 + \exp(-\kappa h)],$$

and V_a as a first approximation by

$$V_a = -Aa/12h,$$

where A is a material constant for the system known as the Hamaker constant (Hamaker 1937; Mahanty & Ninham 1976). For practical purposes ψ_a is often replaced by ζ . A full discussion of these equations can be found elsewhere (Verwey & Overbeek 1948; Ottewill 1977, 1982; Smith 1969). For the present purposes we can assume that the total interaction energy, V_t , is given by

$$V_t = V_r + V_a + V_B,$$

where V_B is a very close range Born repulsion. From these equations we can examine the influence of ionic strength and diffuse layer potential on the form of the potential energy of

interaction. Some schematic energy curves are given in figure 8. It is immediately clear from 8a that if salt is added to a system, at constant ψ_a , the maximum is depressed until at *ca.* 0.1 mol dm^{-3} it occurs at *ca.* $V_t = 0$, or in other words, since the particles no longer have to surmount a kinetic energy barrier, they can go into a deep energy minimum and come into close contact where they touch. Thus the onset of instability in colloidal dispersions can be correlated with the depression of the kinetic energy barrier to association. This can be achieved by addition of salt (compression of the electrical double layer), by reduction of the surface potential (specific adsorption), or by a combination of both effects.

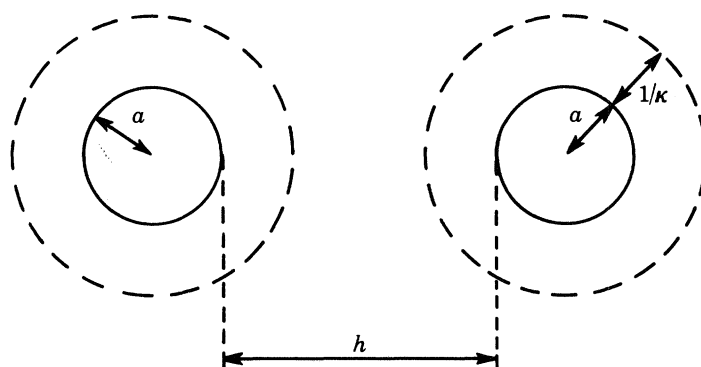


FIGURE 7. Interaction between two spherical particles.

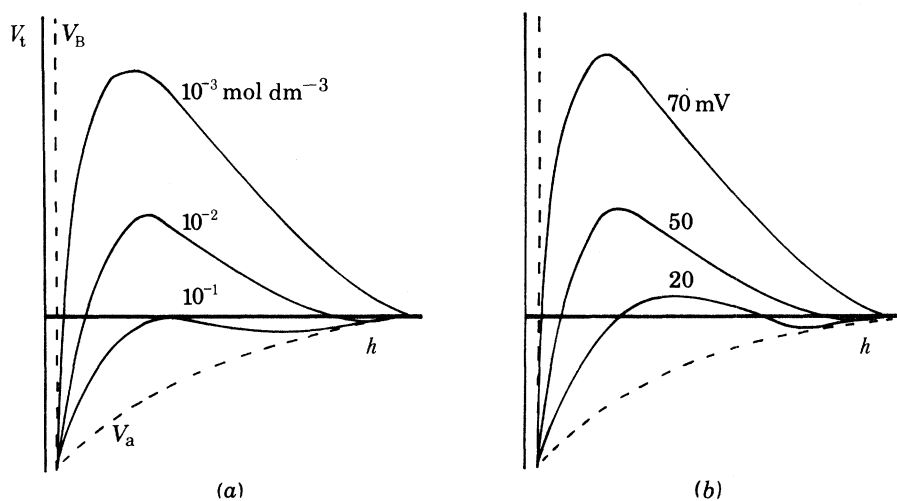


FIGURE 8. Schematic potential energy diagrams: (a) effect of salt concentration; (b) effect of surface potential.

The arguments advanced show quantitatively that the electrolyte concentration at which loss of stability occurs, the so-called critical coagulation concentration, is dependent inversely on a power of the valency ($1/v^n$, where $n = 2$ for coagulation at low potentials and $n = 6$ for coagulation at high potentials (Ottewill 1982). This provides a theoretical basis for the valency dependence in coagulation known as the Schulze–Hardy Rule (Kruyt 1952).

However, as we have discussed earlier, ion exchange can occur in the inner part of the electrical double layer and lead to specific effects of the ions at surfaces. Thus ions of the same

valency are frequently found to form sequences which reflect their own properties, e.g. extent of hydration and polarizability, and their interaction with the surface. A good example is found with the alkali metal ions where the concentration required to produce coagulation is frequently in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$, the lyotropic series (Kruyt 1952).

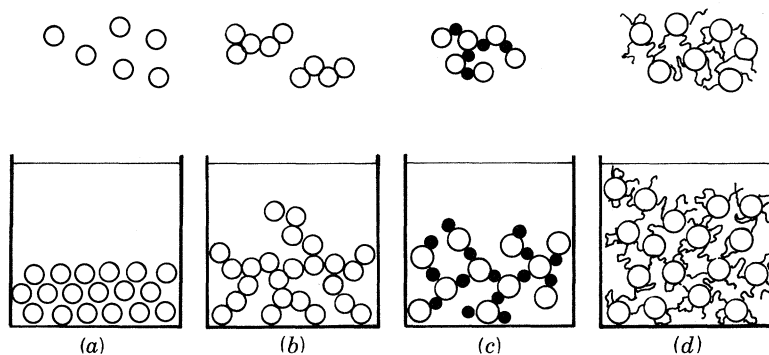


FIGURE 9. States of colloidal dispersions (upper sketch) and settled volumes (lower sketch): (a) stable dispersion, (b) coagulation, (c) heterocoagulation, (d) flocculation.

Another important concept that arises from these considerations is the way in which particles pack in concentrated dispersions. The repulsive forces are dominant for stable systems; these keep the particles apart, maintain a fluid layer between them, and hence allow the particles to assemble, say in sedimentation, into a close packed array with a low sedimentation volume. Under coagulation conditions the particles contact at the point where they kinetically impact. Furthermore, the liquid film is essentially lost, leading to contacts with high friction, and hence the particles pack to form a disordered array with a high void space. These effects are illustrated in figure 9.

Two other considerations can be added. First, if positively charged particles are added to negatively charged particles, the phenomenon of heterocoagulation is observed (figure 9). This is also an effect that can sometimes be obtained with particles of the same sign of charge but with different potentials and different sizes. Second, if polymeric species are present in a system, either by deliberate addition or by formation *in situ*, these can link the particles by a 'bridging' mechanism at low concentrations or 'protect' the particles by extensive adsorption at higher concentrations (Napper 1982). Addition of polymers frequently leads to flocculation, a state in which the primary particles remain separated by the liquid phase but are linked by the polymer. The consequence is the formation of units of high volume requirements, i.e. a high sediment volume, which visually often have a woolly or fluffy appearance.

The illustrations given in figure 9 are an attempt to illustrate schematically the different states that can be realized in practice. It should also be emphasized that combinations of these can occur.

Figure 10 shows the change in sedimentation volume of silica particles in the presence of $5 \times 10^{-2} \text{ mol dm}^{-3}$ calcium chloride as the pH is increased. Taking the sedimentation volume at pH 8 as unity, it can be seen that above pH 9.5 an increase occurs, which rises rapidly above pH 10.6 (Holloway 1974). These results can be correlated with figure 6, which indicates that as pH 9.5–10.0 is approached the electrophoretic mobility approaches zero and hence coagulation would be expected. Above pH 10.0, reversal of charge by the adsorption of calcium would

be expected, leading to the formation of positively charged particles. Moreover, as the pH rises dissolution of the silica must occur (figure 3) to give silicate species in the solution phase, probably polymeric, which lead to flocculation.

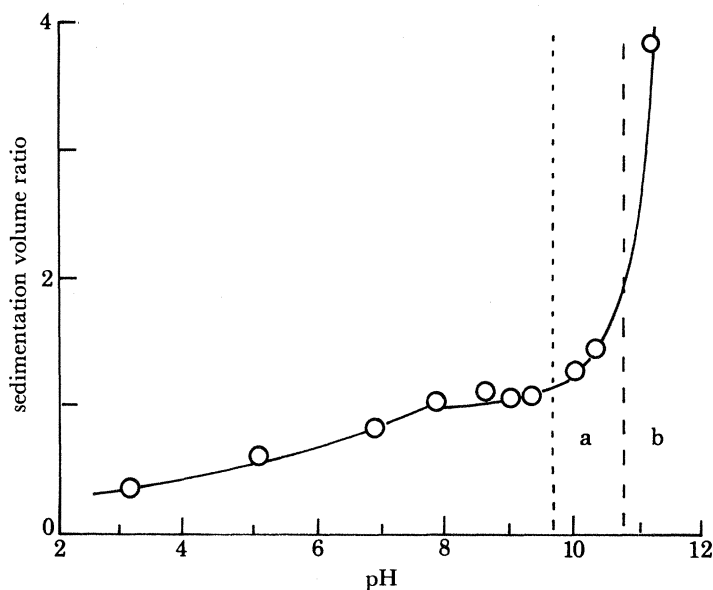
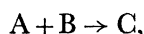


FIGURE 10. Sedimentation volume ratio against pH for silica in 5×10^{-2} mol dm^{-3} calcium chloride solution; a, coagulation, and b, flocculation.

6. FORMATION OF NEW PARTICLES

If two soluble species A and B are mixed to give a reaction



where C is an insoluble compound, then initially the concentration of C increases with time, $C(t)$, as shown in figure 11. The concentration exceeds the solubility limit but new particles are not formed at this point. Nucleation only occurs once the critical supersaturation value has been reached and the rate of nucleation, R_n , becomes finite. Once nucleation occurs the solution concentration falls. In fact, it will fall back, after a short time interval Δt , below the critical supersaturation so that no further nucleation occurs and growth on the existing particles occurs by diffusion of the solute species on to the existing nuclei. If the formation of nuclei is over a small time span, Δt , then monodisperse particles can be formed. More frequently $C(t)$ rises until $R_n \rightarrow \infty$ and nucleation lasts over a long time period thus giving very heterodisperse dispersions.

The fate of the particles formed depends on the environment in which they find themselves, for example, just to take a few cases,

- (i) if there is a low salt concentration and the particles have a high ψ_d then a stable colloidal dispersion would be formed;
- (ii) if there is a high salt concentration and the particles have a low ψ_d then the particles would coagulate as they formed;
- (iii) if the particles are formed in the presence of a polymeric species, or are generated simultaneously with a polymer species, then a flocculated dispersion could well result;

(iv) if nucleation occurs in the presence of existing particles it could occur preferentially at the surface of those particles (*surface* nucleation), leading to overcoating or the growth of new particulate units on the surface.

In the formation of highly hydroxylated materials it is frequently found that the resulting dispersion, whether stable or unstable, is composed of amorphous units. These can be highly hydrated and contain ions. With time, the units reassemble to form new crystalline particles. Ostwald ripening, the preferential dissolution of small particles with growth of the larger particles, also plays a role in this process. Several changes can occur, frequently slowly, until the most stable thermodynamic species is formed.

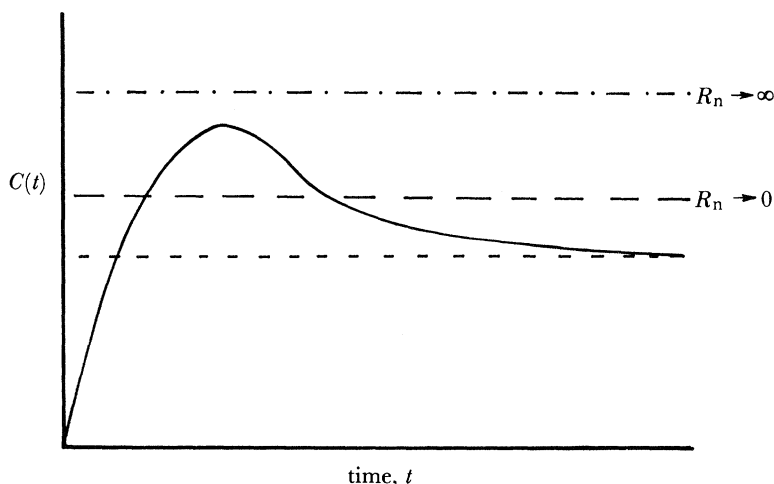


FIGURE 11. Concentration against time for a precipitating system: - - -, solubility; — — —, critical super-saturation curve; · — · —, critical limiting supersaturation.

7. COMMENTS ON CEMENT HYDRATION

The background considerations given in the previous sections can now be applied to speculate about the processes that might occur during the hydration of cement. As soon as the cement comes into contact with water it is apparent that the pH rises rapidly to *ca.* 12.5 (Birchall *et al.* 1978). At this pH both silica and calcium hydroxide are soluble. Hence, if the particles are separated we can visualize diffusion processes (figure 12) in which soluble silica species diffuse outwards from the silica particles and Ca^{2+} and $\text{Ca}(\text{OH})^+$ diffuse from the calcium hydroxide. These ions must meet in a zone in which nucleation can occur to form a colloidal dispersion. Whether this is close to the silica or the calcium hydroxide will depend on the rate of dissolution of each and this rate will also be dependent on factors such as, the chemical nature of the particles, particle size, surface area, temperature, porosity etc.

The silica and calcium hydroxide will be present in the same aggregate unit together with tricalcium silicate, dicalcium silicate etc., for cement, so that the situation is more complex. It has already been demonstrated that calcium has a high affinity for silica surfaces at high pH. The fact that the calcium content of the solution rises rapidly with time, whereas little silica is found in solution (Thomas & Double 1981), might well suggest that the nucleation zone for colloidal particle formation is near to the silica grain surface and that in the high electrolyte concentration the particles thus formed would immediately flocculate to give a gel-like layer at,

or near to, the surface. With continuous diffusion this region would continue to grow and expand away from the surface. Also, while the dissolution continued under attack by OH^- ions, there would accumulate an ion imbalance between this interphase and the solution, leading to osmotic gradients, as suggested by the osmotic membrane hypothesis (Birchall *et al.* 1978; Double *et al.* 1978; Birchall 1980). As a function of time, crystallization of this amorphous material might reasonably be expected to occur and to lead to a contraction and the creation of void space. The role of carbon dioxide must also be considered since this could also lead to the formation of calcium carbonate particles.

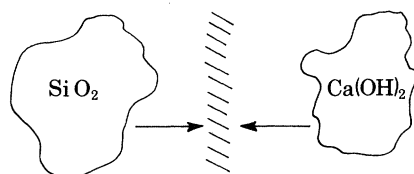


FIGURE 12. Schematic diagram showing formation of a precipitation zone.

It seems likely that since silica is the more slowly dissolving species, it is this factor that is the rate controlling process. It is also possible that the attack on the silica by OH^- ions occurs at or near the surface and for this reason material is pushed outwards in the form of needle-like growths. Moreover, since we are suggesting a particle association process, probably with bridging by polysilicic species, the gel matrix so formed is likely to be amorphous and to have a variable composition.

In the light of this suggested mechanism some indication should be possible as to the likely effect of additives. In terms of electrolyte addition it would be expected that valency effects would be important in controlling coagulation and that these should give a Schulze–Hardy dependence but with some ions showing a pronounced specificity. Materials such as ionic surface active agents, provided they are stable in the alkaline region, would be expected to have a pronounced effect on the nucleation, leading to the formation of smaller particles. In addition there would be adsorption on the larger aggregates, which would help to maintain a fluid layer between the macroscopic surfaces and aid flow and particle packing.

The effect of polymer addition would depend on a number of factors, such as, molecular mass, charge type, degree of branching etc. In the nucleation phase the effect would be uncertain in that either flocculation or stabilization could occur according to conditions. With the larger particles, i.e. large in comparison with the size of the polymer, adsorption of the polymer at the inorganic interface would be expected to give a layer with a thickness of the order of 10 nm or greater (Eirich 1977; Bangham *et al.* 1979) with a high degree of hydration. Macromolecules such as hydrolysed polyvinylacetate or carboxymethylcellulose, which have been shown to be effective as steric stabilizers for aqueous dispersions, might be expected to aid flow by preventing the inorganic solids of high surface energy from coming into intimate contact. These materials, as shown by Birchall *et al.* (1983), are likely to produce much better particle packing thus reducing void volume and ultimate porosity.

I wish to express my sincere thanks to Professor J. D. Birchall, F.R.S., for introducing me to this topic and for a number of stimulating discussions on the subject.

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Discussion

K. S. W. SING (*Brunel University, Uxbridge, U.K.*). Complex ageing mechanisms are involved in the hydration of Portland cement and this gives rise to changes in the microstructure over long periods. The classical process of Ostwald ripening appears to operate in the growth of the calcium hydroxide (Portlandite) crystals, but cannot explain the changes in C–S–H gel structure. The observed *increase* in the area of the solid–liquid interface appears to be due to the development of short-range order, which accompanies the removal of the water ligands. It seems to me important to attempt to distinguish between crystal growth and the ageing of poorly ordered gels such as C–S–H.

R. H. OTTEWILL. Probably the most important aspect of cement ageing, as in many inorganic materials that precipitate as gels, is the slow transformation of amorphous materials into crystalline products.

J. BENSTED (*Blue Circle Industries p.l.c., Research Division, Greenhithe, U.K.*). Can Professor Ottewill comment on the effect of temperature on the coagulation of colloidal silicates? Has he any experience of the colloid chemistry of silicon having 6 co-ordination by hydroxyl?

R. H. OTTEWILL. On the coagulation process alone temperature effects are usually small because they scale with kT , and on the absolute scale of temperature there is only a small change between say ambient temperature and 50° C. On the other hand, processes such as the transformation of amorphous gels to crystalline products, which involve reactions leading to the elimination of water molecules for the product initially formed, can be temperature sensitive.