The Microstructure and Chemistry of Tricalcium Aluminate Hydration [and Discussion]

J. E. Bailey, C. J. Hampson and J. Bensted

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The microstructure and chemistry of tricalcium aluminate hydration

By J. E. Bailey and C. J. Hampson
Department of Metallurgy and Materials Technology, University of Surrey,
Guildford, Surrey, U.K.

Electron optical techniques have been used to study the hydration of tricalcium aluminate in the presence of gypsum at various pH levels. Calcium aluminosulphate hydrates are precipitated, which have compositional variations and structures that range from highly disordered to highly ordered. Results derived from solubility measurements are able to account for the metastability of ettringite with respect to calcium aluminate monosulphate hydrate at pH more than about 12.8.

It is shown that the increased surface area of the precipitates formed at high pH is not sufficient to account for the observed increase in solubility. Consideration of the crystal structure of ettringite and the monosulphate hydrate suggests a further proposal for the type of defect occurring in the ettringite structure at high pH.

Introduction

Examination of the hydration products of ordinary Portland cement (O.P.C.) by electron microscopy has shown that the major aluminium-containing phases found during the early stages of hydration are tricalcium aluminate (C_3A), calcium aluminoferrite (C_4AF) and calcium aluminosulphate hydrate. The last is found in the form of fibres, usually radiating from another aluminium-containing phase. Analyses of these fibres indicate a composition close to that of the mineral ettringite ($Ca_6(Al(OH)_6)_2(SO_4)_3 . 26H_2O$), which has been detected in X-ray diffraction studies of the early stages of O.P.C. hydration (Chatterji & Jeffery 1963). At longer hydration times calcium aluminate monosulphate hydrate ($Ca_4(Al(OH)_6)_2SO_4 . 6H_2O$) may be detected. Bailey & Chescoe (1980) have identified both crystalline and apparently interfacial, amorphous forms of the fibrous material and their evidence that some of the amorphous fibres are hollow has been confirmed by Goodhew & Chescoe (1981).

The existence of two types of calcium aluminosulphate hydrate fibres was proposed long ago (Schwiete *et al.* 1966) and it was suggested that one type was formed by precipitation from solution and the other topochemically on the tricalcium aluminate surface. In the same paper the question of the transformation of ettringite, detected in hydrating cements by X-ray diffraction, to calcium aluminate monosulphate hydrate, in spite of the well established instability of the latter compound with respect to a mixture of ettringite and tricalcium aluminate hydrate (C_3AH_6), was raised.

We have attempted to throw some light on this situation by studying simple model systems, thus reducing the number of variables to a more manageable level. A typical Portland cement contains eight to ten elements at levels greater than 5% by mass, combined in five or six different compounds, at least two of which exhibit several polymorphs. On reaction with water, a solution containing significant levels of up to eight ions is formed. Several of these can exist in various states depending on their concentration and environment and there are many possible interactions between them. We started our work with the simplest cement related system that would produce calcium aluminosulphate hydrates, namely the tricalcium aluminate, calcium sulphate dihydrate (gypsum), water system. From this comparatively simple system we have moved on to study the effect of pH in an attempt to produce microstructures similar to those observed in O.P.C. hydration. In order to provide some rational explanation of our results we have had to make a very careful reappraisal of the chemistry of these systems and its relation to the thermodynamic properties of the various compounds formed. Some of this work will be referred to in the discussion that follows, and details have been published elsewhere (Bailey & Hampson 1982*a*, *b*; Hampson & Bailey 1982).

EXPERIMENTAL

Tricalcium aluminate was prepared by firing mixtures of calcium carbonate and alumina to 1450 °C for 2 h, grinding and refiring until X-ray diffraction indicated that no other phases were present. Chemical tests for free lime (CaO) were not used as, in general, they are not sufficiently sensitive to yield useful information. For instance, at a water to solids ratio of unity, only 0.14 % of CaO in the solid phase is sufficient to saturate the aqueous phase with respect to calcium hydroxide. It was therefore our practice to make up at least one sample from each batch of tricalcium aluminate produced, in sufficient quantity for its pH to be measured. Other samples were produced in quantities *ca.* 1 g in order to allow control of the water to solids ratio and to eliminate the large random variations in CaO content that might occur if the much smaller quantities required for preparation of electron microscopy samples were used.

Samples for transmission electron microscopy (t.e.m.) were prepared by using the method of Bailey & Chescoe (1980), hydration being terminated by vacuum drying. The water to solids ratio was unity and, as explained above, each microscopy sample was a portion from a mixture containing *ca.* 1 g of solids. Details of the procedures used in preparing samples for scanning electron microscopy (s.e.m.) have already been reported elsewhere (Hampson & Bailey 1983). In this case, as only the surface of the tricalcium aluminate pellet reacts, it is not possible to control the ratio of sulphate to aluminate. The aluminate is hydrated in a solution saturated with respect to gypsum, for a given time. In order to simulate the effect of a limited supply of gypsum, such as exists in Portland cement, the pellet of aluminate could be moved at a given time from a solution saturated with respect to gypsum to one of lower sulphate concentration. This has not yet been attempted as it introduces two further variables into the system, namely a second hydration time and the sulphate activity of the second solution.

RESULTS

The results of the electron microscope examinations have already been outlined in the literature (Hampson & Bailey 1983) but it is instructive to assemble some of them in the form of a diagram. In figure 1 the t.e.m. observations concerning the hydration of tricalcium aluminate/gypsum mixtures are summarized as a function of sulphate to aluminate ratio and hydration time. Hexagonal platelet phases are only observed in the region below the dashed line. At sulphate to aluminate ratios greater than unity the only phases observed are calcium aluminosulphate hydrate fibres and gypsum. The absence of tricalcium aluminate has been confirmed by X-ray and infrared examinations (Hampson & Bailey 1983). The initial pH of all these systems is 11.5. The calcium aluminosulphate hydrate fibres were generally 1 μm long × 0.1 μm diameter. Microanalysis showed that the platelet phases contained sulphur.

When the pH of the system was raised by the addition of sodium or calcium hydroxide, or both, the picture changed. In the pH range 12.4–13.0 smaller fibres of calcium aluminosulphate were observed, growing on the surface of the tricalcium aluminate grains. The rate of consumption of the tricalcium aluminate was greatly reduced compared to that at pH 11.5 and the addition of the gypsum at the higher pH range could then be said to retard the tricalcium aluminate hydration. The reduction in fibre size to 0.2 µm × 0.05 µm was also noted by Schwiete *et al.* (1966) and Mehta (1973). There was evidence of a precursor platelet phase being formed at the surface of the tricalcium aluminate grains, similar to that observed by Tinnea & Young (1977) and, during the hydration of tricalcium aluminate without gypsum, by Breval (1976).

At pH 13 the tricalcium aluminate was consumed rapidly and no fibres or platelets were observed on its surface.

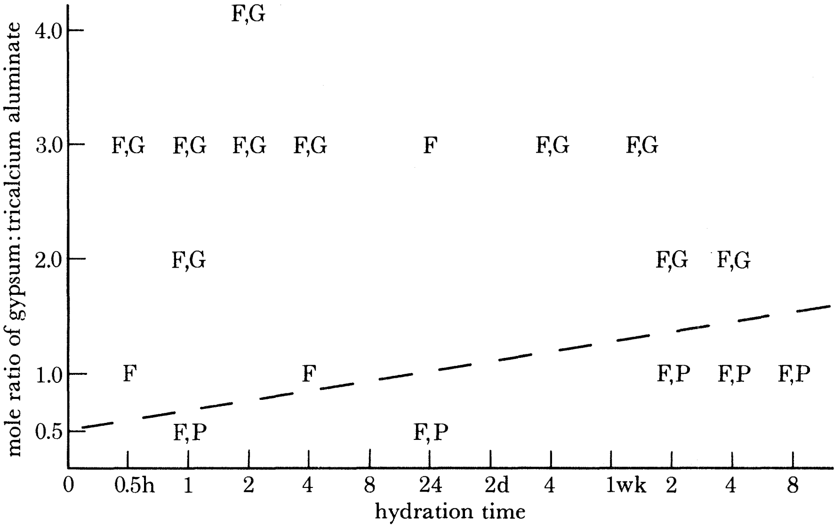


FIGURE 1. Phases observed during the hydration of mixtures of tricalcium aluminate and gypsum. Abbreviations: F, fibres; G, gypsum; P, platelets.

DISCUSSION

These results, and a careful reassessment of the chemical data available for the aqueous phase of the system $CaO/Al_2O_3/SO_3/H_2O$ have led us to make several proposals as a basis for a model of the hydration process of tricalcium aluminate in the presence of gypsum (Hampson & Bailey 1983). These are:

(i) the first hydration product is a platelet phase, being a solid solution between

$$Ca_2(Al(OH)_6)_2.2H_2O \quad \text{and} \quad Ca_4(Al(OH)_6)_2.(OH)_2.12H_2O$$

(or, in the usual cement chemists notation: C_2AH_8 and C_4AH_{19}).

(ii) The location of the next product depends on the solubility of this phase, which in turn depends on the pH of the surrounding aqueous phase. In particular, it depends on the aluminate ion solubility (Bailey & Hampson 1982*b*).

(iii) At low pH (*ca.* 11.5) this second product is produced by through solution precipitation. It consists of crystalline fibres of calcium aluminosulphate hydrate with a crystal structure similar to ettringite, but with a composition deficient in both calcium and sulphate ions with respect to that mineral. The limit of this non-stoichiometry appears to be a composition of approximately $Ca_4(Al(OH)_6)_2SO_4 . xH_2O$, i.e. a material with the same sulphate to aluminate ratio as calcium aluminate monosulphate hydrate.

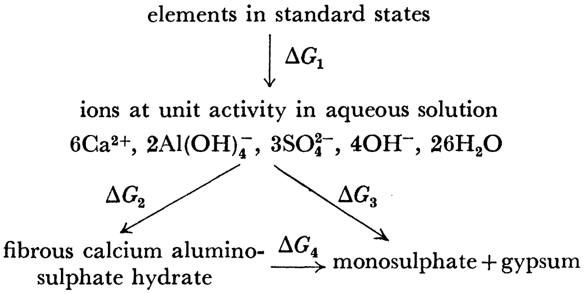
(iv) At pH *ca.* 12.5 the second product is formed at the tricalcium aluminate surface and covers or replaces the layer of platelets. The fibres are smaller than those observed at lower pH and have a less ordered structure. The latter is reflected in the increased solubility of such materials, and their decreased stability in the electron microscope. We have previously suggested that this disorder is due to a deficiency of aluminium in the fibres (Hampson & Bailey 1982) and noted an empirical correlation between the solubility product of the ettringite-like phase and the product of the activities of the sulphate and hydroxide ions in the surrounding solution.

The first three proposals appear to correspond well with our observations and are based on accepted theories of physical chemistry. The fourth, however, raises certain problems. The proposed aluminium deficiency in the fibres formed at high pH was made on the basis of the reduction in aluminate activity observed in solutions in equilibrium with ettringite as the pH is raised from *ca.* 11.5 to 12.5. However, it is observed that it is in alkali-containing systems with pH *ca.* 12.5 that the greatest increase in the ettringite solubility product occurs. Under these conditions the aluminate level in solution rises with increased pH (Bailey & Hampson 1982*b*). Such a rise in aluminate activity in solution does not seem consistent with a reduction in the aluminium content of the fibres. In general the composition of non-stoichiometric precipitates reflects that of the solution around them; such an effect is, for instance, observed in apatite precipitates (McClean & Budy 1964). Thus while we retain the hypothesis that the increase in solubility of ettringite at high pH, and the other changes observed, are due to the observed disorder in its crystal structure, we wish to revise our opinion as to the nature of these defects. We will therefore devote the remainder of this paper to a careful consideration of some of the observations relating to calcium aluminosulphate hydrates at high pH.

The most readily quantifiable parameter is the increase in molar free energy of the solid phase implied by its increased solubility product (K_s). The latter varies from 10^{-45} to 10^{-35} as the pH is raised from 11.5 to *ca.* 13 (Hampson & Bailey 1982), which corresponds to a molar free energy increase ΔG, from -250 to -170 kJ/mol of calcium aluminosulphate hydrate, when formed from the appropriate ions at unit activity. (The relation $\Delta G = RT \ln K_s$ is derived in the majority of physical chemistry texts, for example, Moore (1972)). At pH *ca.* 12.8 the fibrous calcium aluminosulphate hydrate is unstable with respect to a mixture of the plate like monosulphate and gypsum (Jones 1944; Kalousek 1941). The change in molar free energy when the fibrous 'ettringite' phase is transformed to such a mixture can be calculated from the molar free energies of formation of the species involved, as in table 1. The desired result is the quantity ΔG_4, which is clearly equal to $\Delta G_3 - \Delta G_2$. ΔG_2 is the quantity already obtained from the solubility products of the fibrous aluminosulphate hydrate phase. To obtain ΔG_3 we begin by applying our calculation of solubility product to the data of D'Ans & Eick (1954) for solutions in equilibrium with calcium aluminate monosulphate hydrate. An average value of 10^{-27} is obtained for the solubility product of the monosulphate, corresponding to a free energy change of -154 kJ/mol. To this must be added twice the molar free energy change for the formation of gypsum from ions at unit activity, namely -52 kJ/mol, giving a total of -206 kJ/mol for ΔG_3. Thus if $\Delta G_2 = -250$ kJ/mol then $\Delta G_4 = -206-(-250) = +44$ kJ/mol whereas if $\Delta G_2 = -170$ kJ/mol $\Delta G = -36$ kJ/mol. In the first case the 'ettringite' is the stable phase, while in the second the mixture of monosulphate and gypsum has the lower free energy. The change from one situation to the other occurs when $\Delta G_2 = -206$ kJ/mol. This corresponds to K_s *ca.* 10^{-36}, a value that is observed at pH 12.5 in systems saturated with gypsum. Thus the observed metastability of calcium aluminosulphate fibres at pH more than about 12.8 may be explained by the increased molar free energy of such materials.

The second characteristic of fibrous calcium aluminosulphate hydrate precipitates is the reduction in size that is observed as the pH at which they are formed is raised. The increase in the vapour pressure of liquid droplets and in the solubility of precipitates as their particle size is decreased is well known and it has been suggested that the change in solubility product that we have observed for ettringite is due to the change in fibre size. From an estimate of the surface energy we can calculate the increase in the energy of the fibres due to their decreased size. A cylindrical fibre of radius r and length l, with surface energies γ_e, and γ_s for the ends and sides respectively has a minimum surface energy when

TABLE 1. FREE ENERGY CHANGES IN THE FORMATION OF ETTRINGITE AND CALCIUM ALUMINATE MONOSULPHATE HYDRATE



$$\gamma_e/\gamma_s = l/2r,$$

and in this state the total surface energy of the ends is half that of the sides. For ettringite the easier of the two surface energies to estimate is that of the cylindrical surface, γ_s. Analysis of the crystal structure of ettringite (Moore & Taylor 1970) shows it consists of positively charged calcium aluminate hydrate columns, joined laterally by hydrogen bonds and separated by sulphate ions. These columns are parallel to the axis of the fibres and it is therefore the hydrogen bonds that have to be broken if the cylindrical surface of the fibres is to be created. Each unit cell of the structure consists of one column, approximately a cylinder of radius 0.56 nm, length 2.15 nm, containing 52 water molecules in addition to the calcium and aluminate ions plus its associated sulphate ions. The cylindrical surface of each cylinder amounts to 8×10^{-18} m^2 and is crossed by 52 hydrogen bonds, each with an energy 0.1 eV or 1.6×10^{-20} J (Kittel 1971). To a first approximation the surface energy γ_s is therefore

$$\gamma_s = \left(\frac{52}{2}\right)\frac{1.6 \times 10^{-20}}{8 \times 10^{-18}} = 0.05\ \mathrm{J\ m^{-2}}.$$

Ignoring the ends, the specific surface of a cylindrical fibre of radius r and density ρ is equal to $2/r\rho$. For ettringite $\rho = 1764$ kg m^{-3} and r is observed to vary from 0.05 μm to 0.2 μm. The corresponding surface areas are 23 and 57 m^2/g respectively. The relative molecular mass of ettringite is 1254 so the surface area of 1 mole of the fibres changes by 34×1254 m^2 as the pH of formation is raised from 11.5 to 12.5. If the surface energy is 0.05 J m^{-2} the corresponding increase in energy is 2.1 kJ/mol. Over the same pH range the observed increase in molar free energy, calculated from the solubility product, is 60 kJ/mol so it is not possible that the decrease in fibre size accounts for the increase in solubility.

We have already suggested (Hampson & Bailey 1982) that at high pH levels there is some form of defect in the calcium aluminate hydrate columns that form the basis of the ettringite structure and that it is this defect that increases the free energy. Since the monosulphate is stable at high pH, its structure is presumably not affected in the same way. Studies of the related compound $Ca_4(Al(OH)_4)_2(OH)_6 . 6H_2O$ (C_4AH_{13}) (Ahmed & Taylor 1967) showed it to consist of positively charged sheets of formula $(Ca_2Al(OH)_6^+)_n$ interleaved with negative ions (OH^-, SO_4^{2-} or $Al(OH)_4^-$) and water molecules. In the case of ettringite the basic unit of the crystal structure is, as already described, a column of formula $(Ca_3Al(OH)_6^{3+})_n$. Both these columns and the sheets in the monosulphate structure contain water. Aluminate ions in the aqueous phase of Portland cements and related systems exist in the form $Al(OH)_4^-$, while a significant fraction of the calcium in solution is in the form of the ion pairs $CaOH^+$ and $CaSO_4$ (Bailey & Hampson 1982*a*). This fraction increases as the pH and sulphate activity of the aqueous phase increase.

In order to form sheets, as in the monosulphate, each aluminate ion must combine with two Ca^{2+} and two OH^- ions or two $CaOH^+$ ion pairs. To form columns, as in ettringite, however, three Ca^{2+} ions and two OH^- ions are required, or two $CaOH^+$ ion pairs and one Ca^{2+} ion. It seems likely that it is the reduction in Ca^{2+} ion activity at elevated pH and sulphate levels that leads to the disorder in the fibrous calcium aluminosulphate hydrates, and that the defect is again a calcium deficiency in the columns, accompanied presumably by a deficiency of sulphate ions to maintain the charge balance. In this case it is caused by a lowering of the Ca^{2+} activity in the aqueous phase, whereas at lower pH the cause may be a kinetic one relating to the comparatively rapid dissolution of the tricalcium aluminate.

Conclusions

The observed increase in solubility product, and hence molar free energy, of fibrous calcium aluminosulphate hydrates at high pH (*ca.* 12.8) is sufficient to account for their metastability with respect to calcium aluminate monosulphate hydrate and gypsum. It is unlikely that the increase in molar free energy is due to the apparently increased surface area of the fibres formed at high pH.

Consideration of the crystal structures of ettringite and the monosulphate, and of the ions present in solution, leads us to suggest that disorder in the structure of fibres formed at high pH is in the form of calcium deficiency in the calcium aluminate hydrate columns and is due to the reduction of Ca^{2+} activity in solution. This is the same type of defect as was previously proposed for the initial fibrous precipitate formed in tricalcium aluminate/gypsum mixtures at pH *ca.* 11.5.

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Discussion

J. Bensted (*Blue Circle Technical Research Division, Greenhithe, U.K.*) Perhaps, in view of the variability in composition found in the ettringite phase, a change in name away from 'ettringite' would be useful?

J. E. Bailey and C. J. Hampson. We agree; these calcium aluminosulphate hydrates should not be referred to as ettringite.