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The microstructure of the hydration products of tri-calcium aluminate in the presence of gypsum

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The hydration of tri-calcium aluminate in the presence of gypsum has been examined by electron optical methods as a function of pH and hydration time. The location of the alumino-sulphate phase has been related to the solubility of aluminate ions from the precursive platelet phase. At pH ~ 11.5 the alumino-sulphate precipitate is crystalline and precipitates from solution. When first formed it is deficient in calcium and sulphate with respect to ettringite. If the deficiency is too great, transformation to calcium aluminate monosulphate hydrate may occur as an intermediate step before the equilibrium phases are obtained. At a higher pH (~ 12.5) the fibres of alumino-sulphate are smaller and more rounded. Long tubular fibres similar to those seen in portland cement were not observed. This has been explained as a consequence of using pure tri-calcium aluminate, rather than alkali-containing material. The information obtained has been used to predict the effect of some inorganic additives on the phases produced during the setting of portland cement.

1. Introduction

This paper describes investigations of the microstructure of calcium aluminate hydrates and calcium alumino-sulphate hydrates formed during the hydration of tri-calcium aluminate under various conditions in the presence of gypsum. The work is a continuation of previously reported studies by Bailey and Chescoe [1, 2]. In recent papers [3, 4] we have discussed the chemistry of the aqueous phase of portland cement and the chemistry of the calcium alumino-sulphate hydrates; an important conclusion from this work is that the calcium alumino-sulphate phases appear to have a structure that is strongly dependent upon chemical environment, particularly pH and sulphate activity.

This paper commences, therefore, with a study of tri-calcium aluminate (C_3A)/gypsum mixtures of varying molar ratios and proceeds to include the effect of pH. We then examined the hydration of C_3A in solutions saturated with respect to both gypsum and calcium hydroxide. Both transmission electron microscopy (TEM) and scanning electron microscopy (SEM) techniques have been used and the latter technique provides most useful data for initial examination of the system, particularly at an early stage of hydration.

The implications of these observations and their interpretation for the behaviour of C_3A in portland cement are also discussed in this paper.

2. Experimental methods and observations

2.1. TEM study of the hydration of tri-calcium aluminate/gypsum mixtures

Tri-calcium aluminate was produced by firing mixtures of calcium carbonate and alumina to 1450° C for 2 h, grinding and re-firing. Samples were re-fired until no phases other than C_3A were detected by X-ray diffraction. Mixing with gypsum was carried out in a vibratory mill. Samples for microscopy were prepared using the method developed by Bailey and Chescoe [1] and hydration was terminated by vacuum drying. Molar ratios of gypsum ($C\bar{S}H_2$) to C_3A varied from 0.5 to 4

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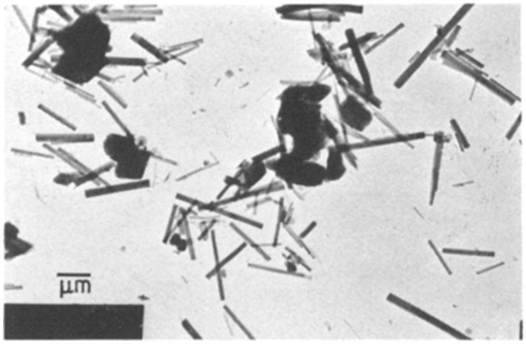

Figure 1 Tri-calcium aluminate/gypsum (1:3) hydrated for 2 h (TEM).

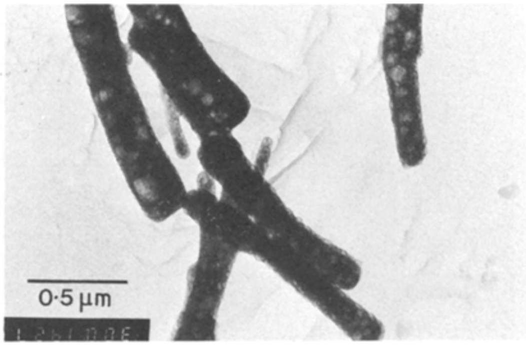

Figure 3 The effect of electron beam damage on ettringite fibres (TEM).

and hydration times from 0.5 to 24 h. The water/solids ratio (wt/wt) was approximately unity and the pH of the mixtures was around 11.4.

In the majority of samples only fibres having a composition similar to ettringite and crystals of gypsum were observed (Figs. 1 and 2). Even after only 30 min hydration, no unreacted tri-calcium aluminate was observed. Most of the fibres were loosely dispersed, suggesting that they had been precipitated from solution. The fibres were usually ~ 1 μm × 0.1 μm and had a well-defined rectangular silhouette. They were extremely sensitive to electron-beam damage, which led to re-crystallization and a characteristic bubbled appearance (Fig. 3). The diffraction pattern from the damaged fibres (Fig. 4) was found to correspond to a structure for dehyrated ettringite determined by Bannister [5]. With extreme care, diffraction patterns could be obtained from undamaged fibres (Fig. 5), and these usually consisted of a single row of spots parallel to the fibre axis. Mixtures of fibres and gypsum crystals were observed at $C\bar{S}H_2/C_3A$ ratios $\geqslant 1.0$. When the molar ratio was reduced to 0.5, however, a mixture of fibres and hexagonal platelets was observed after 30 min (Figs. 6 and 7). The platelets were crystalline and contained sulphur. Electron diffraction patterns could be obtained from them if low beam currents were used: excessive currents led to a loss of crystalline order but no morphological change. Some of the fibres were more rounded and energy dispersive analysis showed a significant deficiency in sulphur compared to well crystallized ettringite.

2.2. The effect of pH on the hydration of C_3A in the presence of gypsum

As a preliminary experiment, samples of $C\bar{S}H_2/C_3A$ mixtures were hydrated in plastic containers, dried at 40° C and examined by X-ray diffraction and infrared spectroscopy. Their pH was found to be ~ 11.5 and the results confirmed the conclusions drawn from the TEM observations. However, when the pH was raised to ~ 12.8 by addition of sodium hydroxide, a totally different picture emerged. Substantial amounts of C_3A remained in the system for several hours and very little crystalline ettringite was detected (Fig. 8). TEM

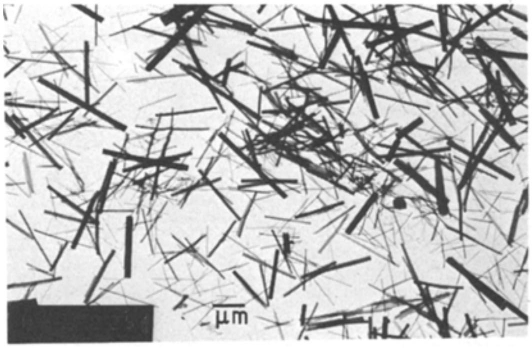

Figure 2 Tri-calcium aluminate/gypsum (1:3) hydrated for 24 h (TEM).

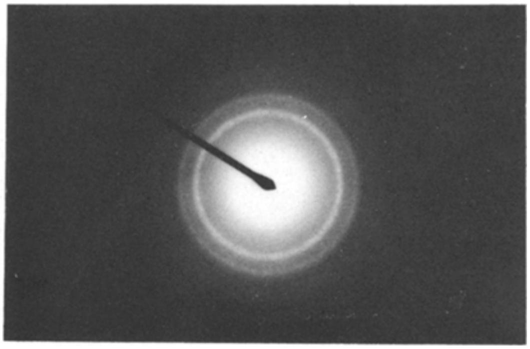

Figure 4 Electron diffraction pattern obtained from beam-damaged ettringite fibres.

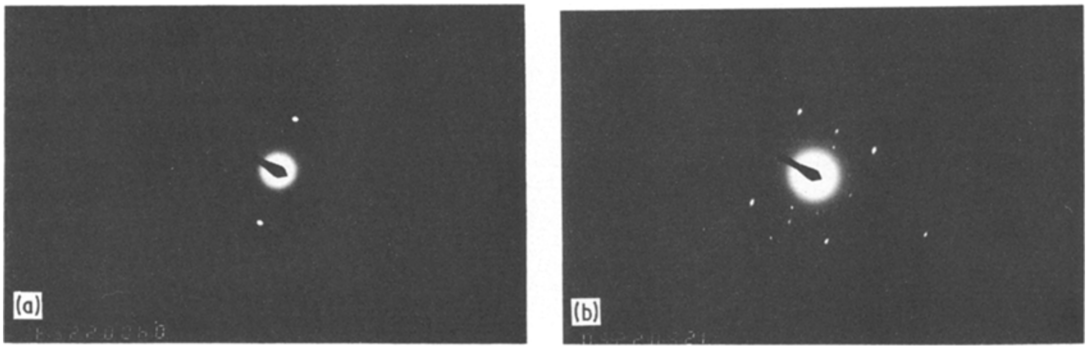

Figure 5 Electron diffraction patterns from undamaged ettringite fibres.

showed large grains of C_3A enveloped by short protruding calcium alumino-sulphate fibres (Fig. 9).

In order to distinguish fibres of ettringite formed in solution from those formed at the surface of the C_3A, samples of the aluminate were embedded in epoxy resin. After polishing to expose the aluminate the blocks were dipped in solutions of calcium sulphate. The pH of these solutions was adjusted by the addition of sodium hydroxide. The blocks were subsequently washed with distilled water, dried with acetone and then examined by SEM. Examination of the micrographs (Figs. 10 and 11a to f) showed that fibres were attached to the C_3A grains from pH 12.6 to 13.0. At pH 13 the fibres were much smaller than at lower pHs and at pH 13.2 no fibres were observed after 30 min. At pH $\lesssim$ 12.4 foils or platelets were observed. It is not yet certain what these are: probably they are calcium aluminate hydrates which are formed at the surface and re-dissolve to precipitate ettringite from solution. They have not been observed in the earlier TEM studies and are perhaps only seen because the geometry of the samples impedes the dissolution of the C_3A.

2.3. Hydration of C_3A in the presence of gypsum and calcium hydroxide

SEM samples were produced by sintering pressed discs of C_3A (2 mm × 10 mm diameter) at ~ 1250° C. These were glued to copper stubs with "Durofix" and attached to corks which were floated in stirred suspensions of gypsum and calcium hydroxide for various times. Hydration was stopped by washing with absolute alcohol and vacuum drying. Since the samples were suspended upside down and subsequently washed, only material which was attached to the C_3A surface remained when they were examined.

The micrographs (Fig. 12) show that the first precipitate on the surface is again of platelets similar to those seen by Breval [6] but this is rapidly replaced by, or covered with, a coating of short fibres. These are rounded and typically 0.2 μm × 0.5 μm. The shortened fibre length of this type of precipitate was also observed by Schwiete *et al.* [7]. Eventually, after about 4 h this coating begins to break up and larger (~ 1 μm × 0.2 μm) hexagonal fibres appear, from underneath the coating. Platelets are also sometimes observed at the ruptures in the coating.

There is no evidence of the long, tubular

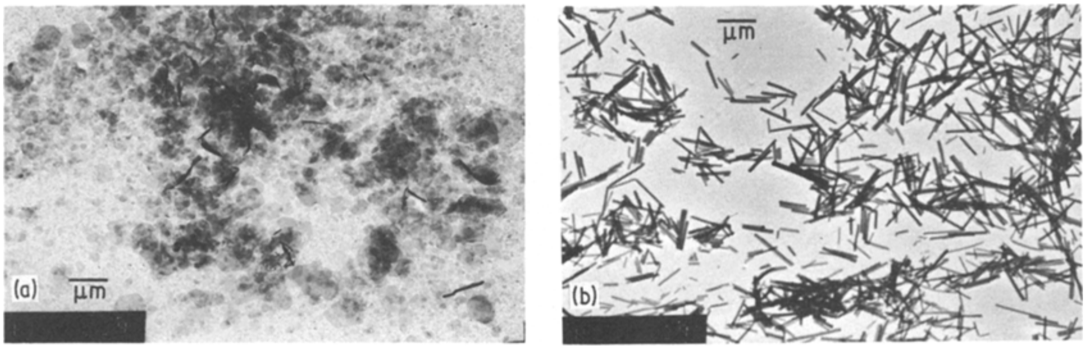

Figure 6 Tri-calcium aluminate/gypsym (1:0.5) hydrated for 30 min (TEM).

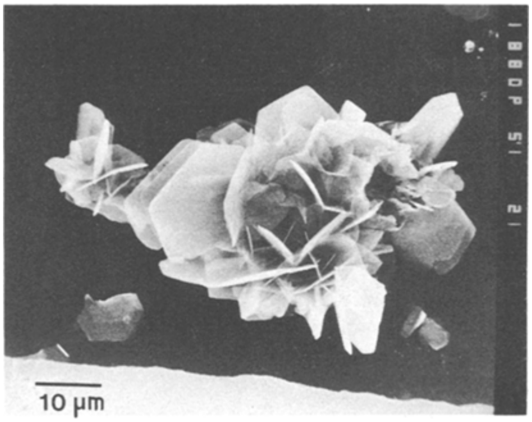

Figure 7 Tri-calcium aluminate/gypsum (1:0.5) hydrated for 24 h (SEM).

calcium alumino-sulphate hydrates fibres which are seen in suspensions of portland cement.

3. Discussion

3.1. Hydration of tricalcium aluminate–gypsum mixtures

From the TEM studies it appears that the initial fibrous precipitate formed on hydrating a C_3A/$C\bar{S}H_2$ mixture is an ettringite-like phase deficient in both calcium and sulphate ions. It may be represented by the formula $Ca_{3+n}(Al(OH)_6)_2(SO_4)_n xH_2O$.

Since we observed mixtures of only fibrous products and gypsum at $C\bar{S}H_2/C_3A$ ratios down to unity, we conclude that fibres can be formed even when n is reduced to one. A further reduction in the overall molar ratio of $C\bar{S}H_2/C_3A$ in the system, however, resulted in the production of a hexagonal platelet phase. This was shown to be crystalline and sulphur-containing and we conclude that it is a member of the solid-solution series between di- and tetra-calcium aluminate hydrates (C_2AH_8 and C_4AH_{19}) and calcium aluminate monosulphate hydrate ($C_3A\,C\bar{S}H_{12}$). The crystal structure of these materials consists of calcium aluminate hydrate sheets separated by layers containing water and the substituent ions. These ions are loosely bound and it is their easy replacement which leads to the wide range of compositions observed in these materials.

We would account for our observations by proposing that the initial precipitate in a mixture of tri-calcium aluminate and gypsum is a crystalline product with a structure similar to that of ettringite and a fibrous morphology. Its composition is represented by the formula given above with $0.5 < n < 1$. The course of further reactions depends on the ratio of $C\bar{S}H_2/C_3A$ in the initial mixture. If this is less than n, then the gypsum is consumed very rapidly leaving a mixture of C_3A and the initial fibrous phase. The remaining C_3A reacts rapidly with the water to form hexagonal hydrate phases and the fibrous phase redissolves, transferring ions through the solution to the hexagaonal platelet phase. Thus, as we observe, the fibres disappear and are replaced by platelets of the type described above (e.g. Fig. 7). The hexagonal phases in the $CaO/Al_2O_3/H_2O$ system are metastable [8] so, eventually, one would expect them to transform to a mixture of stoichiometric ettringite and the cubic tri-calcium aluminate hydrate (C_3AH_6). This was observed by Schwiete *et al.* [7] after 60 days hydration of $C_3A/C\bar{S}H_2$ mixtures. Each transformation from one set of phases to another is such as to cause a reduction in the total free energy of the system. Thus a mixture of tri-calcium aluminate, gypsum and water has a

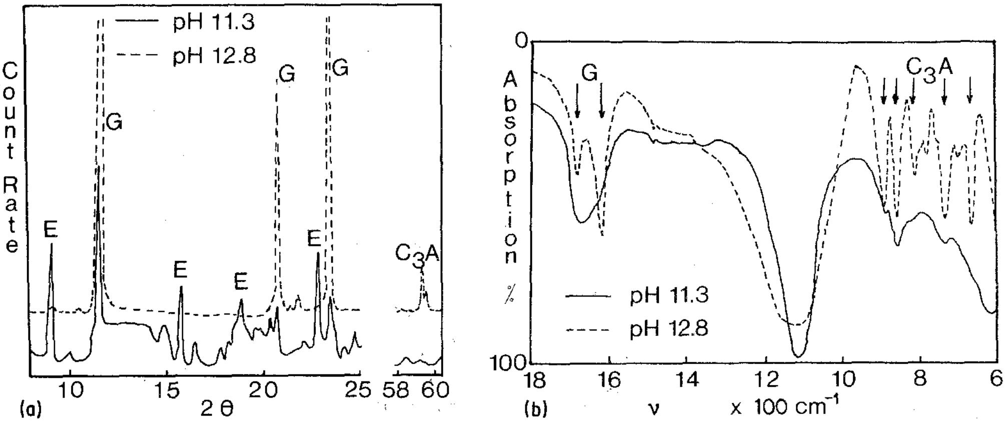

Figure 8 X-ray diffraction (a) and infrared spectrum (b) of a tri-calcium aluminate/gypsum paste (1:3) after 6 h hydration at pH 11.3 (no addition) and pH 12.8 (NaOH added).

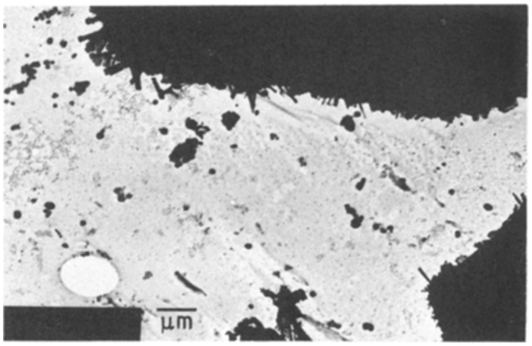

Figure 9 Tri-calcium aluminate/gypsum (1:3) hydrated at pH 12.8 for 2 h. Radial fibres growing from a grain of tri-calcium aluminate (TEM).

higher free energy than a mixture of our proposed initial fibrous product with gypsum and water and this, in turn, has a greater free energy than a mixture of stoichiometric ettringite, gypsum or C_3AH_6 (depending on the composition of the initial mixture) and water. The well-established metastability of the hexagonal platelet phases [8] with respect to the ettringite and C_3AH_6 implies that they also have a greater free energy than the latter mixture. Since the solubility product of a phase is simply related to its molar free energy, it follows that a phase such as calcium aluminate monosulphate hydrate is more soluble than the lower energy mixture of C_3AH_6 and ettringite. Thus provided that nucleation of the latter phases can occur the monosulphate will dissolve and they will be precipitated. Conversely, our observation of a fibrous, ettringite-like phase which dissolves and is replaced by a hexagonal platelet-phase implies that the initial fibres have a higher free energy than that of stoichiometric ettringite. Our proposed disordered, calcium and sulphate deficient initial precipitate would satisfy this condition. The greater the departure from stoichiometry, the higher the free energy of the precipitate until eventually the free energy of the hexagonal phases is exceeded and they can be produced as an intermediate step between the initial and final fibrous precipitates.

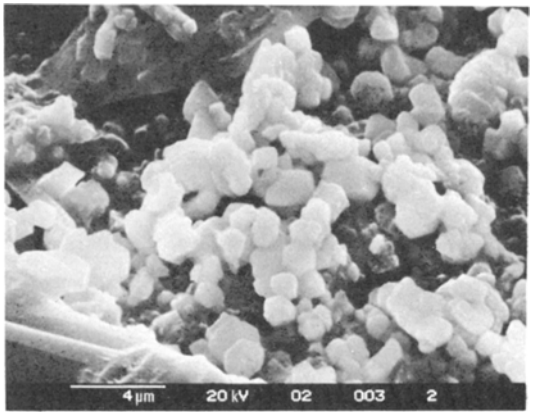

Figure 10 Tri-calcium aluminate before hydration (SEM).

3.2. The effect of pH

The results obtained in the preliminary experiments confirm the conclusions of Schwiete *et al.* [7] as to the effect of pH on the precipitation of ettringite. We have previously [4] proposed a model to explain both the disordering of the crystal structure at high pH observed by Schwiete *et al.* and the results of the equilibrium studies of Jones [8] in terms of removal of aluminium from the ettringite structure as the pH is increased. The model does not, however, explain the change in the location of the alumino-sulphate precipitate.

From the SEM results it appears that at pH ~ 11.8 platelets of an amorphous calcium aluminate hydrate similar to those observed by Breval [6] in the early stages of C_3A hydration are formed on the aluminate surface. These re-dissolve and the fibrous calcium alumino-sulphate is precipitated from solution. Reference to the data of Jones [8] suggests that the platelets would be similar to di-calcium aluminate hydrate, (C_2AH_8) for which Nikushchenko *et al.* [9] determined a solubility product of $10^{-13.75}$. This provides us with one relationship between the calcium, aluminate and hydroxide ion activities in the aqueous phase. The concentrations of the ions are also related by the requirement that the solution be electrically neutral. Thus

$$2[Ca^{2+}] - [Al(OH)_4^-] - [OH^-] = 0$$

If we now choose a value for the hydroxide ion activity we define the pH of the system and leave two variables, i.e., the calcium and aluminate ion concentrations. By estimating these values we may calculate the ionic strength of the aqueous phase and, thence, a set of activity coefficients for the ions. Using these the solubility product of C_2AH_8 may be expressed in terms of ionic concentrations, rather than activities. Thus we obtain two relationships between the remaining two variables and these can be calculated by successive approximations, using each new set of concentrations to re-calculate the ionic strength and activity coefficients and hence obtain a further, more accurate

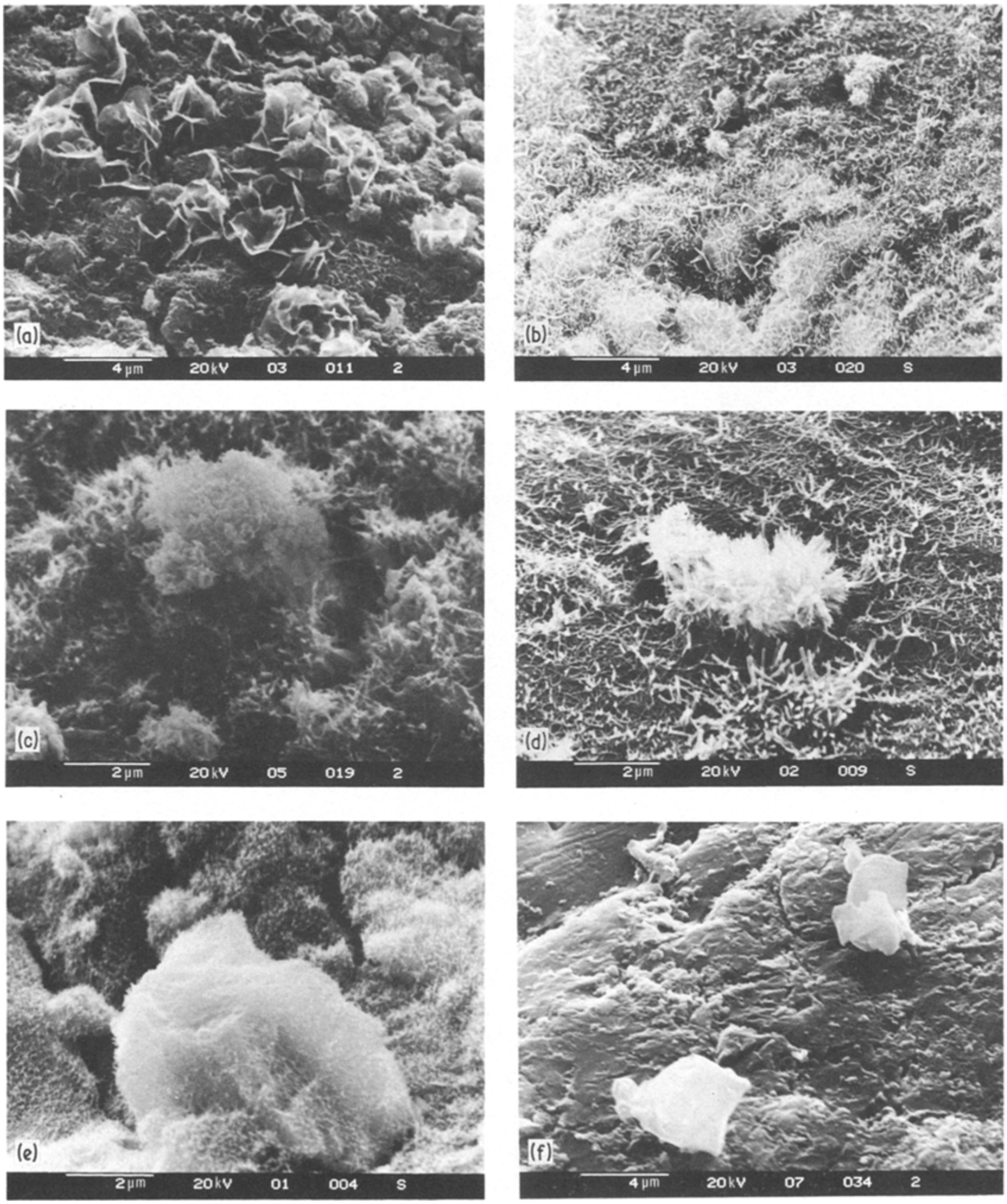

Figure 11 Tri-calcium aluminate hydrated in gypsum suspensions at various pH levels for 45 min (SEM). (a) pH 11.7, (b) pH 12.4, (c) pH 12.6, (d) pH 12.7, (e) pH 13.0, (f) pH 13.2.

set of concentrations. Using this method we predict the following concentrations at pH 11.8 in a system saturated with respect to C_2AH_8:

$$[Ca^{2+}] = 6.5\,\mathrm{mmol\,l^{-1}}$$

$$[Al(OH)_4^-] = 6.1\,\mathrm{mmol\,l^{-1}}$$

$$[OH^{-1}] = 7.0\,\mathrm{mmol\,l^{-1}}.$$

Let us consider what we should expect to occur if this solution was mixed with a solution saturated with respect to gypsum and held at the same pH (11.8). The sulphate activity in such a solution would be $\sim 10^{-2}$ M. Mixing this with the aluminate containing solution would lead to a system in which the ionic activity product of ettringite would be $\sim 10^{-37}$. Using the expression derived in

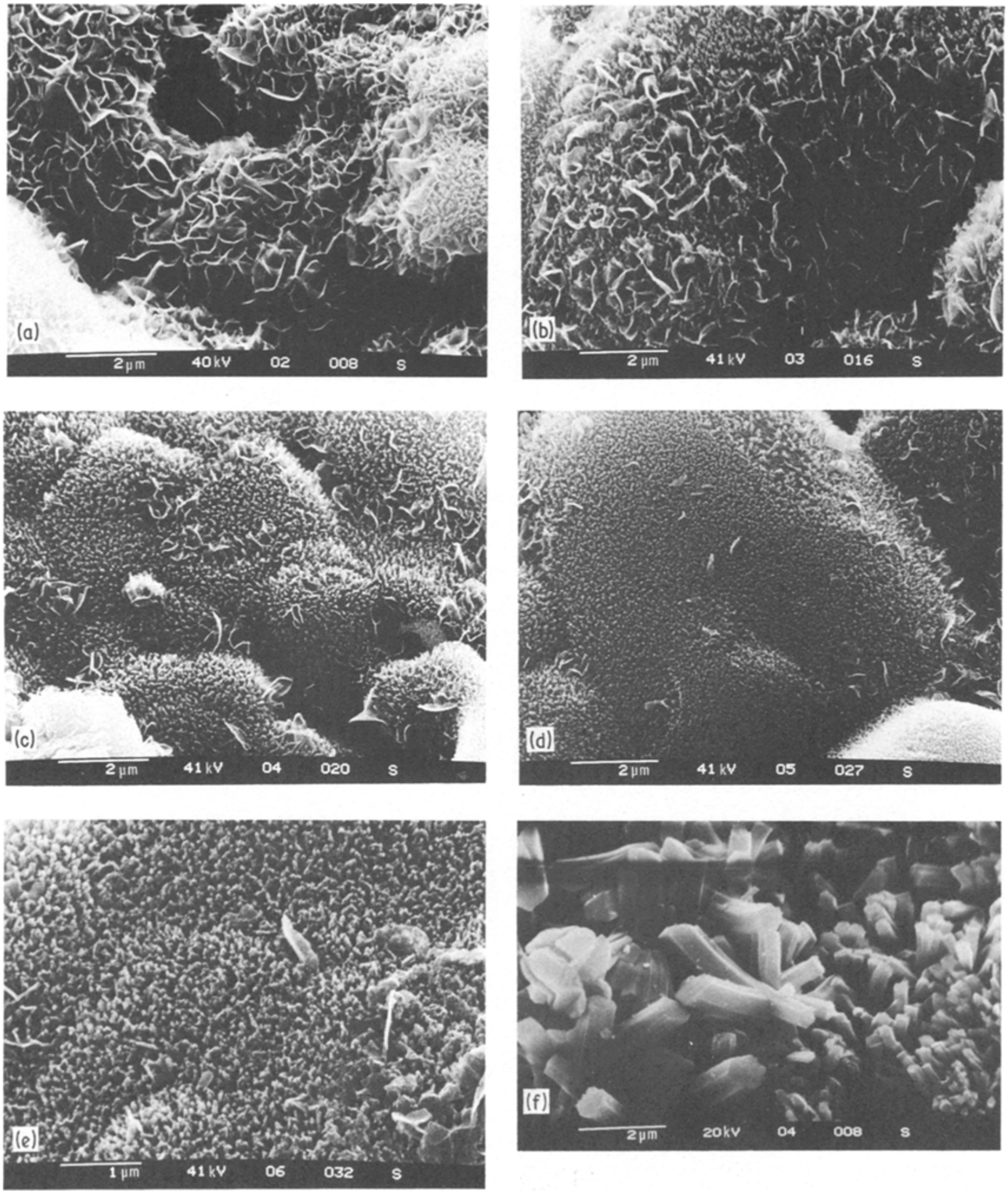

Figure 12 Hydration of tri-calcium aluminate in suspensions of gypsum and calcium hydroxide for various times (SEM). (a) 0.5 min, (b) 1 min, (c) 2 min, (d) 5 min, (e) 30 min, (f) 4 h.

our previous paper [4] we predict that the solubility product of ettringite under these conditions would be $\sim 10^{-40}$. The resulting mixture would thus be highly supersaturated and it is not surprising, therefore, that in practice we observe rapid precipitation of a fibrous calcium alumino-sulphate hydrate at a distance from the dissolving phases.

If the pH is raised to ~ 12.6 then we would expect the immediate hydration product of the C_3A to change to a mixture of tetra-calcium aluminate hydrate (C_4AH_{19}) and calcium hydroxide. Using the calculation described above the following concentrations are predicted:

$$Ca^{2+} = 17\,\text{mmol}\,l^{-1}$$

$$Al(OH)_4^- = 0.14\,\text{mmol}\,l^{-1}$$

$$OH^- = 33\,\text{mmol}\,l^{-1}.$$

It is immediately apparent that the concentration of aluminate in solution has dropped to 2% of the previous level. A mixture of this solution with a solution saturated with respect to gypsum at the same pH would have an ionic activity product for ettringite of $\sim 10^{-34}$. The predicted solubility product at these levels of hydroxide and sulphate activity is $\sim 10^{-35}$. The degree of saturation of our imaginary mixture is thus much less than at the lower pH. Transport of aluminate through the solution will be limited by its low solubility from the platelet phase and will restrict alumino-sulphate precipitation to regions adjacent to the aluminate surface.

When the pH is raised still further by the addition of alkali to the system, calcium alumino-sulphate hydrates are no longer stable with respect to calcium hydroxide. This decomposition and the reported stability of calcium aluminate monosulphate hydrate at pH ~ 12.8 have been discussed in our previous paper [4]. Our observations of rapid dissolution of C_3A at pH 13.2, and no surface precipitates on the dissolving grains, are consistent with this.

3.3. Systems saturated with calcium hydroxide

The SEM observations confirm that a platelet phase is still the first product to be formed on the C_3A surface but show that it is rapidly replaced by a fibrous precipitate. The fibres are considerably smaller than those precipitated from solution at lower pH levels, and appear to be more rounded. This may be a reflection of the internal disorder which we believe to exist in these precipitates at high pH. In spite of the space available around the aluminate surface, there is no evidence of the long fibres which are readily obtained in dilute suspension of portland cement. Instead, after 4 h hydration, large well-formed crystals are seen, apparently emerging from underneath the layer of fine fibres (Fig. 12f). We suggest that these crystals are formed underneath the coating of fine fibres in a lower pH environment: this may be a reaction in solution-filled space between the aluminate grain and the coating or it may be a recrystallization of the inside of the coating itself.

The reduction in the rate at which the C_3A is consumed when the pH of a $C_3A/C\bar{S}H_2$ mixture is raised to ~ 12.5 implies that the layer of fine fibres is a significant barrier to the access of the calcium sulphate solution to the aluminate surface. It has been suggested [10] that the layer is semi-permeable and that further reaction occurs because water is drawn in through the alumino-sulphate coating by osmosis. Semi-permeable calcium alumino-sulphate hydrates have been produced [11] and this model appears to account quite well for the long tubular fibres observed in cement.

In view of the failure of these experiments to produce similar long fibres, it is worth estimating the concentrations of the various species inside and outside the alumino-sulphate layer. For the outside the data of Jones [8] can be used directly since we know the phases present; for the inside it has been assumed that alumina gel, C_2AH_8 and ettringite are the relevant phases.

The results in Table I show that it is most unlikely that water would be drawn in through the alumino-sulphate layer by osmosis. In a cement clinker, however, most of the sodium is present as a substituent in the C_3A and some of this could be released into any solution within the alumino-sulphate layer, causing the anion levels to rise and possibly exceed those of the outside solution. Osmosis could then occur and the inner solution would contain a higher aluminate concentration than the outer solution. Hence when the two came into contact a calcium alumino-sulphate hydrate could be precipitated.

3.4. Application to the setting of portland cement

In order to avoid "flash set" in portland cement it is necessary to prevent rapid hydration of the tri-calcium aluminate. When the setting is controlled by the addition of gypsum it is the formation of an alumino-sulphate coating on the C_3A surface which prevents the rapid hydration. Our observations suggest that in order for a surface coating to form it is necessary that the

TABLE I Probable concentrations inside and outside the calcium alumino-sulphate hydrate layer when C_3A is hydrated in a gypsum/calcium hydroxide suspension

Species	Concentration	
	Inside (mmol l^{-1})	Outside (mmol l^{-1})
Ca	4.5	31.6
SO_4	0.075	12.4
OH	7.4	38.3
$Al(OH)_4$	1.5	0.12

solubility of aluminate ions from the initial calcium aluminate hydrate phase should be low ($< 10^{-4}$ M). This condition is satisfied in systems saturated with calcium hydroxide and gypsum at pH ~ 12.5. The production of a disordered calcium alumino-sulphate hydrate under these conditions makes the formation of a continuous, coherent coating more likely because there is less tendency to produce a precipitate with a well-defined morphology. If the pH is lowered we would expect a crystalline alumino-sulphate precipitate to form away from the calcium aluminate surface and rapid setting could occur because of the poor packing of the ettringite fibres produced. Alakali additions raising the pH above ~ 12.8 would also cause rapid setting, since the surface coating would dissolve and either calcium aluminate monosulphate or calcium hydroxide would be formed. Reductions in pH can be obtained with chemicals such as $CaCl_2$ which leave an anion in solution whereas increases occur if the cation (e.g., Na^+, K^+) is left in solution and the anion is precipitated.

4. Conclusions

The first product in the hydration of tri-calcium aluminate in the presence of gypsum is a disordered phase with an irregular platelet morphology similar to the calcium aluminate hydrates observed by Breval [6].

The position of the subsequent alumino-sulphate precipitate is governed by the solubility of aluminate ions from this disordered precipitate. This, in turn, depends on the pH of the surrounding solution. If this solubility is low, precipitation naturally occurs close to the calcium aluminate surface. At the high pH levels (~ 12.5) at which this is the case the evidence indicates that the precipitate is a disordered ettringite-type calcium alumino-sulphate hydrate and the reduced fibre length observed is consistent with our previous predictions as to the mechanism of the disordering [4]. It is not a result of high supersaturation in solution. The precipitate is capable of forming a coherent coating over the tri-calcium aluminate grains. In the presence of calcium hydroxide (pH 12.5) the alumino-sulphate coating is eventually ruptured and large hexagonal rods of ettringite appear. These have grown in a lower pH environment within the coating. They are not often observed in portland cement because the gypsum can be consumed and the protective coating removed before they are produced. These crystals grow more slowly and to a larger size than those precipitated at pH ~ 11.5. Samples formed at pH 12.5 do not grow long fibres by an osmotic mechanism. This may be explained as a consequence of the chemical environment inside the protective coating. If, however, a sodium containing tri-calcium aluminate was used, osmosis and long-fibre growth might be expected.

At lower pH (~ 11.5) the potential supersaturation of the system with respect to ettringite is much higher and crystalline precipitate is rapidly formed by a through-solution mechanism. This precipitate is initially deficient in calcium and sulphate compared to stoichiometric ettringite. In extreme cases the fibres are smaller and more rounded than for a stoichiometric precipitate, and may redissolve, precipitating a platelet phase which, in turn, is metastable with respect to ettringite and tri-calcium aluminate hydrate.

The control of the setting of portland cement by the addition of gypsum is only possible in the pH range ~ 12.3 to 12.8. Additives which remove the pH of the system from this range will cause rapid setting.

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