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On the structure of some precipitated calcium alumino-sulphate hydrates

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The chemistry of the calcium alumino-sulphate hydrates has been re-assessed using the methods developed in a previous paper [10]. Ettringite does not have a constant solubility product. The rise in the ionic activity product of solutions in equilibrium with "ettringite" as a function of pH and sulphate activity is attributed to disordering of the crystal structure. This is due to removal of aluminium from the calcium aluminate hydrate columns which form the framework of the ettringite structure. The columns are terminated by these defects and estimates of the expected column length under various conditions are made. Qualitative explanations of changes in the stability of "ettringite" with respect to calcium aluminate monosulphate hydrate and of the action of certain admixtures on portland cement are made on this basis.

1. Introduction

It is now generally accepted that the retardation of the setting of portland cement by the addition of gypsum is due to the formation of a barrier layer calcium alumino-sulphate hydrate phase. Some workers [1] maintain that this is a crystalline phase while others [2] have obtained evidence of a non-crystalline alumino-sulphate gel. Many studies of calcium alumino-sulphate hydrates have been made and there appears to be considerable confusion as to the stability of certain phases. The concept of an amorphous calcium alumino-sulphate hydrate gel is not new – the earliest reference appears to be a paper by Forsen [3], who produced semipermeable membranes in porous glass plates from calcium aluminate and saturated lime or lime and gypsum solutions. Jones [4] discussed the reactions of hydrated alumina with a lime–gypsum suspension and of tri-calcium aluminate hydrate (C_3AH_6) with gypsum, both of which gave "ettringite" coatings. He observed that the addition of iron or silicon to tri-calcium aluminate encouraged coating formation, in reactions with calcium or alkali sulphates whereas a pure aluminate would all be converted rapidly to ettringite. The discussion in a paper by Lerch [5] in 1946 includes a contribution by Kalousek referring to a metastable semipermeable membrane formed during the hydration of portland cement. Kalousek [6] had already investigated the effect of alkali on the system $CaO/Al_2O_3/SO_3/H_2O$, and had managed to obtain a gel from an aqueous phase similar to that found in portland cement but he was not able to determine the composition of the material. Ettringite was found to be unstable in alkali solutions stronger than 0.25 M and to decompose in 0.8 M alkali over a period of 4 weeks forming a calcium aluminate monosulphate solid solution with considerable replacement of sulphate by hydroxide ions. The monosulphate was found to be metastable at alkali concentrations less than 0.15 M. Jones [7] also studied the $CaO/Al_2O_3/SO_3/H_2O$ system and found that the monosulphate and the related hexagonal calcium aluminate hydrates were all metastable at 20° C. He also demonstrated that there is no equilibrium between gypsum and C_3AH_6. More recently, Schwiete *et al.* [8] have claimed that two distinct types of calcium alumino–sulphate hydrate may be formed during the hydration of cement. They defined two ranges of pH in which these were formed:

(1) pH 11.5 to 11.8 – precipitation from solution to form crystalline ettringite;

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(2) pH 12.5 to 12.8 – topotactic formation of non-crystalline material with a composition similar to ettringite.

Both crystalline and non-crystalline fibres with compositions similar to ettringite have been identified by Bailey and Chescoe [2] in samples of portland cement and in synthetic systems.

In order to throw light on these findings we have re-assessed the chemical analyses of solutions in contact with various phases in the $CaO/Al_2O_3/SO_3/H_2O$ system using the methods set out in our previous paper [10], and attempted to calculate a solubility product for ettringite. In addition we have related the past observations described above to the pH of the systems and investigated the formation of ettringite at high pH levels. From these results we have made various predictions concerning the hydration of tri-calcium aluminate/gypsum mixtures and portland cements. Experiments to test these predictions will be reported in a future paper.

2. Phase equilibria in the calcium alumino-sulphate hydrate system

The analyses by D'Ans and Eick [9] and Jones [7] of solutions in equilibrium with the various solid phases in this system have been re-assessed. Hydroxide ion concentrations, which were not reported in the original data, were calculated by assuming that the solutions were electrically neutral and the computer program developed previously [10] was then used to calculate the true activities of the hydroxide ions and hence the pH of the solutions. This calculation involved corrections both for the effect of the ionic strength of the solution on the activity coefficients of the various ions and for the formation of complex ions and ion-pairs. Activity values were calculated because, unlike concentrations, they can be used to calculate the free energy of a solution, and therefore of solid phases in equilibrium with the solution. Values calculated for solutions in equilibrium with two or three solid phases define the limits of stability of the compounds in the system. Those relevant to ettringite are shown in Fig. 1. This is a projection of the results on to a plane representing zero aluminate ion concentration: for the stable phases in the system the aluminate concentrations are low and this two-dimensional approximation provides a useful presentation of the results. It is apparent that in an alkali-free system ettringite is stable almost up to the pH of saturated calcium hydroxide (pH 12.45). Higher pH values can only be obtained by the addition of alkalis. The pH range quoted by Schwiete *et al.* [8] for formation of a calcium alumino-sulphate hydrate gel therefore starts at, or above, the maximum pH attainable in an alkali-free system. Jones [7] studied alkali-containing systems and provided analyses of solutions in equilibrium with gypsum, ettringite and portlandite (calcium hydroxide) at various alkali levels, from which pH values were calculated as before (Table I). A pH of 12.8 was attained in 0.25 M alkali solution. We note that this corresponds to both the stability limit for ettringite determined by Kalousek [6] and the upper pH limit of Schwiete *et al.* [8] for their non-crystalline phase.

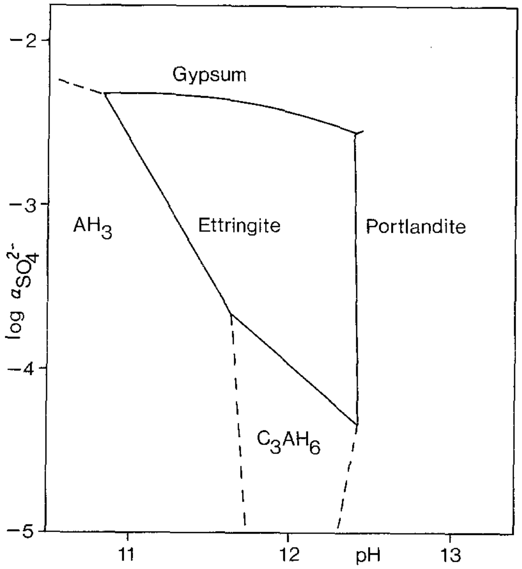

Figure 1 Stability fields in the system $CaO/Al_2O_3/SO_3/H_2O$ (projected onto the plane $[Al(OH)_4^-] = 0$).

Using the same data [9] it is possible, in theory, to calculate a solubility product for ettringite. Similar calculations have been carried out for the calcium aluminate hydrates by

TABLE I pH of solutions in equilibrium with gypsum, ettringite and portlandite calculated from results of Jones [7]

Alkali (mmol l^{-1})	pH
0	12.41
178	12.74
250	12.81

Nikushchenko *et al.* [11] with considerable success.

Using the same assumptions, namely that the aluminium in solution exists as $Al(OH)_4^-$ ions and that the electrical neutrality of the solution is maintained by the formation of hydroxyl ions we would expect the ettringite to dissolve thus:

$$Ca_6(Al(OH)_6)_2(SO_4)_3 26H_2O \rightarrow 6Ca^{2+} + 2Al(OH)_4^- + 3SO_4^{2-} + 4OH^- + 26H_2O,$$

and therefore that the solubility product would be given by:

$$K_E = a^6_{Ca^{2+}} a^2_{Al(OH)_4^-} a^3_{SO_4^{2-}} a^4_{OH^-},$$

where a_x is the activity of the ion X in the solution. It is possible to establish an upper limit for the value of K_E from the observation of Jones [7] that gypsum and C_3AH_6 do not co-exist. This implies that the change in molar free energy under standard conditions (ΔG°) for the reaction

$$Ca_3(Al(OH)_4)_2(OH)_4 + 3\ CaSO_4 \cdot 2H_2O + 20H_2O \rightarrow Ca_6(Al(OH)_6)_2\ (SO_4)_3 \cdot 26H_2O$$

is negative. If we split the reaction into two hypothetical stages we may calculate ΔG° for each stage in terms of the solubility products of the solid phases:

$$Ca_3(Al(OH)_4)_2(OH)_4 + 3\ CaSO_4 \cdot 2H_2O + 20H_2O \rightarrow 6Ca^{2+} + 2Al(OH)_4^- + 3SO_4^{2-} + 4OH^- + 26H_2O$$

for which

$$\Delta G_1^\circ = RT \ln K_1$$

where

$$K_1 = \frac{a^6_{Ca^{2+}} a^2_{Al(OH)_4^-} a^3_{SO_4^{2-}} a^4_{OH^-} a^{26}_{H_2O}}{a_{Ca_3(Al(OH)_4)_2(OH)_4}\, a^3_{CaSO_4 \cdot 2H_2O}\, a^{20}_{H_2O}}$$

i.e.

$$K_1 = K_{C_3AH_6} K_G^3 a^6_{H_2O}$$

where $K_{C_3AH_6}$ and K_G are the solubility products of tri-calcium aluminate hydrate and gypsum, respectively.

Similarly,

$$Ca_6(Al(OH)_6)_2\ (SO_4)_3 \cdot 26H_2O \rightarrow 6Ca^{2+} + 2Al(OH)_4^- + 3SO_4^{2-} + 4OH^- + 26H_2O$$

$$\Delta G_2^\circ = RT \ln K_E.$$

For the original reaction, by Hess' law

$$\begin{aligned}\Delta G^\circ &= \Delta G_1^\circ - \Delta G_2^\circ \\ &= RT(\ln K_{C_3AH_6} + 3\ln K_G + 6\ln a_{H_2O}) \\ &\quad - RT\ln K_E,\end{aligned}$$

and therefore, if ΔG° is negative it follows that

$$\ln K_E < 3\ln K_G + \ln K_{C_3AH_6} + 6\ln a_{H_2O}.$$

For a dilute solution, $a_{H_2O} = 1$ so that

$$K_E < K_G^3 K_{C_3AH_6},$$

which implies that $K_E < 10^{-36}$.

When the solubility product was calculated from the data of both Jones [7] and D'Ans and Eick [9] using the corrections for complex ion formation and activity coefficients described in our previous paper [10], it was found that the values varied from 10^{-35} to 10^{-45}. Inspection of the results suggested a nonlinear relationship between K_E and the product of the hydroxide and sulphate activities (Fig. 2), showing a rapid rise from a lower limit $\sim 10^{-45}$ when the product $\sim 10^{-6}$: for the majority of the data it could be approximated by the relationship:

$$\log K_E \propto 4 \log (a_{OH^-} \cdot a_{SO_4^{2-}}).$$

The wide variation in the ionic product emphasizes the need to examine a wide range of solution compositions when attempting to establish a solubility product; a precaution which has not always been taken [12].

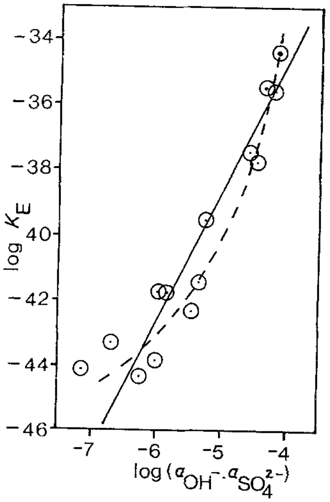

Figure 2 Calculated solubility products for ettringite as a function of hydroxide and sulphate activities.

3. The formation of ettringite at high pH

It follows from the previous section that at high pH levels ettringite may be converted to calcium hydroxide, leaving sulphate and aluminate ions in solution:

$$\begin{aligned}&Ca_6(Al(OH)_6)_2(SO_4)_3 \cdot 26H_2O\\ &+ 8OH^- \rightleftharpoons 6Ca(OH)_2 + 2Al(OH)_4^-\\ &+ 3SO_4^{2-} + 26H_2O.\end{aligned}$$

The reaction was assumed to have an equilibrium constant given by

$$K = a^2_{Al(OH)_4^-} a^3_{SO_4^{2-}}/a^8_{OH^-},$$

and was investigated by taking stoichiometric mixtures of calcium hydroxide, sodium aluminate and sodium sulphate. The sodium salts were made up into solutions of various concentrations and allowed to react with the corresponding quantities of calcium hydroxide in sealed plastic containers. The state of each mixture at equilibrium was assessed by measuring the pH. Since the initial concentrations of aluminate and sulphate were in the ratio of 2:3 the mathematics of the system is very simple: if we characterize the initial concentrations by C_0 and the degree of reaction by x then the equilibrium constant for the reaction may be expressed in terms of C_0, x and the activity coefficients, γ, of the various ions.

	$8\,OH^-$	$\rightleftharpoons 2\,Al(OH)_4^-$	$+\ 3\,SO_4^{2-}$
Initial concentration	0	$2C_0$	$3C_0$
Equilibrium concentration	$8x$	$2(C_0-x)$	$3(C_0-x)$

$$\begin{aligned}K &= \gamma^2_{Al(OH)_4^-}[2(C_0-x)]^2\gamma^3_{SO_4^{2-}}\\ &\quad \times [3(C_0-x)]^3/\gamma^8_{OH^-}(8x)^8\\ &= 108Y/a^8_{OH^-}\end{aligned}$$

where

$$Y = \gamma^2_{Al(OH)_4^-}\gamma^3_{SO_4^{2-}}(C_0-x)^5.$$

The activity of the hydroxyl ions, a_{OH^-}, was obtained from the pH measurement and the activity coefficients of the other ions were calculated from the ionic strength of the system which was calculated to be $11C_0 - 3x$. The quantity Y could then be calculated and plotted as a function of a_{OH^-} (Fig. 3), from which it was deduced that

$$\log Y = -1.78 + 8.9 \log a_{OH^-},$$

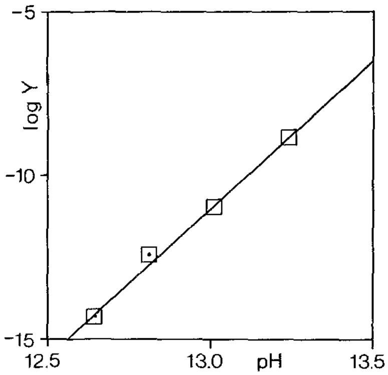

Figure 3 The composition of solutions in contact with ettringite at high pH ($Y = a^2_{Al(OH)_4^-}a^3_{SO_4^{2-}}$).

implying that $K \simeq 1.7$. Since the solution was in equilibrium with both calcium hydroxide and ettringite, K could be expressed in terms of their solubility products, K_P (for portlandite), and K_E (for ettringite):

$$K = K_E/K_P^6.$$

This leads to values of $\sim 10^{-31}$ for K_E; much higher than the "maximum" value predicted from Jones' observations. Substitution of typical values for hydroxide and sulphate activity from Table II into the expression derived for K_E in the previous section gives $K_E \simeq 10^{-30}$. Therefore, there appears to be reasonable agreement between the two sets of results.

Conversion of the calcium hydroxide to ettringite was virtually complete below pH 12.3 but fell to 50% at pH 12.8. The degree of conversion depends on the solid/liquid ratio and reflects the amount of solid which must dissolve to give the required levels of ions in solution.

4. Discussion

The wide variation in the ionic activity products of solutions in equilibrium with "ettringite"

TABLE II Change in free energy, ΔG, and predicted column length, l, for various values of ionic activity product, K_E

$\log K_E$	ΔG (kJ mol^{-1})	l (μm)
−45	0	∞
−43	11.4	0.17
−40	28.5	0.067
−35	57	0.034
−30	86	0.022

implies that the solid phase varies in some way. The most obvious variations are a change in composition or a change in the degree of order. Two groups of workers have reported substitution of hydroxide ions for sulphate ions in ettringite in aged cements and synthetic samples [13, 14] but the apparent dependence of K_E on the product of the sulphate and hydroxide activities rather than their ratio does not seem consistent with such a replacement. The crystal structure of ettringite [15] consists of columns of composition $[Ca_3Al(OH)_6^{3+}]_n$ arranged in a hexagonal array with the sulphate ions in the interstices. Adjacent columns are linked by hydrogen bonding. Disordering could occur if the columns were terminated by removal of aluminium, leaving two neutral $[Ca_3(OH)_6]$ ends. The reduction in charge could easily be accommodated by removal of interstitial sulphate ions.

A rough estimate of the increase in free energy due to the formation of such a defect may be made if we ignore any relaxation in the crystal structure and assume that the energy change is solely due to the replacement of one set of ions by another.

$$Al(OH)_4^- + 1.5\,SO_4^{2-} \rightarrow 4\,OH^-$$

$$\Delta G^\circ = 1780\ \text{kJ mol}^{-1}$$

The observed change in K_E, over the range of solution compositions examined, of a factor of 10^{15}, corresponds to a change in the free energy of the solid phase of $\sim 85\ \text{kJ mol}^{-1}$ which corresponds to replacement of 2.5% of the aluminium, a level at which the change in composition would only be detected by very careful analyses. Each aluminium atom removed creates two terminations in its column so the average column will contain 40 aluminium atoms or 20 formula units. The unit cell of ettringite contains two formula units and may be regarded as one column 2.15 nm long plus its associated sulphate ions.

Thus the average column length in the most disordered system examined is predicted by our calculation to be 20 nm or 0.02 μm. This is very short compared to the average observed fibre dimensions for samples prepared at pH ~ 11.3 (~ 1 μm long × 0.2 μm diameter). If we assume that the lowest value of K_E obtained from the data of Jones [7] and D'Ans and Eick [9] represents a perfectly crystalline material, then the increase in free energy due to disorder is given by

$$\Delta G = 5.7 \log (K_E/10^{-45})\ (\text{kJ mol}^{-1})$$

and the average column length is

$$l = 1.9/\Delta G\ (\mu\text{m}).$$

Values obtained from these relations are given in Table II.

We may next consider the energetics of the system and attempt to correlate our calculations with the observations of other workers referred to earlier in this paper. These are the decomposition of "ettringite" to calcium aluminate monosulphate hydrate in alkali solutions stronger than ~ 0.25 M, in spite of the metastability of the latter phase with respect to ettringite in an alkali-free system and the two modes of "ettringite" formation proposed by Schwiete *et al.* In order to assess the decomposition of ettringite to monosulphate quantitatively we need to assemble values of standard free energy for all the species involved. This will be done in a future paper. Meanwhile we may consider the situation qualitatively. The implied decomposition is:

$$Ca_6(Al(OH)_6)_2\,(SO_4)_3 \cdot 26H_2O \rightarrow$$

$$Ca_4(Al(OH)_4)_2\,SO_4(OH)_4 \cdot 6H_2O$$

$$+\ 2\,CaSO_4 \cdot 2H_2O + 16H_2O.$$

This is obviously likely to occur if the gypsum is removed in some way (e.g. by reaction with tricalcium aluminate) but there is no immediate reason to suppose that the reaction should be affected by a change in pH. However, if it is accepted that the free energy of the "ettringite" is raised considerably at higher pH levels then it is possible that it eventually exceeds that of a mixture of calcium aluminate monosulphate hydrate, gypsum and water. It is then possible for the monosulphate to persist as a stable phase. The implication of the reported results is that a sufficiently high pH can only be attained by addition of alkali to the system.

The two types of "ettringite" proposed by Schwiete *et al.* are said to form below pH 11.8 and above pH 12.5, respectively. It has already been shown that the ionic activity product, K_E, is related to the product of the activities of the hydroxide and sulphate ions.

If we consider a pH of 12.2 and an average sulphate activity for the system ($\sim 10^{-3}$) then we obtain a value of $\log K_E = -37.5$, corresponding to a predicted column length of

~ 0.05 μm or ~ 25 unit cells. X-ray diffraction lines would then have a typical width of ~ 1° 2θ, compared with 0.01° 2θ for a 2 μm crystal size. The broadening of the lines should be easily detectable with a diffractometer but the sample should still yield a recognizable diffraction pattern. However, it seems likely that a well-defined morphology is no longer produced when the column length is less than this.

If it is accepted that the retardation of the setting of portland cement by the addition of gypsum is due to the formation of a coating of disordered ettringite, then normal retardation can only occur in the pH range defined by Schwiete *et al.* [8]. The aqueous phase of the cement is approximately in equilibrium with calcium hydroxide: the pH is therefore altered if either soluble anions or cations are added to the aqueous phase. Addition of NaOH or Na_2CO_3, for example, leaves sodium ions in solution, the anions being precipitated as calcium compounds: the extra cations in solution lead to an increase in the pH at which equilibrium with calcium hydroxide is attained. Conversely, addition of a material such as $CaCl_2$ leaves the anion in solution and lowers the equilibrium pH. In either case it is possible to obtain pH levels outside the range 12.5 to 12.8 and accelerated setting is observed.

5. Conclusions

Ettringite does not exhibit a constant solubility product. The ionic activity product, K_E, of solutions in equilibrium with "ettringite" rises as a function of hydroxide and sulphate activity. This rise reflects an increase in the molar free energy of the solid phase which we attribute to defects in the crystal structure, namely the removal of aluminium from the calcium aluminate hydrate columns resulting in columns of finite length. Rough estimates of column length based on thermodynamic data for free ions suggest a value of ~ 0.2 μm at pH ~ 11.5, decreasing to ~ 0.02 μm at higher pH levels. These values are consistent with the observed crystal size of ettringite. It should be possible to detect significant X-ray line broadening for $(h k l)$ lines with $l \gg h + k$ in samples prepared or stored at high pH and sulphate levels and an extra infrared absorption band due to the terminal OH groups should be detectable in such samples. We also expect that "ettringite" could lose its characteristic fibrous habit at high pH levels and be capable of forming a coherent coating over other particles. This would be unstable with respect to calcium aluminate monosulphate hydrate above a certain pH level and with respect to ordered crystals below a second, lower, pH level. These phases would not be capable of forming coherent coatings. This provides an explanation of the acceleration of the setting of portland cement when the pH is either lowered or raised. We predict that when the pH is lowered large amounts of ettringite will be detected in the initial product whereas when it is raised calcium aluminate monosulphate hydrate or extra calcium hydroxide will be produced.

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