

THE C₃A - GYPSUM SYSTEM IN ALKALI SULFATE SOLUTIONS

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An investigation series is carried out on the mechanism of hydration of C₃A in the presence of gypsum in excess solutions of 0.1 and 1 molar alkali metals sulphates, for one week at room temperature. The effect of lime and alite on the progress of hydration is studied. In sulphate-rich solutions, the mechanism of C₃A hydration is interpreted in terms of the change in the calcium ions concentration of the solution with time. The dormant period is indicated by a plateau of the dissolved calcium and the acceleration period by its depletion. The hydration of C₃A in the presence of gypsum is strongly retarded in 0.1 molar alkali sulphate solutions saturated with lime, the dormant period is extended, and the mechanism becomes diffusion controlled. The hydration is, however, accelerated in 1 molar sodium sulphate solution of the same mixture because of the precipitation of hydroglauberite (Na₁₀(CaSO₄)₈·6H₂O) which is accompanied by the depletion of the dissolved calcium. The hydroglauberite transforms to ettringite (C₃A·3CaSO₄·30-32H₂O) with time.

INTRODUCTION

The influence of alkali metals sulphates on the progress of hydration of ordinary Portland cement and its individual components is becoming of an increasing importance because of the enhanced degree of sulphatization in modern cement industry as well as of the enrichment of alkalies in concrete from its ingredient. As soon as cement is mixed with water alkalies pass rapidly into the solution. Alkali concentration in the pore fluid of concrete range between 0.2 to 0.7 moles, depending on the cement content and the concrete components. The rise of pH-values as a result of dissolved alkalies favours the precipitation of portlandite [1].

In Portland cement clinker, alkalies not combined with sulphate are preferentially incorporated in the aluminate and belite [2]. C₃A has an inclusion limit of 2.25 % Na₂O and 4.39 % K₂O [3]. Whilst sodium oxide dissolves in the lattice of C₃A, K₂O and SO₃ give rise to potassium sulphate or double salts that coat the C₃A crystals partly or fully [4]. In laboratory clinkers, K₂SO₄ was detected from 60 % sulphatization onwards whereas Na₂SO₄ was not detectable until a sulphatization of 90%. The clinker may contain arcanite (K₂SO₄), aphtitalite (K₃NS₄) and rarely thernadite (Na₂SO₄) all of which along with calcium langbeinite (KC₂S₃) react very rapidly with water [5].

Sulphur combined in the clinker phases was reported to have an accelerating effect on the cement setting while the sulphate combined as alkali sulphate has a retarding effect [2]. Potassium sulphate increases the early hydration but lowers the ultimate strength [6]. Rapid setting by potassium sulphate is due to the syngenite (K₂(CaSO₄)₂H₂O) formation with a reduction of the sulphate from the solution which prevents satisfactory retardation of C₃A hydration. K₂SO₄ causes a decrease of the flow value of fresh mortar specimen and lowers the bleeding and slump values of concrete specimens [7, 8]. Sodium sulphate is found to be ineffective on the progress of hydration of C₃A [9].

A closer understanding of the effect of the alkali metal sulphates on the hydration behaviour of C₃A shall through more light on its mechanism of hydration. In this paper the mechanism of the C₃A hydration in the presence of gypsum, lime and alite in different concentrations of sodium and potassium sulfates solutions is studied.

EXPERIMENTAL

The C₃A was prepared through burning a stoichiometric mixture of calcite and alumina three times at 1350°C, the free lime content was 1.7 % [10]. The preparation of alite was performed by burning calcite with silica, alumina and magnesium carbonate with a mole

ratio of 3:0.88:0.05:0.05 at 1450 °C four consecutive burnings, three hours each. The alumina and magnesia were added to the reaction mix as fluxes in order to obtain the phase at a relatively low temperature of 1450 °C, the free lime content was 5.4 %. The X-ray diffraction patterns of the two phases prepared are illustrated in Figures 1 and 2 respectively. Their chemical formulae were not elucidated, as the results of the respective X-ray diffraction analysis were satisfactory.

The gypsum phase ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) used as well as the anhydrous sodium and potassium sulphate salts were reagent grade. Lime was obtained from calcining chemically pure calcite.

The mixtures studied comprised a starting weight of 0.3g C_3A and the respective weights were calculated according to the mole ratios cited in Table 1.

Table 1. The reactants used in 100ml alkali sulphate solutions.

System	Mole ratio	Weight used (g)
I. $\text{C}_3\text{A-G}$	1:1.5	0.3-0.2867
II. $\text{C}_3\text{A-G-C}$	1:1.5:1	0.3-0.2867-0.0623
III. $\text{C}_3\text{A-G-C-A}$	1:1.5:1:1	0.3-0.2867-0.0623-0.2535

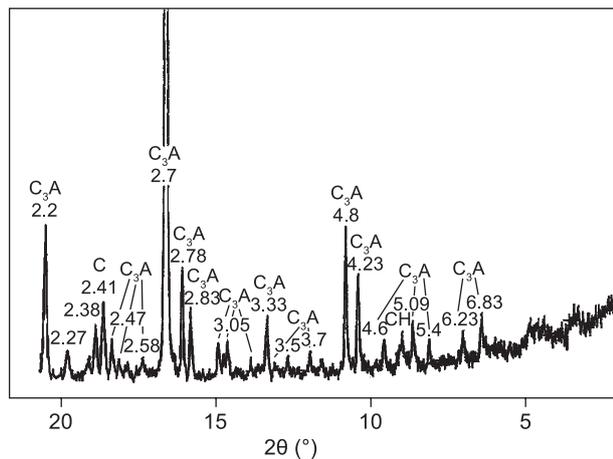


Figure 1. The X-ray diffraction patterns of the C_3A .

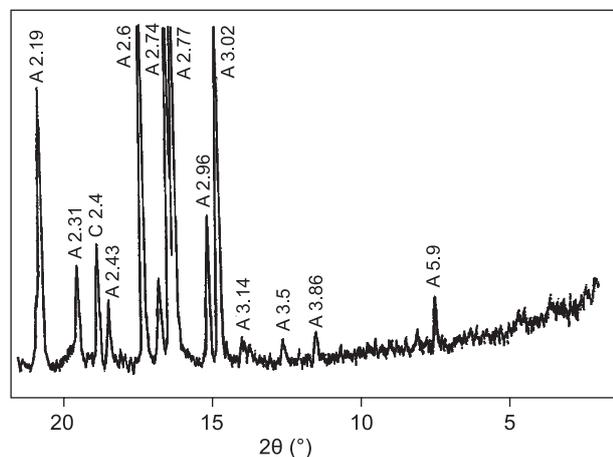


Figure 2. The X-ray diffraction patterns of the alite (A).

The hydration reaction was carried out by stirring the solid mixtures in 100ml of 0.1 molar solution of each of the sodium and the potassium sulphate as well as in 1molar sodium sulphate at time intervals from 2 min up to 7 days at room temperature. The 1mole potassium sulphate solution could not be prepared because of the formation of supersaturated solution at room temperature. At the definite time intervals the solutions were filtered off, analyzed volumetrically for the determination of calcium and colourimetrically for aluminum [11]. The sulphate concentration of the solution was measured turbidimetrically [12].

RESULTS AND DISCUSSION

The change in the concentration of the ions dissolved in 0.1 and 1molar alkali sulphate solutions of the different C_3A systems studied are illustrated in Figures 3 and 4 respectively, on semi-logarithmic scales. In Figure 3, the solubility curves of 0.1 molar sodium and potassium sulphate solutions are denoted by (1) and (2). The results obtained from hydrating the systems in 1molar sodium sulfate solutions are compared with those carried out in 0.1 molar solutions in Figure 4, the corresponding curves are given the No. (3). As previously mentioned the investigation series with 1molar potassium sulphate solution was not carried out due to the formation of supersaturated solution of this salt at this concentration in water at room temperature.

In the figures, the concentrations of the dissolved sulphate and aluminum are expressed as gram $\text{SO}_4^{2-}/\text{l}$ and gram Al/l respectively. The amount of dissolved calcium is presented as gram CaO/l to compare the values obtained with the saturation value of lime at room temperature ($\sim 1.13\text{gCaO}/\text{l}$).

Systems in 0.1molar alkali sulphate solutions

It is clear from Figure 3 that the concentration of the sulphate ions dissolved in 0.1molar alkali sulphate solutions tends to decrease with time. The sulphate depression is pronounced in the solutions of potassium (curves 2) compared to that in the case of sodium (curves 1). The solubility curves of systems II and III are slightly lower than those of system I.

Aluminum is detected clearly in the solutions of system I. Its initial concentration is lowered with time then rises again. The solutions of system II shows a slight increase of the dissolved aluminum at a later hydration time. No aluminum is observed in the solution of system III.

The dissolved calcium ions behave quite in a similar way in the solutions of both alkali metals. In systems I and II, the ions released at the reaction start remain constant for 30 minutes and 24 hours respectively, then deplete. In

mixture III the lime concentration approach its saturation value at room temperature and remains constant during 7 days. The calcium ion concentration of the solutions increases from systems I to II to III. This is expected, as in system I the sources of the dissolved calcium are the ions released from the hydration of C_3A and from the solubility of gypsum. The increase in the concentration of the dissolved calcium in system II is attributed to the addition of 0.6gram/liter CaO to the mixture (see Table 1). The further increase in the concentration of the dissolved calcium in system III is due to the presence of alite beside the lime added. The alite acts as an important source of lime. The pH-values lying in the range of 11 to 12 in the three systems are a further indication for the increase of lime concentration in solution. The data of the calcium ions concentrations of the three systems are cited in Table 2 as gram CaO/liter.

Systems in 1molar sodium sulphate solution

Figure 4 illustrates the change in the concentration of the ions dissolved in 1 molar sodium sulphate solutions of the three systems studied, with time. The results are drawn together with those obtained in 0.1molar solutions for the purpose of comparison.

The sulphate ions dissolved in 1molar solutions are 10 times greater than in the case of 0.1 molar. In system I, the solubility curve of sulphate remains constant over the duration studied (7 days). The curves show a slight decrease in system II and a clear depletion in system III.

In the solution of system I, the dissolved aluminum does not pass through a minimum as in the case of 0.1molar solutions but remains high in solution. The aluminum is weakly dissolved in system II and totally depressed in system III.

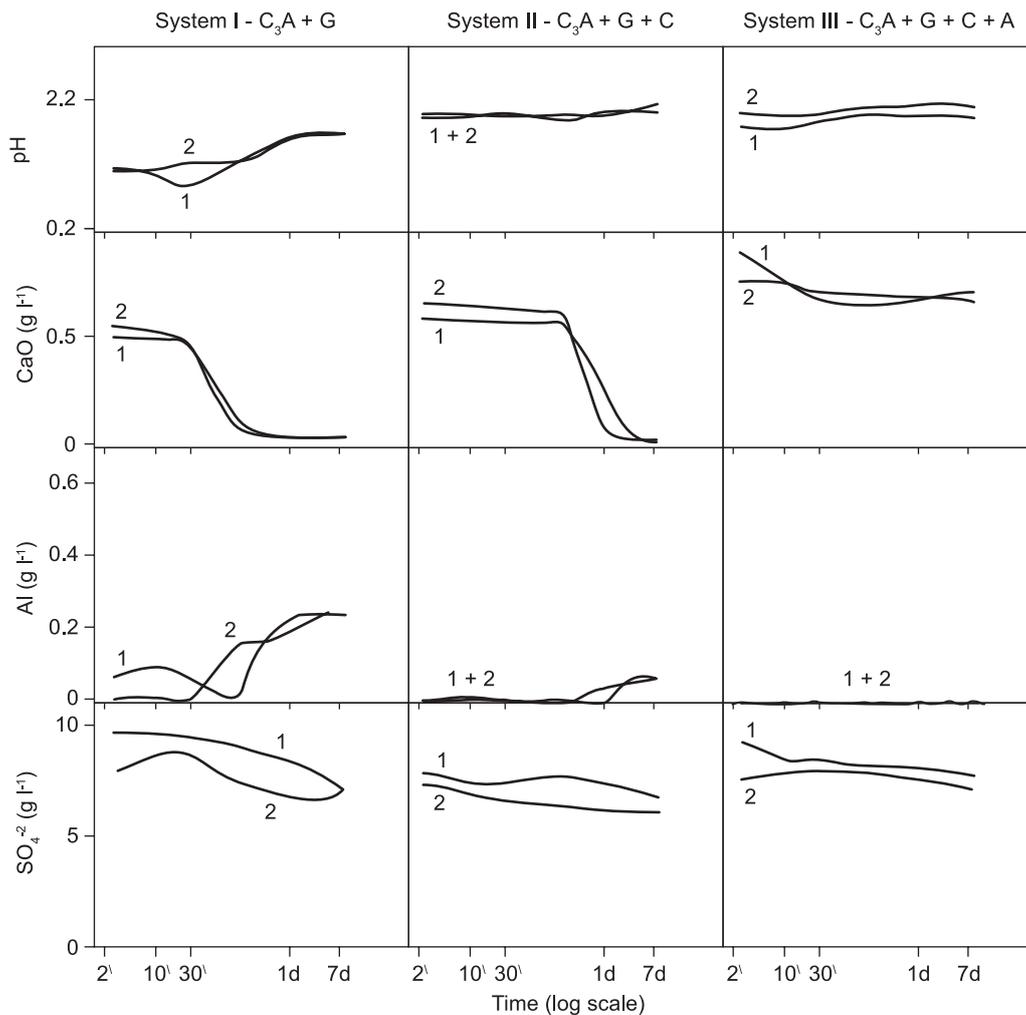


Figure 3. The change in the concentration of the ions dissolved in the solutions of the mixture C_3A -gypsum, also in the presence of lime and alite in 0.1M sodium sulphate solution (curves no1) and 0.1 M potassium sulphate solution (curves no 2) at room temperature (G - Gypsum, C - Lime, A - Alite).

Table 2. The variation in the calcium ion concentration expressed as gram CaO/liter in 0.1 and 1 molar solutions of sodium sulphate (NS) and 0.1 molar solution of potassium sulphate (KS) of the systems studied.

Time	CaO (g/l) in 0.1 molar alkali sulphate solution			CaO (g/l) in 1 molar sodium sulphate solution		
	System I	System II	System III	System I	System II	System III
	NS - KS	NS - KS	NS - KS	NS	NS	NS
2 ^c	0.503-0.556	0.599-0.669	0.909-0.769	0.741	0.800	0.974
10 ^c	0.493-0.524	0.591-0.703	0.012-0.785	0.708	0.503	0.937
30 ^c	0.470-0.477	0.580-0.643	0.013-0.731	0.687	0.288	0.867
3h	0.134-0.050	0.578-0.626	0.009-0.710	0.119	0.076	0.791
6h	0.063-0.046	0.569-0.626	0.006-0.704	0.079	0.081	0.671
1d	0.031-0.044	0.379-0.031	0.000-0.704	0.071	0.089	0.671
3d	0.031-0.044	0.048-0.034	0.000-0.693	0.077	0.088	0.585
7d	0.046-0.044	0.031-0.031	0.000-0.731	0.102	0.084	0.476

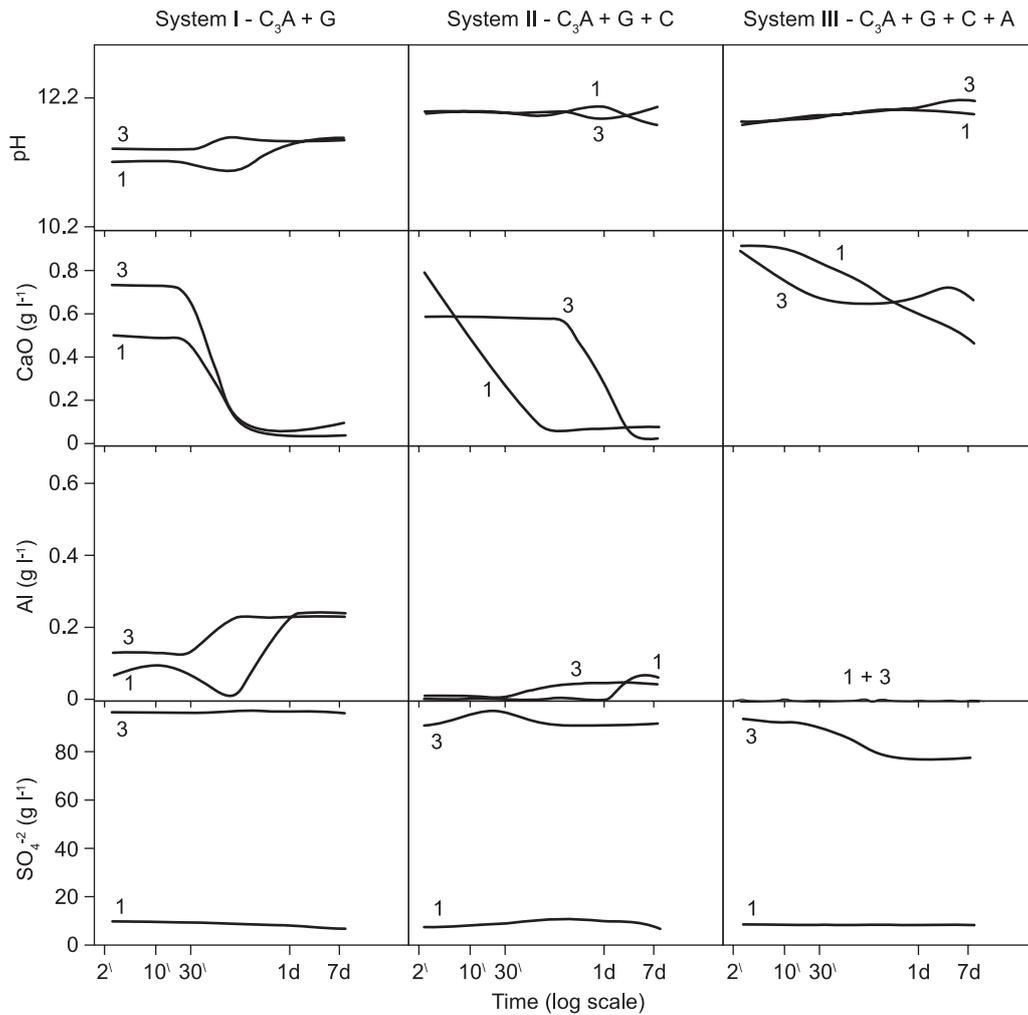


Figure 4. The change in the concentration of the ions dissolved in the solutions of the systems C₃A-gypsum, also in the presence of lime and alite in 1 M sodium sulphate solution (curves no 3) with time. The results obtained in 0.1 M sodium sulphate solutions (curves 1) are included in the figure for purpose of comparison (G - Gypsum, C - Lime, A - Alite).

The calcium ions dissolved in the solutions of system I behave in the same way as in the case of 0.1 molar solutions i.e. they show a plateau for 30 minutes then decrease with time up to a complete depletion. The calcium ions deplete rapidly from the solutions of system II and in system III, they are consumed at a slower rate. In these last two cases, no dormant period occurs but the reaction passes directly to the acceleration stage.

X-ray diffraction

The hydration of the different C₃A systems in 0.1 and 1 molar alkali sulphate solutions leads to the formation of ettringite (C₃A.3CaSO₄.30-32H₂O); the monosulphate hydrate (C₃A.CaSO₄.10-12H₂O) does not appear in these systems.

In 0.1 molar alkali sulphate solution, clear ettringite patterns are detected in system I after 2 minutes from the reaction start. The ettringite patterns weaken in the

presence of lime and alite in systems II and III. The ettringite salt crystallizes better from 0.1 molar solutions of the potassium sulphate compared to that of the sodium salt. Neither hydroglauberite (Na₁₀(CaSO₄)₈6H₂O) nor syngenite (K₂(CaSO₄)₂H₂O) form at this molar concentration,.

In 0.1 molar solution, the C₃A is consumed after 3 days during the hydration of systems I and II, but in system III the solid is clearly detected on the 7th day (Figure 5). In 1molar sodium sulphate solution the diffraction patterns of C₃A disappear early i.e. after 10 min to 3 hours in the different systems studied.

Hydroglauberite precipitates after 7days from 1 molar sodium sulfate solution of system II at a solution concentration of 92.2 gram SO₄²⁻/liter, 0.047 gram Al/liter and 0.084 gram CaO/liter. It appears earlier in system III (after 3 hours) at a solution concentration of 78 gram SO₄²⁻/liter, 0.61 gram CaO/liter with no dissolved aluminum but transforms to ettringite after 3 days (Figure 6).

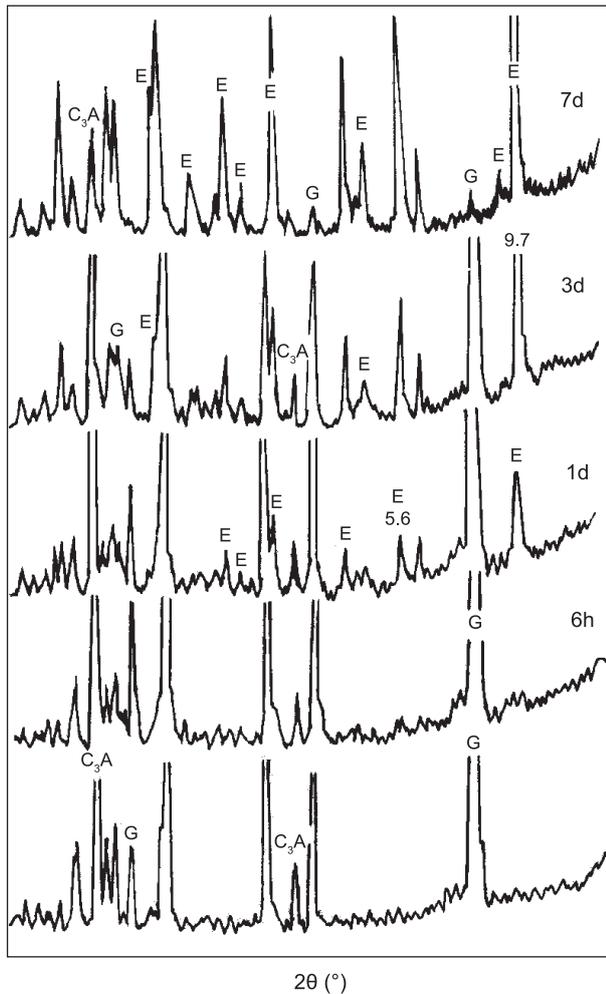


Figure 5. The X-ray diffractograms of the solids obtained from hydrating the mixtures of C₃A and gypsum in the presence of lime and alite (system III) in 0.1 molar sodium sulphate solution (G = Gypsum, E = Ettringite).

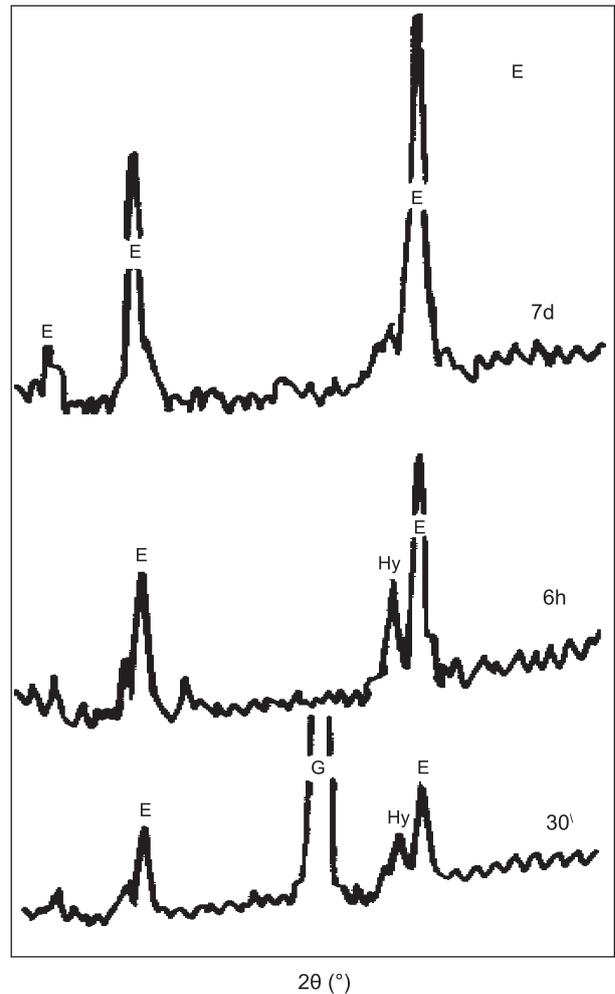


Figure 6. The X-ray diffractograms of the solids obtained from hydrating the mixtures of C₃A and gypsum in the presence of lime and alite (system III) in 1molar sodium sulphate solution (G = Gypsum, Hy = Hydroglauberite, E = Ettringite).

DISCUSSION

The hydration reaction of C_3A in the presence of gypsum in an excess amount of water was previously studied for a mole ratio of 1:1.5 at room temperature [13], the effect of lime and alite on the progress of reaction was also investigated. The mechanisms of the reactions were interpreted in terms of the change in the sulphate ion concentration of the solution with time. This mechanism was valid as long as the gypsum phase was the only source of sulphate in the system and its concentration was below the value of its saturation value at room temperature.

The reaction kinetics of C_3A with gypsum followed the three-stage route illustrated in Figure 7, which can be explained as follows. Point (a) represents the instantaneous reaction. Line (a-b) represents the dormant period and the route (b-c-d) expresses the acceleration period. At point (a), there is a direct release of the sulphate ions from the gypsum phase to the solution. This stage is accompanied by an instantaneous coating of the C_3A grains with a layer of calcium sulphoaluminate hydrates, which type and morphology depend on the concentrations of lime, sulphate ions, and hydroxyl ions of the solution as well as temperature. During the dormant period (line a-b), the solution does not take part in the reaction and the reaction becomes diffusion controlled. Line (b-c) represents the first part of the acceleration period: At (b) the hydrate salts coating the C_3A grains precipitate and new C_3A surfaces are exposed to further reaction. At (b-c) the C_3A reacts with the dissolved calcium sulphate present in the solutions and causes its depletion to form ettringite. The dissolved calcium sulphate is depleted at (c) and the excess C_3A reacts with ettringite to form the monosulphate hydrate.

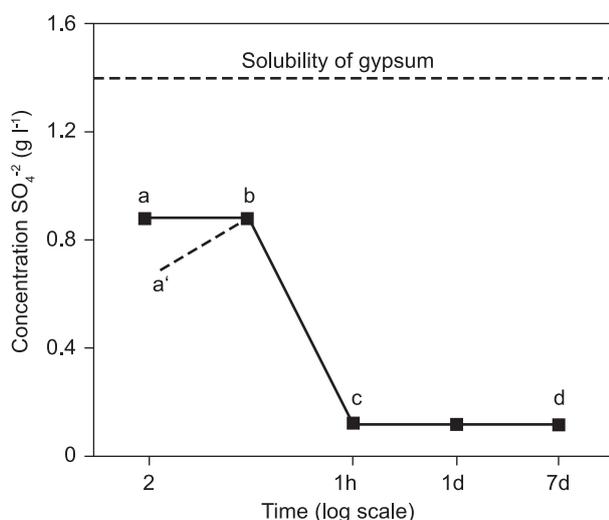


Figure 7. The change of the sulphate ions concentration with time in the solutions of C_3A and gypsum (G) at room temperature [13].

Alkali sulphate solutions with concentrations equal to or greater than 0.1 mole are sulphate-rich. The change in the concentration of the dissolved sulphate with time is therefore no more indicative for the mechanism of hydration due to its presence in an excess amount, instead the variation in the calcium ion concentration of the solution with time is significant.

In 0.1 molar alkali sulphate solutions, the behaviour of the dissolved calcium follows the same qualitative path as that of the sulphate ions in water shown in Figure 7. This applies to systems with CaO concentration lying below the saturation value of lime at room temperature. Under these conditions, the dissolved lime shows a constant value corresponding to the dormant period of C_3A then depletes during the acceleration period. This is observed in system I where the C_3A hydrates with gypsum in 0.1 and 1 molar alkali sulfate solutions with no added lime or alite. It is also seen in 0.1 molar alkali sulphate solutions of system II, in the presence of a low concentration of lime. In this system, the lime added to the reactant amounts to 0.6 gram CaO/liter which value is significantly lower than the saturation value at room temperature and means that the lime added should dissolve. Under these conditions, the dormant period extends only slightly.

The further increase of lime concentration in the solution of 0.1 molar alkali sulphates of system III, leads to a clear retardation of the dormant period. System III has a higher lime concentration due to the presence of alite, the dormant period extends further, and a longer plateau of the dissolved calcium lasting 7 days long is observed. The solution does not take part in the reaction and the mechanism becomes diffusion controlled. This explains the retardation of C_3A hydration.

The sulphate depletion shown at b-c in Figure 7 indicates the acceleration period of C_3A i.e. the reaction of its newly exposed surface with the dissolved calcium sulfate to form the ettringite. In sulfate-rich solution (≥ 0.1 molar alkali sulfate solutions), the acceleration period of C_3A in the presence of gypsum is indicated by the depletion of the calcium ions from the solution. The calcium depletion in 0.1 molar alkali sulphate solutions of systems I, II and III and in 1 molar sodium sulfate solution of system I, is accompanied by the formation of ettringite. In 1 molar sodium sulphate solution of systems II and III with no dormant period, the rapid depletion of the calcium ions is accompanied by the precipitation of hydroglauberite.

The hydration reaction of a mixture composed of C_3A , gypsum and alite (molar ratio of 1:1:1.5) was previously studied in 0.5 molar solutions of each of the sodium sulphate and potassium sulphate salts [14, 15]. The hydration procedure was the same as that of the present paper. The results proved the precipitation of hydroglauberite and syngenite from the respective alkali sulphate solutions at this molar concentration. This means that the precipitation of the double salts occurs in

these systems readily in alkali sulfate solutions of molar concentrations equal to or higher than 0.5 moles but not at a molar concentration of 0.1. Further investigations are necessary to define the exact concentration of the alkali sulphate solutions lying in the range of 0.1 to 0.5 moles at which the double salts precipitate in these systems.

CONCLUSION

In alkali sulphate solutions, the hydration of C_3A in the presence of gypsum (mole ratio 1 : 1.5) depends on the concentration of the dissolved calcium, sulfate ions, and lime at room temperature. In sulphate-rich solutions, the mechanism of hydration is indicated by the variation in the calcium ions concentration of the solution with time. In 0.1 molar alkali sulphate solution, the hydration of C_3A in presence of gypsum is retarded significantly when the lime concentration of the solution reaches saturation. The hydration is accelerated in 1 molar solutions due to the precipitation of hydroglauberite, which transforms to ettringite with time.

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