Pergamon

Cement and Concrete Research, Vol. 28, No. 1, pp. 53–61, 1998

0008-8846/98 $19.00 + .00

PII S0008-8846(97)00253-6

STUDIES ON THE STABILITY OF THE CALCIUM SULFOALUMINATE HYDRATES. PART II: EFFECT OF ALITE, LIME, AND MONOCARBOALUMINATE HYDRATE

H.Y. Ghorab,[1]* E.A. Kishar,† and S.H. Abou Elfetouh†
*Helwan University, Cairo, Egypt
†Ain Shams University, Cairo, Egypt

(Received March 20, 1995; in final form November 5, 1997)

ABSTRACT

The variation of the solubility values of ettringite in the presence of alite, lime, and monocarboaluminate hydrate at 30 and l00°C is studied. The solubility product of ettringite is found to be 1.98×10^{-37} in pure water, 1.11×10^{-40} in the presence of alite with a mole ratio of l0, and insoluble in the presence of saturated lime solution as well as in an excess amount of monocarboaluminate hydrate.

The ettringite phase reacts with the calcium silicate hydrates with the weakening of its X-ray diffraction intensity; at the boiling water temperature the tobermorite phase forms, in the presence of lime or monocarboaluminate hydrate the hydrogarnet phase appears beside the monophase solid solution. *© 1998 Elsevier Science Ltd*

Introduction

The behaviour of the calcium aluminate hydrates and their derivatives in aqueous solutions has attracted the attention of many investigators, the problem of their stability being directly related to the physical and mechanical properties of Portland cement. These phases are the first responsible for the setting behaviour of cement and affect the hardening process at later stages of hydration. The nature of the calcium sulfoaluminate hydrates is better known than that of the calcium carboaluminate hydrate and relatively more concern has been focused on the ettringite than the monosulfate hydrate.

Experimental

The ettringite and the monocarboaluminate hydrate were prepared by stirring a stoichiometric ratio of powdered tricalcium aluminate and gypsum or calcium carbonate in an excess amount of redistilled water. The alite phase was prepared by mixing calcium oxide (from calcium carbonate), silica, aluminium oxide, and magnesium carbonate with a mole ratio of

---

[1] To whom correspondence should be addressed.

3:0.88:0.05:0.05.The mixture was burned for 5 h at 1450°C followed by three other times, the duration of each being 3 h.

The systems studied are ettringite-alite-water, ettringite-lime-water, and ettringite-monocarboaluminate hydrate-water with mole ratios 1:1 and 1:10, expressed relative to the ettringite phase. The weight of ettringite used was 0.5 g and the respective weights of alite, lime, or monocarboaluminate hydrate were calculated.

The mixtures were stirred at 30°C or boiled for 1 h and up to 14 days in l00 mL redistilled water. At the desired time interval the solutions were filtered off and the dissolved calcium, sulfate, aluminium, silicon, carbon dioxide, and the pH value were determined (1,2). The solid phases were analysed by means of X-ray diffraction.

Results

The behaviour of the ettringite phase in pure water was reported in part 1 of this series (3) and the stability of both types of calcium sulfoaluminate hydrates in alkaline solutions at different temperatures is published elsewhere (4).

The solubility values of the system alite-ettringite-water and lime-ettringite-water at 30 and 100°C are illustrated in Figure 1(a & b), those of the pure ettringite are inserted in the figures for comparison. The solubility curves of the ettringite-monocarboaluminate hydrate-water system at 30 and 100°C are shown in Figure 2. The details of the solubility values are given in Tables 1 to 6.

At 30°C, the sulfate ion concentration of the solution of the pure ettringite phase, having an average value of 0.2 g/L, undergoes a stepwise lowering in the presence of alite. The first stage lasts 6 h at values 0.157 and 0.112 g SO_4^{2-}/L for the mixtures with mole ratios of 1 and 10, respectively followed by constant values at 0.068 and 0.045 g SO_4^{2-}/L for both mixtures studied (Fig. 1a). In the lime-ettringite-water system, the sulfate ion concentration of the ettringite solution decreases from 0.2 to 0.045 and 0 g SO_4^{2-}/L in the mixtures with mole ratios 1 and 10, respectively. It is constant during the reaction time studied and does not undergo a stepwise lowering (Fig. 1b).

Both systems of alite- and lime-ettringite mixtures with a mole ratio of 1 cause a depression in the amount of the dissolved aluminium from average 30 to 4 ppm. A complete depression however is seen in the presence of 10 mol lime to ettringite. The calcium ion concentrations increases in the presence of alite as well as lime from 0.08 to average 0.174 and 1.08 g CaO/L in the mixtures with mole ratios of 1 and 10. The average pH value of the solutions is 11.4 in the ettringite-water system and 12.5 in the alite mixture with a mole ratio of 1 and in the presence of lime. At higher alite concentration, it shows a value of 13.1 at 1 day and 13.5 after 14 days.

The silicon concentration, whose only source is alite, is constant in the ettringite-alite mixture with a mole ratio of 1. It is lowered by higher alite additions but increases with time attaining the solubility value of the dilute alite solution (Table 1).

The sulfate ion concentration of the solution of ettringite in water is appreciably affected by the monocarboaluminate hydrate at 30°C. An early decrease is seen with a mole ratio of 1 followed by a rerise after 6 h attaining almost the value of the pure ettringite solution after 2 weeks stirring; the amount of dissolved sulfate is completely depressed by the monocarboaluminate hydrate when present with a molar ratio of 10 (Fig. 2). The aluminium concentration is averaged 50 ppm in the solution of ettringite-monocarboaluminate hydrate

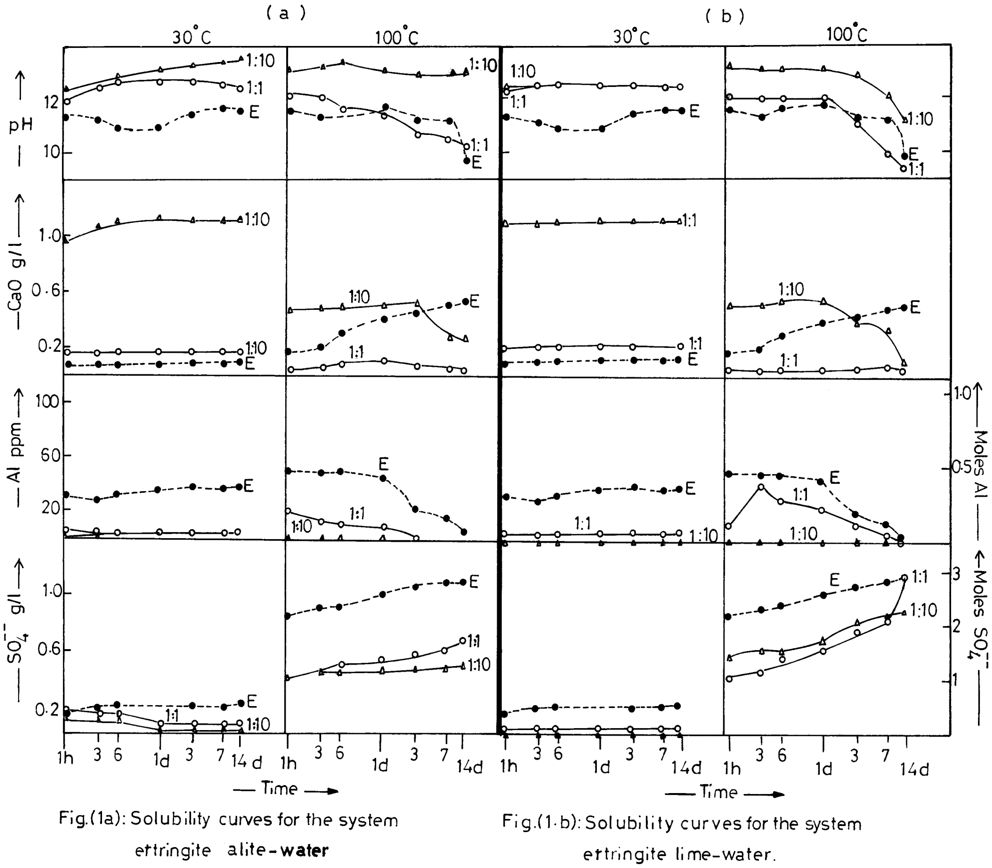

FIG. 1.

Solubility curves for the system *a*) ettringite-alite-water and *b*) ettringite-lime-water.

(mole ratio = 1), which value is higher than the aluminium solubility of the solutions of each of the pure hydrates. The addition of the carbonate-bearing phase with a mole ratio of 10 leads to a low aluminium concentration at first and rises with time to reach the value of the mixture with a mole ratio of 1. In this system, the maximum calcium oxide concentration of the solution is 0.19 g CaO/L. The average pH value of the carbonate-bearing mixture is 11.4 and 11.9 for the mole ratios 1 and 10, respectively. The amount of carbon dioxide dissolved is constant and increases with the rise of monocarboaluminate hydrate concentration in the mixture.

Both ettringite and monocarboaluminate hydrate phases are stable at room temperature and the hydrogarnet phase appears in both series studied after 6 h stirring. In the presence of alite the X-ray diffraction patterns of the ettringite phase remain unchanged in the mixture with a mole ratio of 1 except for an increased intensity of calcium hydroxide after 7 days, at which time the diffraction lines of alite disappear. At higher alite concentration, the ettringite patterns weaken with time. In the lime-bearing system, however, no variation or weakening in the ettringite patterns is observed.

On the other hand, a boiling solution of the pure ettringite showed a maximum release of

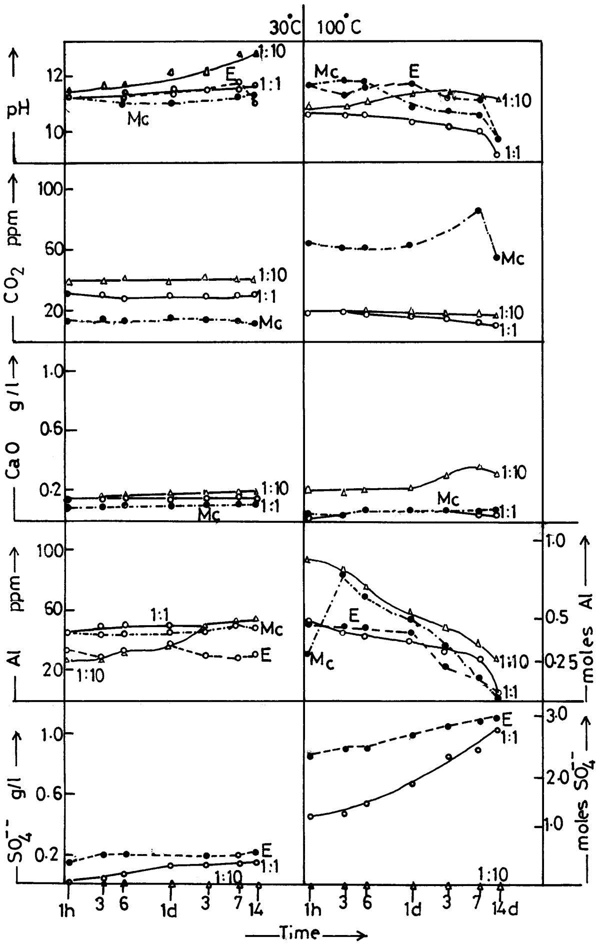

Fig.(2): The solubility curves for the system ettringite-monocarboaluminate hydrate-water.

FIG. 2.
Solubility curves for the system ettringite-monocarboaluminate hydrate-water.

2.8 moles sulfate after 2 weeks stirring (3). In the presence, of alite the total sulfate release amounts to 1.76 and 1.29 moles for the mixtures containing mole ratios of 1 and 10 (A:E). The effect of lime is, however, less than that of alite and a total of 2 mol go to the solution containing concentrated lime during 2 weeks time (Fig. 1). The amount of dissolved aluminium in the boiling ettringite solution decreases with time and is consumed after 14 days. The same behaviour is observed in the presence of low alite concentration with an obvious depression in the measured values and an early consumption (after 3 days). At higher alite additions, the concentration of aluminium is zero all over the reaction period. In the lime-bearing system with a mole ratio of 1, the total depression of aluminium from the solution is delayed and their dissolved values at earlier ages are higher than the comparative alite system. At higher lime concentration, no dissolved aluminium is detected. Generally the

TABLE 1
The solution concentration of the system ettringite-alite-water, mole ratio (1:1) and (1:10) at 30°C.

	Mole ratio (1:1)									(1:10)								
		SO_4^-		Al		Si		CaO			SO_4^-		Al		Si		CaO	
time	pH	g/L	moles	ppm	moles	ppm	moles $\times 10^3$	g/L	moles $\times 10^2$	pH	g/L	moles	ppm	moles $\times 10$	ppm	moles $\times 10^5$	g/L	moles $\times 10$
1 h	12.0	0.18	0.47	5.5	0.051	0.014	0.122	0.172	0.43	12.4	0.135	0.353	3.5	0.325	0.002	0.17	0.96	0.24
3 h	12.5	0.1574	0.41	4.5	0.042	0.014	.122	0.168	0.42	12.5	1.1125	0.294	4.0	0.372	0.002	0.17	1.08	0.27
6 h	12.7	0.1574	0.41	4.0	0.037	0.014	0.122	0.179	0.45	12.9	0.1125	0.294	4.0	0.372	0.005	0.43	1.10	0.275
1 day	12.7	0.068	0.18	4.0	0.037	0.014	0.122	0.168	0.42	13.1	0.045	0.118	4.0	0.372	0.009	0.78	1.12	0.28
3 days	12.8	0.068	0.18	3.5	0.033	0.014	0.122	0.168	0.42	13.3	0.045	0.118	4.0	0.372	0.009	0.78	1.10	0.275
7 days	12.7	0.068	0.18	3.5	0.033	0.014	0.122	0.180	0.45	13.4	0.045	0.118	4.0	0.372	0.012	1.04	1.11	0.277
14 days	12.5	0.068	0.18	4.0	0.037	0.014	0.122	0.184	0.46	13.5	0.045	0.118	4.0	0.372	0.014	1.22	1.12	0.28

values of the calcium ion concentration of the boiling solutions of the systems studied is lower than that of 30°C. In the dilute alite system, the solubility of calcium is less than that of the pure ettringite (average 0.06), whereas at higher alite concentration the calcium ion of the solution exceeds that of the ettringite system (average 0.41) but decreases after 3 days. The behaviour of calcium in the solutions of lime-ettringite mixture is similar to the alite at 100°C except for lower values at later reaction time in the mixtures with concentrated lime. The pH values of the solutions tend to decrease with time with an obvious similarity between the system of ettringite, dilute alite, and lime-bearing mixtures; in those solutions containing higher amount of alite, the depression is less noticed.

At the boiling water temperature, the monocarboaluminate hydrate is seen to delay the release of the dissolved sulfate in the solution of the mixture compared to that of the pure ettringite phase; this takes place with a mole ratio of monocarboaluminate hydrate to ettringite of 1. At higher carbonate phase, the sulfate ion is completely depressed from the

TABLE 2
The solution concentration of the system ettringite-calcium oxide-water, mole ratio (1:1) and (1:10) at 30°C.

	Mole ratio (1:1)							(1:10)				
		SO_4^-		Al		Calcium oxide					CaO	
time	pH	g/L	moles	ppm	moles	g/L	moles $\times 10^3$	pH	SO_4^- g/L	Al ppm	g/L	moles $\times 10$
1 h	12.4	0.045	0.118	4.00	0.0372	0.192	0.48	12.5	0.00	0.00	1.10	0.1964
3 h	12.5	0.045	0.118	4.0	0.0372	0.200	0.50	12.5	0.00	0.00	1.104	0.197
6 h	12.6	0.045	0.118	4.0	0.0372	0.208	0.513	12.5	0.00	0.00	1.112	0.1985
1 day	12.6	0.045	0.118	4.0	0.0372	0.200	0.50	12.5	0.00	0.00	1.12	0.20
3 days	12.6	0.045	0.118	4.0	0.0372	0.200	0.50	12.5	0.00	0.00	1.12	0.20
7 days	12.5	0.045	0.118	4.0	0.0372	0.200	0.50	12.5	0.00	0.00	1.12	0.20
14 days	12.5	0.045	0.118	4.0	0.0372	0.200	0.50	12.5	0.00	0.00	1.12	0.20

TABLE 3
The solution concentration of the system ettringite-monocarboaluminate-water, mole ratio (1:1) and (1:10) at 30°C.

	Mole ratio (1:1)							(1:10)					
		SO_4^-		Al	CO_2						CaO		
time	pH	g/L	moles	ppm	ppm	moles	CaO g/L	pH	SO_4^- g/L	Al pp	ppm	moles ×10	CaO g/L
1 h	11.2	0.0225	0.0588	45.00	32.00	0.2066	0.14	11.4	0.00	27.00	39.00	0.2518	0.152
3 h	11.3	0.045	0.11765	49.00	30.00	0.1937	0.144	11.5	0.00	27.00	40.00	0.2583	0.16
6 h	11.4	0.0675	0.1765	49.00	29.00	0.1872	0.144	11.6	0.00	30.00	42.00	0.2712	0.168
1 day	11.5	0.135	0.3529	50.00	30.00	0.1937	0.144	12.0	0.00	34.00	39.30	0.2537	0.176
3 days	11.4	0.135	0.3529	50.00	30.00	0.1937	0.152	12.0	0.00	51.00	43.00	0.2776	0.176
7 days	11.5	0.157	0.4105	54.00	29.50	0.1905	0.152	12.60	0.00	54.00	40.70	0.2628	0.184
14 days	11.6	0.157	0.4105	54.00	30.70	0.1982	0.152	12.60	0.00	54.00	40.20	0.2596	0.192

solution (Fig. 2). The aluminium concentration decreases with time tending to a zero value after 2 weeks with a parallel decrease in the pH value. The amount of calcium is seen to be low with a steady value of 0.2 g CaO/L, increasing slightly between 1 and 14 days, and that of the carbon dioxide in the solution of the mixture is less than that of the pure boiling solution of the monocarboaluminate hydrate.

According to the X-ray diffraction analysis, the pure ettringite phase was converted to the monosulfate hydrate after an hour boiling in water, which persisted to 11 days then decomposed to gypsum and hemihydrate (3). In the presence of alite with a molar ratio of 1, the monophases solid solution forms instead. The end product appears after 14 days as anhydrite and tobermorite. In the lime-ettringite system, the hydrogarnet phase is stabilised beside the monophase solid solution.

Both the ettringite and the monocarboaluminate hydrate in their mixture convert to the monophase solid solution at the boiling water temperature. At the 7th day the hydrogarnet appears and remains the main hydration product beside calcite up to 2 weeks (mole ratio Mc:E = 1). In

TABLE 4
The solution concentration of the system ettringite-alite-water, mole ratio (1:1) and (1:10) at 100°C.

	Mole ratio (1:1)									(1:10)							
		SO_4^-		Al		Si		CaO			SO_4^-			Si		CaO	
time	pH	g/L	moles	ppm	moles	ppm	moles $\times 10^3$	g/L	moles $\times 10^2$	pH	g/L	moles	Al ppm	ppm	moles $\times 10^5$	g/L	moles ×10
1 h	12.2	0.405	1.059	20.0	0.186	0.024	0.209	0.040	0.100	13.1	0.405	1.059	0.00	0.004	0.349	0.46	0.115
3 h	12.1	0.45	1.176	12.5	0.116	0.034	0.297	0.056	0.140	13.2	0.45	1.177	0.00	0.004	0.349	0.47	0.118
6 h	11.6	0.495	1.294	10.0	0.093	0.034	0.297	0.080	0.200	13.4	0.45	1.177	0.00	0.004	0.349	0.48	0.120
1 day	11.4	0.54	1.412	9.5	0.088	0.034	0.297	0.109	0.272	13.0	0.47	1.229	0.00	0.008	0.698	0.49	0.123
3 days	10.7	0.562	1.470	0.00	0.00	0.034	0.297	0.061	0.152	12.9	0.47	1.229	0.00	0.008	0.698	0.50	0.125
7 days	10.5	0.607	1.587	0.00	0.00	0.028	0.245	0.051	0.128	13.0	0.47	1.229	0.00	0.008	0.698	0.27	0.068
14 days	10.1	0.675	1.765	0.0	0.00	0.004	0.0349	0.026	0.064	13.0	0.495	1.294	0.00	0.004	0.349	0.26	0.065

TABLE 5
The solution concentration of the system ettringite-calcium oxide-water, mole ratio (1:1) and (1:10) at 100°C.

	Mole ratio (1:1)							(1:10)					
		SO_4^-		Al		CaO			SO_4^-			CaO	
time	pH	g/L	moles	ppm	moles	g/L	moles $\times 10^3$	pH	g/L	moles	Al ppm	g/L	moles $\times 10$
1 h	12.0	0.405	1.0588	12.5	0.11628	0.0512	0.128	13.1	0.562	1.469	0.00	0.52	0.130
3 h	12.0	0.470	1.2288	40.00	0.3721	0.0512	0.128	13.0	0.607	1.587	0.00	0.536	0.134
6 h	12.0	0.54	1.4118	30.00	0.2791	0.0512	0.128	13.0	0.607	1.587	0.00	0.560	0.140
1 day	12.0	0.607	1.587	24.00	0.2233	0.0512	0.128	13.0	0.675	1.765	0.00	0.56	0.140
3 days	11.0	0.7425	1.9412	12.5	0.11628	0.0672	0.168	12.8	0.720	1.882	0.00	0.40	0.100
7 days	9.9	0.81	2.1177	7.50	0.06877	0.0816	0.204	12.0	0.765	2.000	0.00	0.368	0.092
14 days	9.4	1.125	2.9413	0.00	—	0.072	0.180	11.1	0.787	2.0576	0.00	0.096	0.024

the mixture with a mole ratio of 10, the monophase solid solution remains well identified allover the reaction period, the hydrogarnet phase forming during the first hour and increasing with time.

Discussion

Table 7 summarizes the equilibrium concentrations of the ions present in contact with the ettringite phase in its aqueous solution at room temperature according to the values reported by different researchers (5–8) beside those found in the present work. The solubility product of the trisulfate form is calculated according to the congruent solubility of this phase as suggested by Zang (8) who used the following dissociation reaction:

$$3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 31H_2O = 6Ca^{2+} + 2AlO_2^{-} + 3SO_4^{2-} + 4OH^{-} + 29H_2O$$

$$\text{Ksp E} = (Ca^{2+})^6\cdot(AlO_2^{-})^2\cdot(SO_4^{2-})^3\cdot(OH^{-})^4$$

TABLE 6
The solution concentration of the system monocarboaluminate hydrate-water, mole ratio (1:1) and (1:10) at 100°C.

	Mole ratio (1:1)							(1:10)					
		SO_4^-		Al	CO_2						CaO		
time	pH	g/L	moles	ppm	ppm	moles	CaO g/L	pH	SO_4^- g/L	Al pp	ppm	moles $\times 10$	CaO g/L
1 h	10.6	0.450	1.1765	52.00	19.00	0.1086	0.199	10.80	0.00	93.00	21.00	0.0120	0.0112
3 h	10.6	0.473	1.2367	45.00	20.00	0.1143	0.184	10.80	0.00	87.00	21.00	0.0120	0.024
6 h	10.5	0.540	1.4118	42.00	17.50	0.1000	0.200	11.00	0.00	75.00	21.00	0.0120	0.072
1 day	10.3	0.675	1.7648	38.00	16.00	0.0915	0.224	11.30	0.00	55.00	20.00	0.01143	0.0736
3 days	10.2	0.855	2.2354	34.00	15.00	0.0857	0.304	11.30	0.00	48.00	19.00	0.01086	0.0640
7 days	10.0	0.900	2.3531	27.00	12.00	0.0686	0.368	11.20	0.00	37.00	18.00	0.01029	0.0380
14 days	9.20	1.035	2.706	7.50	10.00	0.0572	0.309	11.10	0.00	27.00	17.00	0.00972	0.040

TABLE 7
The solubility values and solubility products of ettringite.

Reference	CaO ppm	Al_2O_3 ppm	SO_3 ppm	Solubility product
Lerch (5)	45	12	50	7.6×10^{-46}
Lea (6)	132	35	127	3.5×10^{-37}
Turriziani (7)	35	215	43	1.65×10^{-44}
Zhang (8)	68.5	36.4	301.75	1.1×10^{-40}
Our work in pure water	84	56.2	168	1.98×10^{-37}
E:A (1:1) at 30°C	84	7.55	56.66	2.2×10^{-38}
E:A (1:10) at 30°C	84	7.55	37.5	1.11×10^{-40}

It is clear from the results cited in the table that the solubility product of the ettringite phase lies in the range of 10^{-37} to 10^{-46}. The value obtained in the present work is close to that reported by Lea (6) being 1.98×10^{-37} and 3.5×10^{-37} in both works, respectively. The next closest one is that obtained by Zang, being 1.1×10^{-40} in spite of its relatively high sulfate content. The values calculated on the basis of those found by Lerch (5) and Turriziani (7) are much lower and attain 7.6×10^{-46} and 1.65×10^{-44}. The observed differences may be attributed to the experimental conditions, which are not clear in the individual works.

Hampson and Bailey (9) attributed the variation in the solubility product of the ettringite to disordering in the crystal structure as a consequence of the removal of aluminium from the calcium aluminate hydrate column. According to the authors, this would lead to dependence of the ionic activities of the solution of ettringite upon the pH and sulfate activity. This statement can be checked by evaluating the solubility product of the ettringite as a function of the concentration, which would be a subject of future investigation.

In the present work, the solubility values of the pure ettringite phase in water is calculated according to the assumption of its congruent solubility as suggested by Zhang (8). In the presence of alite and lime, however, the solubility of the ettringite is treated as incongruent, i.e., the amount of calcium released to the solution from the phases added would be just needed to attain the saturation value of lime at the respective temperature, the decrease in the solubility value of ettringite is thus attributed to the depression of the aluminium and sulfate dissolved and not to calcium. The solubility product is thus calculated taking the value of calcium determined in the pure ettringite system beside the lowest values of sulfate and aluminium measured in the alite-ettringite water system at 30°C. These considerations lead to values of 2.2×10^{-38} and 1.11×10^{-40} for the mixtures having mole ratios of alite to ettringite 1 and 10, respectively. In the presence of excess lime or monocarboaluminate hydrate no aluminium or sulfate are measured in the solution, which would lead to a zero value for the solubility.

The stepwise lowering of the sulfate ion concentration observed in the alite-ettringite system is interesting because of its relation to the mechanism of hydration of the alite phase known for its spontaneous coating with a first hydrate layer, which is responsible for the first stage lowering of the sulfate ion concentration, after which precipitation a second hydrate appears and is connected with the second depression stage of sulfate, the CSH phase known to incorporate about 1/6 mole sulfate in its structure (10). Quite a similar behaviour was observed in the alite-tricalcium aluminate-water system, where a stepwise lowering of the dissolved aluminium was observed and was attributed to the mechanism of the alite hydration (11).

The decrease of the ettringite intensity of the X-ray diffractograms is another indication for the interaction taking place between the trisulfate form and alite. Previous work confirmed the interaction through calorimetric analysis of the hydration of the tricalcium silicate in the presence of ettringite considering the morphology of the resulting hydrates (12). It was reported that the addition of ettringite crystals did not change the growth symmetry of the nucleation centers and morphology of the resulting phases but did increase the number of active centers on which the growth of silicate hydrate nucleation centers occurred.

The ettringite phase was found to gain a more colloidal nature when formed instantaneously in an unsaturated lime solution of 0.6 g CaO/L during the hydration of tricalcium aluminate in the presence of gypsum (13). In this work, however, a lime solution of concentration 0.2 to 1.2 g CaO/L is found to be ineffective on the morphology of the readily formed ettringite phase as detected through the intensity of the X-ray diffraction patterns, the main effect lying in the solubility value.

References

1. APHA-AWWA-WPCF, Standard Methods for Examination of Water and Waste Water, American Public Health Association, 5th ed., p. 39, 1980.
2. A.I. Vogel, Quantitative Inorganic Analysis, Longman Green & Co, White Plains, NY, 1961.
3. H.Y. Ghorab and E.A. Kishar, Cem. Concr. Res. 15, 93–99 (1985).
4. H.Y. Ghorab and E.A. Kishar, 8th Int. Congr. Chem. Cem., Rio de Janeiro, 104–109 (1986).
5. W. Lerch, F.W. Ashton, and R.H. Bogue, J. Res. Nat. Bur. Stand. 2, 715 (1929).
6. F.M. Lea, The Chemistry of Cement and Concrete, Edward Arnold Ltd., London, 1956.
7. R. Turriziani and G. Schippa, Ricerca Sci. 25, 2894–2898 (1955). Chemistry of Cement, H.F.W. Taylor (ed.), p. 61, Academic Press Ltd., London, 1964.
8. F. Zang, Z. Zhou, and Z. Lou, 7th Int. Congr. Chem. Cem. 2, 188–193 (1980).
9. C.J. Hampson and J.E. Bailey, J. Mater. Sci. 3341–3346 (1982).
10. I. Odler, 7th Int. Congr. Chem. Cem. 4, 493–495 (1980).
11. H.Y. Ghorab, S.H. Abou El Fetouh, and H.M. Ahmed, Zement-Kalk-Gips 12, 624–627 (1988).
12. R. Dron, Gidratatsiya. Tsem. 2, 208–211 (1976).
13. H.M. Ahmed, M.Sc. Thesis, Ain Shams University, 1989.