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STUDIES ON THE STABILITY OF THE CALCIUM SULFOALUMINATE HYDRATES, PART III: THE MONOPHASES

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ABSTRACT

The effect of ettringite, monocarboaluminate hydrate, alite, and lime on the solubility of the monosulfate hydrate is studied at 30 and 100°C. At the same temperatures, the stability of the monocarboaluminate hydrate in presence of alite and lime is investigated.

At 30°C both types of calcium sulfoaluminate hydrates exist with a total of 0.8 mol sulfate in equilibrium with 0.2 mold sulfate dissolved in solution. The ettringite phase appears with a sulfate content exceeding 3 mol. The monosulfate hydrate resists longer a boiling solution of its mixture with ettringite or lime than with alite or monocarboaluminate hydrate. The hydrogarnet phase appears preferentially in the monocarboaluminate hydrate-bearing systems. The solutions compositions are reported. © *1998 Elsevier Science Ltd*

Introduction

An important derivative of the calcium aluminate hydrate is the monocarboaluminate hydrate, whose significance lies in the fact that it appears readily during the hydration of the tricalcium aluminate in the presence of lime, alkalies, and calcite, and also as a result of the fast carbonation of the tetracalcium aluminate hydrate or its solid solution with the monosulfate hydrate, due to the high susceptibility of the former to atmospheric carbon dioxide. The monophases represent collectively the monosulfate hydrate, the tetracalcium aluminate hydrate and its carbonate-bearing phase, and also the monocarboaluminate hydrate.

The subject of this work is to report the stability-solubility relationship of these phases and their interaction with other cement phases.

Experimental

The monosulfate hydrate was prepared according to the method of Lerch et al. (1) as follows: Freshly prepared saturated lime solution was added to 500 mL of freshly prepared monocalcium aluminate solution. The precipitate was filtered off. To the clear filtrate 200 mL of

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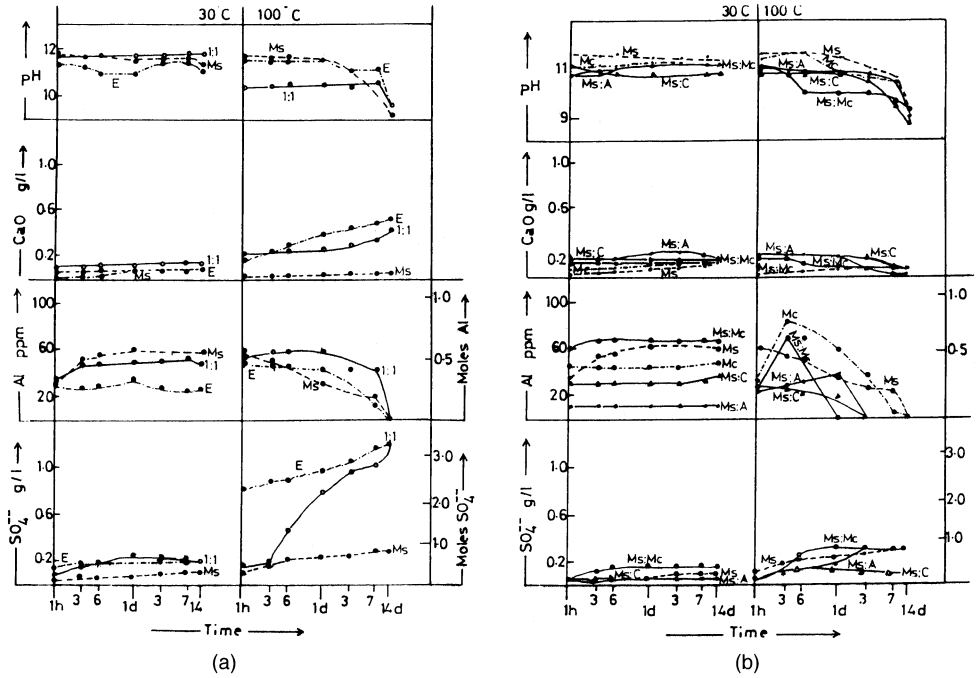

FIG. 1.
(a) The solubility curves of the system ettringite-monosulfate hydrate-water. (b) The solubility curves of the system monosulfate-hydrate-lime, -alite, -monocarboaluminate hydrate-water. E = Ettringite, Ms = Monosulfate hydrate, Mc = Monocarboaluminate hydrate, A = alite, C = Lime, Al = Aluminum.

saturated calcium sulfate solution was added and the mixture was left for 2 h, after which the monosulfate hydrate precipitate was filtered, washed, and dried. The precipitate obtained was chemically analysed and was found to have the formula: $C_{4.02}\ A_{1.0}S_{1.01}H_{12.2}$.

The ettringite phase was prepared by stirring tricalcium aluminate with gypsum with a molar ratio of 1:3 in an excess amount of water for 2 weeks.The washed and dried precipitate had the chemical composition of $C_{5.9}A_{1.0}S_{3.0}H_{32.3}$ (2).

The effect of ettringite, monocarboaluminate, alite, and lime on the solubility and the stability of the monosulfate hydrate was studied by weighing 0.2 g of the latter and adding each individual phase with the corresponding weights forming mixtures with molar ratios 1:1. These mixtures were stirred at 30°C or boiled for 2 weeks (the procedure is detailed in the preceding part of this series). In the monocarboaluminate hydrate series, the weight taken was 0.5 g and the respective mixtures with alite and lime (mole ratios 1:1 and 1:10) were calculated.

Results

The effect of ettringite on the concentration of the dissolved ions in the aqueous solution of the monosulfate hydrate at 30 and 100°C is illustrated in Figure 1a; that of alite, lime, and

TABLE 1
The solution concentration of the system etringite-monosulfate hydrate-water. Mole ratio (1:1) at 30°C and 100°C.

	at 30°C				at 100°C			
		SO_4^{2-}	Al	CaO		SO_4^{2-}	Al	CaO
Time	pH	g/L	ppm	g/L	pH	g/L	ppm	g/L
1 h	11.7	0.113	37.0	0.112	10.4	0.180	55.0	0.224
3 h	11.8	0.158	49.0	0.12	10.5	0.225	60.0	0.272
6 h	11.8	0.225	49.0	0.128	10.6	0.495	60.0	0.272
1 day	11.8	0.270	50.0	0.12	10.6	0.810	60.0	0.272
3 days	11.8	0.248	52.5	0.132	10.5	0.99	45.0	0.296
7 days	11.9	0.248	52.5	0.144	10.6	1.035	45.0	0.336
14 days	11.9	0.22	50.0	0.152	9.7	1.215	0.00	0.432

monocarboaluminate hydrate is shown in part b of the same figure, and the solubility values are given in Tables 1 to 8.

At 30°C the sulfate ion concentration of the solution of the monosulfate hydrate rises with time in the presence of an equimolecular amount of ettringite, exceeding slightly the equilibrium value of the latter (average ~0.2 g SO_4^{2-}/L, ~0.6 mol SO_4^{2-}). The same behaviour takes place in the solution of the mixture of the monosulfate hydrate and the monocarboaluminate hydrate, where the amount of sulfate dissolved increases, approaching the solubility value of ettringite at 30°C. The effect of lime and alite on the sulfate ion concentration of the monosulfate hydrate solution is weaker, and a maximum of 0.2 mol sulfate (~0.068 g SO_4^{2-}/L) is reached after a few hours then remains constant for 2 weeks. The concentration of the dissolved aluminum in the aqueous solution of the pure monosulfate hydrate is relatively higher than that of the pure ettringite, being average 53 and 30 ppm respectively (3). The solution of the mixture of both phases shows an average aluminum value of 48.5 ppm. In the monosulfate hydrate-lime or -alite mixtures the average values of the aluminum concentration in the respective solutions are found to be 31.2 and 11 ppm. In

TABLE 2
The solution concentration of the system monosulfate hydrate-alite-water. Mole ratio (1:1) at 30°C and 100°C.

	at 30°C								at 100°C							
		SO_4^{2-}		Al		Si		CaO		SO_4^{2-}		Al		Si		CaO
Time	pH	g/L	mol	ppm	mol	ppm	mol	g/L	pH	g/L	mol	ppm	mol	ppm	mol	g/L
1 h	10.9	0.045	0.145	11.0	0.127	0.014	0.155	0.160	11.2	0.068	0.220	22.5	0.259	0.002	0.222	0.208
3 h	10.9	0.045	0.145	11.0	0.127	0.014	0.155	0.168	11.0	0.113	0.366	27.0	0.311	0.002	0.222	0.184
6 h	11.1	0.068	0.220	11.0	0.127	0.012	0.133	0.176	11.0	0.135	0.437	30.0	0.346	0.008	0.888	0.184
1 day	11.3	0.068	0.220	11.0	0.127	0.010	0.111	0.20	11.0	0.180	0.583	37.5	0.432	0.007	0.777	0.176
3 days	11.3	0.068	0.220	11.0	0.127	0.008	0.088	0.227	10.9	0.315	1.020	0.00	0.00	0.007	0.777	0.064
7 days	11.4	0.068	0.220	11.0	0.127	0.005	0.055	0.195	10.5	0.315	1.020	0.00	0.00	0.005	0.555	0.038
14 days	11.5	0.068	0.220	11.0	0.127	0.000	0.000	0.173	8.8	0.315	1.020	0.00	0.00	0.001	0.11	0.040

TABLE 3
The solution concentration of the system monosulfate hydrate-calcium oxide-water. Mole ratio (1:1) at 30°C and 100°C.

		at 30°C						at 100°C				
		SO_4^{2-}		Al		CaO		SO_4^{2-}		Al		CaO
Time	pH	g/L	mol	ppm	mol	g/L	pH	g/L	mol	ppm	mol	g/L
1 h	11.2	0.045	0.1458	30.00	0.346	0.168	10.90	0.0675	0.2187	27.00	0.311	0.192
3 h	10.9	0.0675	0.2187	30.00	0.346	0.168	10.90	0.1125	0.3645	25.00	0.288	0.192
6 h	10.9	0.0675	0.2187	30.00	0.346	0.160	10.90	0.135	0.4373	20.00	0.230	0.192
1 day	10.9	0.0675	0.2187	30.00	0.346	0.160	10.90	0.135	0.4373	18.00	0.207	0.192
3 days	10.9	0.0675	0.2187	30.00	0.346	0.160	10.60	0.1125	0.3645	0.00	—	0.176
7 days	10.9	0.0675	0.2187	32.00	0.369	0.160	9.50	0.1125	0.3645	0.00	—	0.088
14 days	10.95	0.0675	0.2187	37.00	0.426	0.176	8.70	0.1125	0.3645	0.00	—	0.072

the presence of the monocarboaluminate hydrate, the amount of dissolved aluminum rises to 68 ppm, the pure carbonate-bearing phase showing a value of 45.8 ppm Al (3). The calcium oxide concentration of the solutions of ettringite and monosulfate hydrate are independently low, with value of 0.08 g CaO/L, which rises to an average value of 0.12 g CaO/L in the solution of their mixture. In the monocarboaluminate hydrate, lime, and alite mixtures the average values are 0.12, 0.l6, and 0.18 g CaO/L respectively. The pH values of all mixtures are between 10.9 and 11.9.

At l00°C the pure monosulfate hydrate depletes its sulfate content (1 mol) through boiling 2 weeks in water; in the presence of ettringite 3 mol are depleted gradually to the solution in the same range of time (Fig. 1a). In the mixture of the monosulfate hydrate-monocarboaluminate hydrate the full release of sulfate is observed at the first day whereas in the presence of alite the total sulfate is depleted after 3 days. Lime depresses the sulfate ion concentration of the boiling monosulfate hydrate solution to 0.36 mol (Fig. 1b).The aluminum concentration of the boiling solution of the monosulfate hydrate-ettringite mixture is

TABLE 4
The solution concentration of the system monosulfate hydrate-monocarboaluminate hydrate-water. Mole ratio (1:1) at 30°C and 100°C.

		at 30°C						at 100°C				
		SO_4^{2-}		Al	CO_2		CaO		SO_4^{2-}		Al	CaO
Time	pH	g/L	mol	ppm	ppm	mol	g/L	pH	g/L	mol	ppm	g/L
1 h	10.9	0.068	0.220	61.00	15.00	0.106	0.1312	11.1	0.068	0.220	27.00	0.168
3 h	11.0	0.135	0.437	68.00	14.00	0.099	0.1424	10.90	0.135	0.437	68.00	0.160
6 h	11.1	0.180	0.583	68.00	12.00	0.085	0.1200	10.00	0.270	0.875	50.00	0.120
1 day	11.3	0.180	0.583	68.00	13.00	0.092	0.1232	10.00	0.315	1.020	0.00	0.078
3 days	11.3	0.180	0.583	68.00	13.00	0.092	0.1288	10.00	0.315	1.020	0.00	0.0736
7 days	11.3	0.180	0.583	68.00	12.00	0.085	0.1104	9.7	0.315	1.020	0.00	0.0752
14 days	11.9	0.180	0.583	68.00	13.80	0.098	0.1184	9.3	0.315	1.020	0.00	0.072

TABLE 5
The solution concentration of the system monocarboaluminate hydrate-alite-water. Mole ratio (1:1) and (1:10) at 30°C.

		Mole ratio (1:1)							(1:10)						
		Al	Si		CaO	CO_2			Al	Si		CO_2		CaO
Time	pH	ppm	ppm	mol $\times 10^3$	g/L	ppm	mol	pH	ppm	ppm	mol $\times 10^3$	ppm	mol	g/L
1 h	11	0.00	0.060	0.251	0.144	25.0	0.067	12.20	0.00	0.060	0.251	40.40	0.108	0.88
3 h	11	0.00	0.065	0.272	0.160	23.60	0.063	12.30	0.00	0.043	0.180	33.0	0.088	0.96
6 h	11.3	0.00	0.069	0.289	0.176	26.0	0.069	12.40	0.00	0.033	0.138	30.0	0.080	1.00
1 day	11.5	0.00	0.071	0.297	0.184	21.00	0.056	12.40	0.00	0.025	0.104	25.00	0.067	1.04
3 days	11.6	0.00	0.078	0.327	0.184	20.00	0.053	12.50	0.00	0.025	0.104	24.00	0.064	1.08
7 days	11.7	0.00	0.092	0.385	0.192	20.00	0.053	12.50	0.00	0.025	0.104	14.00	0.037	1.12
14 days	11.7	0.00	0.127		0.096	18.00	0.048	12.60	0.00	0.028	0.117	7.00	0.019	1.08

higher than that of each of the individual hydrates but decreases at the 7th day and is totally consumed after 2 weeks. In the monocarboaluminate hydrate, alite, and lime-bearing systems the aluminum concentration passes through a maximum then undergoes a complete depression after 1 and 3 days respectively. The calcium oxide concentration is highest in the ettringite-monosulfate mixture, with an average value of 0.25 g CaO/L. The highest value in the other systems shows up in the presence of lime with an average value of 0.18 g CaO/L. The pH value lies in the range of 10–11 and tends to decrease with time.

The X-ray diffractograms of the solid phases obtained from stirring the monosulfate hydrate with the different hydrates as well as alite and lime show that under all conditions the monosulfate hydrate undergoes either a partial or total conversion to the ettringite phase at 30°C. The rate of appearance of the high sulfate form depends on the specific mixture: It appears after 1 h in the presence of lime, 6 h in the monocarboaluminate hydrate mixture and 7 days in the presence of alite. The monosulfate hydrate remains well identified in all systems

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

		Mole ratio (1:1)								(1:10)					
		Al		Si		CO_2		CaO		Al		Si			CaO
Time	pH	ppm	mol	ppm	mol $\times 10^3$	ppm	mol	g/L	pH	ppm	mol	ppm	mol $\times 10^4$		g/L
1 h	11.1	55.0	0.119	0.068	0.285	9.0	0.024	0.224	11.3	11.0	0.024	0.113	0.473		0.480
3 h	11.2	0.00	0.00	0.086	0.360	8.0	0.021	0.160	11.3	7.5	0.016	0.115	0.481		0.488
6 h	11.3	0.00	0.00	0.090	0.377	7.0	0.019	0.144	11.4	0.00	0.00	0.118	0.494		0.496
1 day	11.4	0.00	0.00	0.111	0.465	6.5	0.017	0.120	11.6	0.00	0.00	0.116	0.485		0.520
3 days	11.5	0.00	0.00	0.118	0.494	6.0	0.016	0.112	11.9	0.00	0.00	0.118	0.494		0.520
7 days	11.0	0.00	0.00	0.111	0.465	6.0	0.016	0.104	11.3	0.00	0.00	0.122	0.510		0.528
14 days	10.8	0.00	0.00	0.106		5.9	0.016	0.104	11.0	0.00	0.00	0.115	0.481		0.160

TABLE 7
The solution concentration of the system monocarboaluminate hydrate-calcium oxide-water. Mole ratio (1:1) and (1:10) at 30°C.

		Mole ratio (1:1)					(1:10)				
		Al		CaO	CO_2			Al	CaO	CO_2	
Time	pH	ppm	mol	g/L	ppm	mol	pH	ppm	g/L	ppm	mol
1 h	11.2	11.0	0.024	0.19	18.0	0.048	12.1	0.00	0.88	30.0	0.080
3 h	11.5	11.0	0.024	0.194	17.5	0.047	12.2	0.00	0.96	31.95	0.085
6 h	11.9	11.0	0.024	0.198	19.0	0.051	12.2	0.00	1.00	36.2	0.096
1 day	11.9	11.0	0.024	0.264	18.0	0.048	12.4	0.00	0.96	35	0.093
3 days	12.2	15.0	0.033	0.224	17.0	0.045	12.5	0.00	1.00	32.5	0.0865
7 days	12.3	15.0	0.033	0.232	16.8	0.045	12.6	0.00	1.00	31.4	0.084
14 days	12.3	15.0	0.033	0.224	15	0.040	12.8	0.00	1.04	27.6	0.074

but not that of the ettringite-bearing one in which the trisulfate form appears as the sole hydrate. At the boiling water temperature the pure monosulfate hydrate converted to its solid solution with the tetracalcium aluminate hydrate after 1 h (4). In this work however it resists the boiling solution 7 and 14 days in the presence of ettringite and lime respectively. At 100°C the monocarboaluminate hydrate and alite cause the formation of hydrogarnet at the 6th hour and the 3rd day in both systems respectively. The cubic phase is stable for 2 weeks in the monocarboaluminate hydrate mixture but decomposes to gehlenite hydrate in the presence of alite.

The effect of alite and lime on the solution composition of the monocarboaluminate hydrate in water at 30 and l00°C is illustrated in Figure 2a,b.

At 30°C alite has more effect on the aluminum concentration of the solution of the monocarboaluminate hydrate than lime, where a complete depression is observed at the two alite ratios (mole ratios 1:1 and 1:10), whereas only the high lime concentration (mole ratio 1:10) leads to zero value of the dissolved aluminum. In the mixture with lower lime

TABLE 8
The solution concentration of the system monocarboaluminate hydrate-calcium oxide-water. Mole ratio (1:1) and (1:10) 100°C.

		Mole ratio (1:1)					(1:10)			
		Al		CO_2		CaO		Al		CaO
Time	pH	ppm	mol	ppm	mol	g/L	pH	ppm	mol	g/L
1 h	11.6	18.0	0.039	13.0	0.035	0.14	11.8	0.00	0.00	0.44
3 h	11.6	18.0	0.039	12.0	0.032	0.128	11.8	0.00	0.00	0.432
6 h	11.6	18.0	0.039	11.0	0.029	0.128	11.8	0.00	0.00	0.424
1 day	11.6	18.0	0.039	11.0	0.029	0.120	11.9	0.00	0.00	0.440
3 days	11.5	0.00	0.00	10.0	0.027	0.112	11.9	0.00	0.00	0.44
7 days	11.4	0.00	0.00	9.0	0.024	0.072	11.9	0.00	0.00	0.432
14 days	9.9	0.00	0.00	9.0	0.024	0.04	11.9	0.00	0.00	0.440

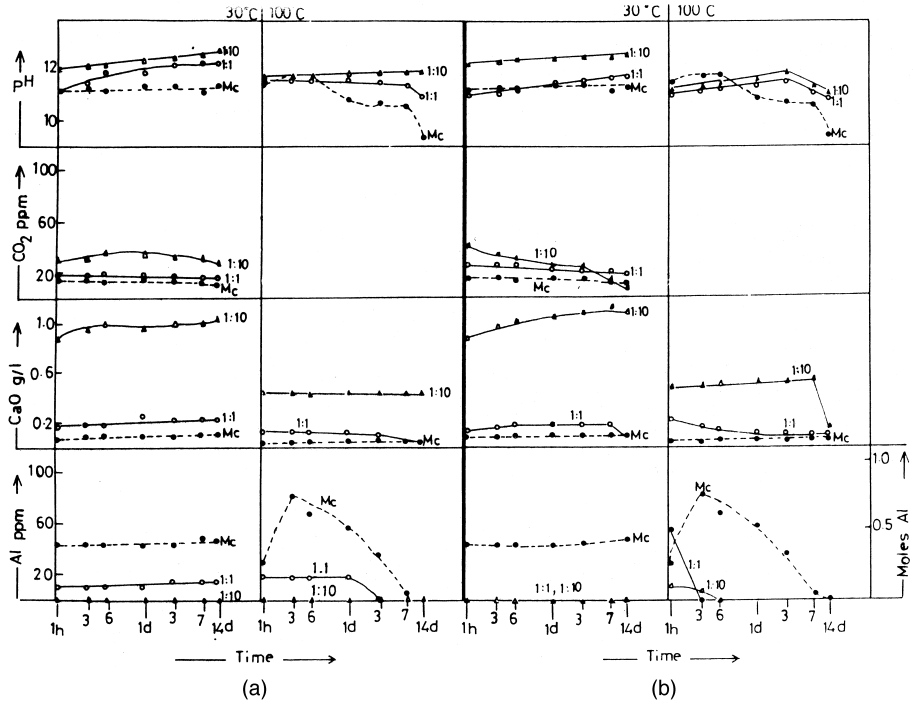

FIG. 2.

(a) The solubility curves of the system monocarboaluminate hydrate-lime-water. (b) The solubility curves of the system monocarboaluminate hydrate-Alite-water. Mc = Monocarboaluminate hydrate, A = Alite, C = Lime, Al = Aluminum.

concentration (mole ratio = 1) an average value of 12.7 ppm aluminum is determined. The calcium oxide concentration of the solution of the monocarboaluminate hydrate in the presence of alite or lime is quite similar: In the mixtures containing a molar ratio of 10 (alite or lime to monocarboaluminate hydrate), the concentration of calcium expressed as calcium oxide per liter attains an average value of 0.97 and 1.02 g CaO/L, which is near the saturation value of lime at 30°C. In the case of molar ratio of one the amount of dissolved lime is much lower and is equal to or lower than 0.22 g CaO/L. It is, however, still higher than the equilibrium value of lime in the solution of the pure monocarboalumniate hydrate being 0.1 g CaO/L. The pH value of the solutions of the mixtures containing lime or alite with a mole ratio of 10 is averaged 12.4, which is higher than that of the pure phase (being 11). The amount of dissolved carbon dioxide increases from 16 ppm in the solution of the pure monophase to an average value of 21.9 and 17.32 in the mixtures containing alite and lime with a mole ratio of 1. At higher mole ratio the average CO_2 concentration is as high as 40 ppm but tends to decrease with time.

At 100°C the amount of dissolved aluminum in the solution of the monocarboaluminate hydrate passes through a maximum at 3 h and is consumed after 2 weeks. In the presence of alite it is consumed after 3 and 6 h for the mixtures with mole ratios of 1 and 10. In the presence of lime (mole ratio of 1) it shows a constant value of 18 ppm after 1 day, long after which it is depressed to zero value. At higher lime concentration no dissolved aluminum is

detected in the solution. The effect of boiling temperature on the dissolved calcium is more pronounced in the mole ratio of 10 (lime or alite) being strikingly lower than the values measured at 30°C (average value 0.4 g CaO/L in both systems). The average pH value of the boiling solutions is between 11 and 11.9 and tends to decrease with time especially in the solutions of lower molar ratio.

The X-ray diffractograms of the solid phases obtained from stirring the monocarboaluminate hydrate with alite and lime show its complete stability at 30°C. In the presence of high lime concentration (mole ratio 10) the portlandite phase precipitates at the first stirring hour and appears after 3 h in the mixture containing alite. The hydrogarnet is identified in the alite mixture with a mole ratio of 1 after 2 weeks at 30°C but forms at the first stirring hour beside the portlandite at the boiling water temperature in the solutions of the mixtures containing high lime or alite concentrations. In the alite monocarboaluminate boiling mixture the hydrogarnet disappears at longer ages in favour of the tobermorite phase.

Discussion

A total of 0.2 g monosulfate hydrate was used in these experiments with a sulfate content of 0.03 g representing 1 mol SO_4^{2-}. When the monosulfate hydrate is stirred in water at 30°C in the presence of lime or alite, it releases about 0.2 mol to the aqueous solution and decomposes partially to the ettringite phases, the sulfate content of both solid phases being 0.8 mol. In other words, the ettringite and the monosulfate hydrate, which are well identified in the X-ray diffractograms, are sulfate deficient compared to their stoichiometric sulfate amount (the ettringite = 3 mol; the monosulfate hydrate = 1 mol SO_4^{2-}). In the mixture containing the monosulfate hydrate and the monocarboaluminate hydrate, the sulfate concentration of the solution amounts to 0.58 mol SO_4^{2-}, and the ettringite phase appears beside the monosulfate hydrate with a sulfate content of 0.42 mol SO_4^{-2} for both hydrates. Both types of the calcium sulfoaluminate hydrate forms are stable in a wide range of aluminum concentration of the solution at 30°C (11–68 ppm), and a calcium ion concentration as low as 0.11 g CaO/L.

On the other hand, the monosulfate hydrate converts completely to the high sulfate form when a stoichiometric ettringite phase is present ($C_3A{\cdot}3CS{\cdot}32H$). The equilibrium sulfate concentration of the solution of this mixture is average 0.2 g/L (0.64 mol SO_4^{2-}), the sulfate content of the solid ettringite phase identified as the sole hydration product would be 3.36 mol SO_4^{2-} exceeding the stoichiometric value of 3.

It is to be concluded that the amount of sulfate incorporated in the calcium sulfoaluminate hydrate phases is variable and deviate from their stoichiometric values. According to the present investigation the ettringite phase appears in a sulfate deficient as well as a sulfate excess form, but the monosulfate hydrate appears only in a sulfate deficient state. One should be able to differentiate these different states perhaps on the basis of their morphology and their specific volume but not by means of their X-ray diffraction patterns, which are identical for the chemically different ettringite or the monosulfate phases.

According to Taylor (5), the sulfate ions incorporated in the channels of the calcium aluminate hydrate columns are bonded to their surface by Van der Waals forces which, in fact do not contradict the former discussion suggesting the incorporation of a wide range of sulfate in the ettringite structure. The main stability of the ettringite is believed to be due to

the calcium aluminate columns and not to the amount of sulfate which agrees further with the finding of Poellman (6).

The monocarboaluminate hydrate is stable in an aluminum concentration range from zero to 60 ppm Al. The low concentration range is caused by the presence of lime or alite.

The hydrogarnet phase appears readily in systems containing monocarboaluminate hydrate at 30°C: It is formed in the monocarboaluminate hydrate-ettringite or alite mixtures. At 100°C the cubic phase appears during boiling the monocarboaluminate hydrate in water, and also in the presence of lime or alite. It is also formed in the following boiling mixtures: ettringite-lime or monocarboaluminate hydrate, and the monosulfate hydrate- alite or monocarboaluminate hydrate. It decomposes to gehlenite hydrate in the monosulfate hydrate-alite mixture.

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