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Hydration reaction of tricalciumaluminate in different systems

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Abstract

The hydration behaviour of tricalciumaluminate in excess magnesium sulfate solution (0.05 molar) in various systems was investigated. The effect of gypsum, gypsum + lime, gypsum + lime + alite on the hydration reaction of tricalciumaluminate at room temperature was studied. The hydration process was carried out in an excess amount of magnesium sulfate solution, and it was followed for a various time intervals up to 7 days. The results obtained from XRD analysis and solution composition have revealed that magnesium sulfate solution (0.05 molar) retards the hydration reaction and prevents the ettringite formation as a result of decreasing alkalinity of the reaction medium.

Keywords: Hydration; Tricalciumaluminate; Ettringite formation; X-Ray diffraction

1. Introduction

Ettringite formation is an important reaction in cement hydration. The effect of different additives on the hydration reactions of tricalciumaluminate have been investigated [1–4]. The soluble sulfates originating from the aggregates or mixing water for example would influence the mechanism of the hydration reaction of cement in concrete. The setting of cement is closely related to the composition of mixing water [5].

The dissolved alkalies increase the pH-value and lower the calcium hydroxide concentration of the solution. This increases the hydration velocity of tricalciumaluminate during the first minutes of hydration. Rapid setting can be avoided by the exact balancing of calcium sulfate content [3,4].

A substantial retardation of hydration in the presence of sulfate occurs only when gypsum is used and enough ettringite is formed. Soluble sulfate in Portland cement strongly retards initial aluminate phase hydration [6] and allows an improvement for both workability of fresh cement past and of ultimate strength of the hardened product.

The hydration of tricalciumaluminate/gypsum mixture with 1 : 1 mole ratio formed a complex phase assemblage. The introduction of sodium cations in solution promotes AFm formation at the expense of ettringite formation. Many studies examined the effects of various ionic species on the formation of ettringite and/or mono sulfate have been reported [7–10].

2. Experimental work

Pure tricalciumaluminate (C_3A) was prepared by well mixing calcite and alumina in the molar ratio of 3 : 1. The mixture was burned at 1350 °C. The alite phase (A) was prepared by mixing calcite, silica, alumina and magnesium carbonate in the molar ratio of 3 : 0.9 : 0.05 : 0.05. The mixture was burned at 1450 °C. The products were examined by means of X-ray diffraction using Ni-filter and Cu-Kα radiation.

Four mixtures namely system (I) C_3A, system (II) C_3A + gypsum with molar ratio of 1 : 1.5, system (III) C_3A + gypsum + lime with molar ratio of 1 : 1.5 : 1, system (IV) C_3A + alite + gypsum + lime with a molar ratio of 1 : 1 : 1.5 : 1 were prepared. The weights of C_3A were 0.30 g, gypsum 0.286 g, lime 0.0623 g and that of alite was

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Table 1
Predominant phases observed by XRD in different systems

Time System (mole ratio)	$2'\rightarrow 6$ h	1 d	3 d	7 d
C_3A	C_3A	C_3A	C_4AH_{13}, C_3A	Gypsum, C_4AH_{13}
C_3A : G(1 : 1.5)	C_3A, gypsum	Gypsum, C_3A C_4AH_{13}	Gypsum, C_4AH_{13}	Gypsum, C_4AH_{13}
C_3A : G : C (1 : 1.5 : 1)	C_3A, gypsum	Gypsum, C_4AH_{13}	Gypsum, C_4AH_{13}	Gypsum, C_4AH_{13}
C_3A : A : G : C (1 : 1 : 1.5 : 1)	Gypsum, C3A, Alite	Gypsum, Ettringite	Gypsum, Ettringite	Gypsum, Ettringite

0.2535 g. The different mixtures were stirred in 100 ml of 0.05 molar magnesium sulfate solutions in well-stoppered glass flasks for different time intervals from 2 min, up to 7 days at room temperature. The solutions were filtered off and the obtained precipitates were washed with isopropyl alcohol, dried at 50 °C for 24 h. The dried precipitates were analyzed by XRD. The dissolved sulfate, in the filtrate, was analyzed turbidimetrically [11], the aluminium and silicon were determined colorimetrically [12], and calcium was determined by compleximetric titration [11]. The pH values were determined using ORION RESEARCH microprocessor ionalyzer/901.

3. Results and disscusion

3.1. X-ray analysis

The predominant phases formed in the different systems studied are shown in Table 1. It can be noticed that the hydration of C_3A in 0.05 molar magnesium sulfate solution gives the tetracalciumaluminate hydrate (*d*-value 8.2 A°) after 3 days, and gypsum was detected after 7 days as a result of the reaction of the liberated calcium hydroxide with magnesium sulfate:

$$Ca(OH)_2 + MgSO_4aq = CaSO_4.2H_2O + Mg(OH)_2$$

Addition of gypsum to C_3A (system II) in the magnesium sulfate solution does not change the hydration products formed. Whereas hydration of the same system (C_3A + gypsum) in pure water [3] and also in sodium or potassium sulfate solutions [4] results in the formation of ettringite. Addition of lime and gypsum to the C_3A (system III) has also no effect on the formed hydration products.

In the system C_3A + alite + gypsum + lime (system IV) ettringite formation takes place after 1 day hydration, while as in pure water [13], the ettringite was formed during the first 10 min of hydration. This proves the retardation of the ettringite formation in the presence of 0.05 molar magnesium sulfate solutions.

3.2. The solution composition

The solution composition of the studied systems at room temperature is shown in Table 2 and Fig. 1. The solutions of these systems contained no aluminium or silicon ions.

In the solution obtained from the hydration of C_3A in 0.05 molar magnesium sulfate (system I), the sulfate ions concentration were almost constant during the first 6 h (Fig. 1-a), then showed a gradual decrease till 7 days. This is due to the precipitation of sulfate as calcium sulfate. The calcium ions concentration (Fig. 1-b) showed a slight increase in the first 6 h, then showed a sharp increase up to 7 days. A slight decrease was observed in the pH values (Fig. 1-c) from 9.09 to 8.30.

Addition of gypsum to C_3A with a molar ratio of 1.5 : 1 (system II) increased the sulfate ions slightly in the first 6 h (Fig. 1-a), then a rapid decrease was shown in the later times up to 7 days. The calcium ions concentration (Fig. 1-b) showed a gradual increase through the hydration times. The pH values were decrease (Fig. 1-c) from 8.55 to 7.75 during the hydration period.

Addition of lime to the previous system (system III) caused a gradual decrease in the sulfate ions concentration (Fig. 1-a), while the calcium ions (Fig 1-b) showed a

Table 2
The solubility values of the different systems studies

System	C_3A			C_3A : G, 1 : 1.5			C_3A : G : C, 1 : 1.5 : 1			C_3A : A : G : C, 1 : 1 : 1.5 : 1		
Time	pH	SO_4^{--} g/l	CaO g/l	pH	SO_4^{--} g/l	CaO g/l	pH	SO_4^{--} g/l	CaO g/l	pH	SO_4^{--} g/l	CaO g/l
$2'$	9.09	2.67	0.06	8.50	2.83	0.52	8.80	3.49	0.57	9.70	2.75	0.70
$10'$	8.80	2.67	0.09	8.45	2.99	0.59	9.00	3.49	0.58	9.69	2.83	0.78
$30'$	8.70	2.66	0.09	8.20	3.17	0.62	9.20	3.40	0.59	9.67	2.83	0.83
3 h	8.57	2.66	0.11	8.17	3.42	0.65	9.30	3.17	0.61	9.71	2.33	0.90
6 h	8.40	2.60	0.15	8.19	3.33	0.67	9.50	3.01	0.65	10.10	1.99	0.93
1 d	8.44	2.42	0.27	7.79	3.33	0.67	9.60	2.30	0.70	10.78	1.17	0.89
3 d	8.36	2.10	0.54	7.80	2.20	0.68	9.70	1.65	0.76	10.80	0.99	0.87

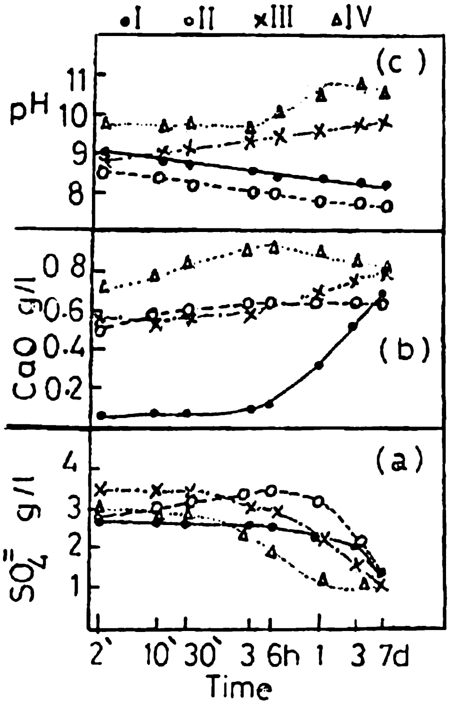

Fig. 1. Solution composition of the studied systems.

gradual increase, the pH values (Fig. 1-c) rose gradually from 8.80 to 9.80 through the hydration period of 7 days.

In system IV (C_3A : A : G : C, molar ratio of 1 : 1 : 1.5 : 1, respectively) we noticed a constant sulfate values through the first 30 min (Fig. 1-a), then a gradual decrease takes place till 3 days, then an almost constant value of sulfate ions was shown till 7 days. The calcium ions showed a gradual increase (Fig. 1-b) in the first 6 h, then it decreased slowly till 7 days. The pH values (Fig. 1-c) showed a constant value of 9.70 in the first 3 h, and then gradually increase up to 10.8 at 7 days of hydration.

3.3. General disscussion

Setting of Portland cement is attributed to the early hydration of C_3A in the presence of gypsum, with a minor contribution of the calcium silicate phases. These conclusions are based on different studies carried out on the phases formed during the initial reaction of the cement pastes [14,15].

In system (IV) the calcium hydroxide concentration exceeded 0.63 g/l CaO which value was found to be the limit causing a total depression of the aluminium from solution [16]. The ettringite phase appear in system IV in a solution containing >0.60 g/l sulfate, >0.63 g/l CaO and pH value of 10.8, while in other systems (I, II, III) the ettringite phase does not appear although the solution contains >0.60 g/l sulfate and >0.63 g/l CaO, but the pH value is also lower than 10.0. We can conclud that the formation of ettringite depends not only on the sulfate ions and CaO concentration, but also on the pH value of the solution.

4. Conclusions

The main conclusions derived from this study can be summarized as follows:

1. Low concentrations of magnesium sulfate solution (0.05 molar) retard the hydration reaction of C_3A.
2. The reaction of C_3A and gypsum was retarded in the presence of 0.05 molar magnesium sulfate solution.
3. The formation of ettringite is accompanied by a high decrease of the sulfate ion concentration in the solution.
4. The ettringite phase is formed even in non-stoichiometric reaction mixtures of gypsum and C_3A.
5. Formation of ettringite occures in systems of pH values not less than 10.0.

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