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INVESTIGATION OF THE EFFECTS OF DIETHYLENE GLYCOL ON THE HYDRATION OF C_3S AND C_3A PASTES

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The effects of diethylene glycol on the hydration characteristics of tricalcium silicate and tricalcium aluminate pastes were studied. Diethylene glycol acts as a retarder in the hydration of C_3S, and as an accelerator in the hydration of C_3A. The amount of $Ca(OH)_2$ found in pastes of C_3S treated with diethylene glycol was lower, the induction period increased and the formation of hydrates was retarded. For C_3A pastes, hydration in the presence of diethylene glycol accelerated the formation of the hexagonal aluminate hydrates and promoted the conversion to the cubic form.

Glycols are used as admixtures for the adaptation of cement pastes so that these may be used even at negative temperatures. Glycols also find considerable use for the protection of fresh concrete surfaces from the quick evaporation of hydration water, which can cause cracking of the concrete. Glycols therefore influence some of the technological characteristics of mortars and concretes. Their physicomechanical effects have been adequately elucidated; our present work deals with the physico-chemical influence of diethylene glycol on the hydration kinetics of single components of cement and with the mechanism of its action.

Experimental

Materials: tricalcium silicate and tricalcium aluminate (synthetically manufactured in the Soviet Union); diethylene glycol (Lachema, Brno).

Methods: thermal analysis, MOM derivatograph, heating rate: 10 deg/min; X-ray analysis, Philips apparatus, PW 1730 generator, PW 1390 goniometer, Cu_K radiation; scanning electron microscopy, JEOL JSM 35 apparatus magnification 5400 ×.

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Results

The tricalcium silicate—water system

A paste of C_3S and water (water/C_3S ratio of 0.8) was prepared without and with the addition of 2.7% or 10% of diethylene glycol to the batch water. After various periods of hydration ranging from 24 h to 28 days the paste specimens were analysed.

Thermal analysis was used to observe and compare the contents of calcium hydroxide formed in the reaction of tricalcium silicate with water. An exothermic peak appears at about 300° in the curves of pastes containing diethylene glycol; and its intensity increases with time (Table 1, Fig. 1).

It was found that the calcium hydroxide content in paste containing 2.7% diethylene glycol was about 50% lower after hydration for 3 days, and about 25% lower after hydration for 7 days as compared to that in pastes not containing diethylene glycol. In pastes containing 10% diethylene glycol, the difference was even more evident.

Table 1 $Ca(OH)_2$ content in hydrated C_3S pastes determined thermogravimetrically

Hydration time	% $Ca(OH)_2$ from the weight loss at 400–500 °C		
	0% deg	2.7% deg	10% deg
3 days	13.7	8.0	6.6
7 days	16.8	13.3	6.6
28 days	16.8	16.8	14.2

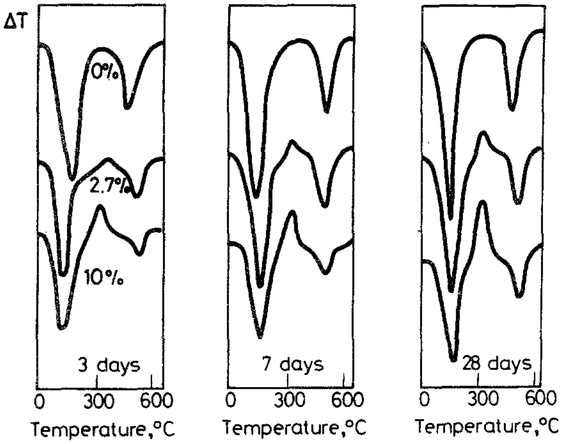

Fig. 1 DTA curves of C_3S pastes hydrated with and without diethylene glycol

The exothermic peak at about 300° in the DTA curves of samples containing diethylene glycol after hydration for 3 day probably indicates the formation of an organic complex of diethylene glycol with Ca ions. This assumption is indirectly confirmed by the result of X-ray analysis (Table 2) which indicate very low contents of calcium hydroxide and carbonate in pastes containing diethylene glycol, though, due to the decrease of unhydrated C_3S, one might expect a higher content of Ca ions released through the hydration of C_3S with water.

Table 2 The intensity of some diffraction maxima, determined by X-ray analysis in C_3S pastes

Hydration time	Sample	Intensity of diffr. maxima counts s^{-1}		
		$Ca(OH)_2$		$CaCO_3$
		0.491 nm	0.293 nm	0.303 nm
3 days	0 % deg	328	147	73
	2.7% deg	109	135	85
	10 % deg	55	95	80
7 days	0 % deg	411	190	80
	2.7% deg	155	170	85
	10 % deg	83	124	95

The formation of CSH gel in C_3S pastes was examined microscopically. In pastes containing diethylene glycol a strong retardation of hydration product formation was observed (Figs 2 and 3).

In the photographs of pastes containing diethylene glycol appear after 7 days of hydration thin stacked leafy plates with rounded edges; these are not observed in the photographs of pastes without diethylene glycol addition (Fig. 4).

This formation occurs in considerable quantity in these pestes even after hydration for 28 days.

The tricalcium aluminate — water system

Pastes of C_3A and water (water C_3A ratio of 0.7) were prepared without and with the addition of 2.7% or 10% of diethylene glycol. After hydration periods of from 5 min to 28 days, the specimens were analysed.

The formation of hexagonal C_4AH_3 and C_2AH_8 hydrates (weight loss up to 200°) and of cubic C_3AH_6 (weight loss from 200° to 400°) was followed by means of thermal analysis [1–3].

The content of metastable hexagonal hydrates varied in a very narrow range for

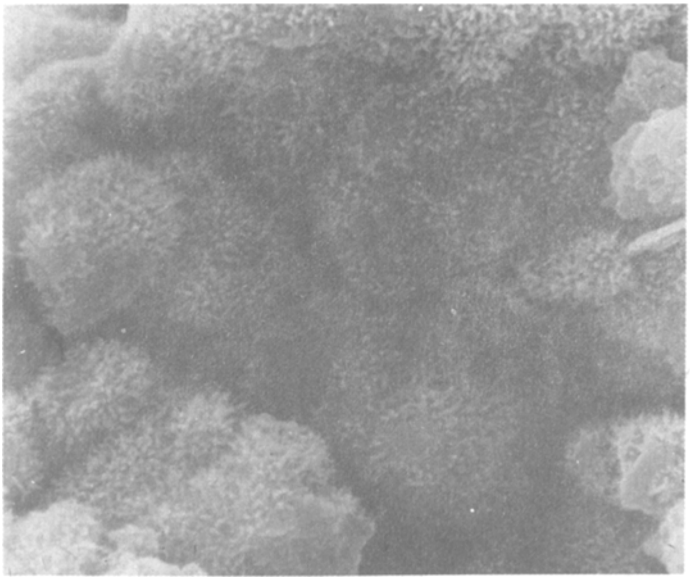

Fig. 2 SEM of C_3S paste hydrated for 3 days without addition, magn. 5400 ×

Fig. 3 SEM of C_3S paste hydrated for 3 days with addition of diethylene glycol, magn. 5400 ×

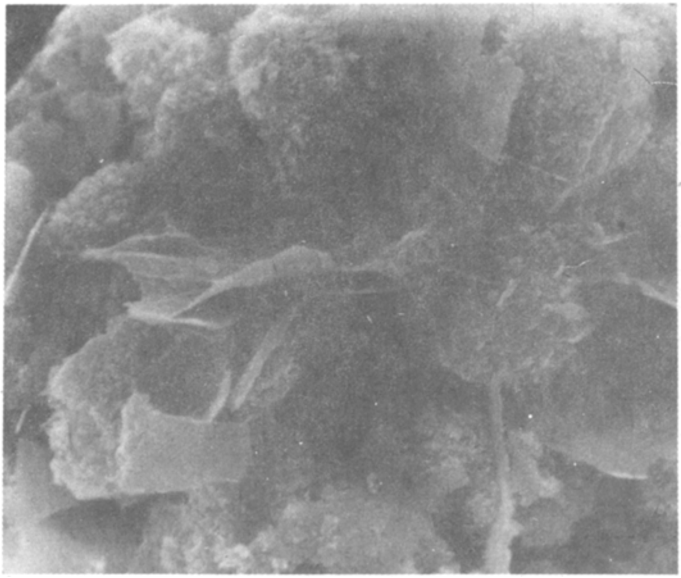

Fig. 4 SEM of C_3S paste hydrated for 7 days with addition of diethylene glycol, magn. 5400 ×

all specimens subjected to analysis. The content of cubic C_3AH_6 in C_3A pastes without diethylene glycol addition increased with time.

In the TG curves of C_3A pastes containing diethylene glycol, the maximum weight loss within the temperature interval from 200° to 400° attained already after 2 or 6 h of hydration, is about 75% higher than that for C_3A pastes containing no diethylene glycol (Table 3). In the DTA curves of hydrating pastes containing

Table 3 Weight losses within the temperature interval from 200 to 400° determined thermogravimetrically

Hydration time	Weight loss in, %		
	0% deg	2.7% deg	10% deg
2 hours	14.3	25.2	19.3
6 hours	14.7	25.0	22.0
24 hours	16.0	25.0	24.5
3 days	17.5	24.2	25.0
7 days	18.7	22.5	21.7
28 days	22.8	23.3	21.7

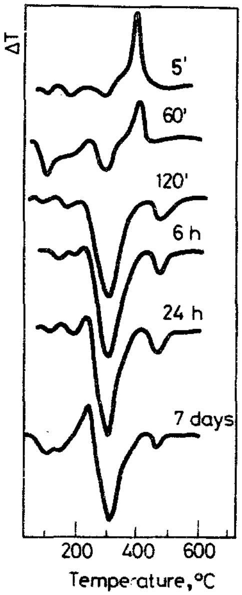

Fig. 5 DTA curves of C_3A pastes hydrated with an addition of diethylene glycol

diethylene glycol an exothermic peak appears at about 400° during the first few minutes of hydration; its intensity decreases with hydration time. After 2 h, it can no longer be detected. For the same pastes, an exothermic peak appears at about 200–250° after 3 days, whose intensity increases with time (Fig. 5).

Table 4 The intensity of some diffraction maxima, determined by X-ray analysis in C_3A pastes

Hydration time	Sample	Intensity of diffr. maxima counts s^{-1}			
		C_3AH_6		C_3A	
		0.513 nm	0.445 nm	0.270 nm	0.408 nm
2 hours	0 % deg	293	112	640	71
	2.7% deg	301	139	38	3
	10 % deg	317	144	376	40
3 days	0 % deg	296	123	350	47
	2.7% deg	384	221	27	2
	10 % deg	360	170	48	—
28 days	0 % deg	299	131	259	21
	2.7% deg	552	235	34	—
	10 % deg	512	184	14	—

This anomaly is explained by the reaction of diethylene glycol with C_3AH_6 to yield an organic complex. This view is indirectly confirmed by the results of X-ray analysis (Table 4), where the decrease in the unhydrated phase in pastes containing diethylene glycol is not equivalent to the relatively small increase in intensities of the diffraction maxima of the hydrate formed.

The X-ray and thermal analyses together confirm the higher content of hydrates in C_3A pastes containing diethylene glycol (Table 4).

The microscopic photographs of C_3A pastes with diethylene glycol addition show a clearly accelerated formation of the cubic hydrate. In pastes without diethylene glycol a hexagonal platy phase prevails (Fig. 6), whereas the surface of samples hydrated for the same time in the presence of diethylene glycol is covered by a large quantity of cubic particles (Fig. 7). Upon further hydration, a further phase appears on the surface of C_3A pastes containing diethylene glycol; this forms layered map surfaces of indefinable shape, with irregular edges (Fig. 8).

Conclusions

It was ascertained that the addition of diethylene glycol did not have equal effects on the hydration kinetics and the structure formation of the silicate and aluminate

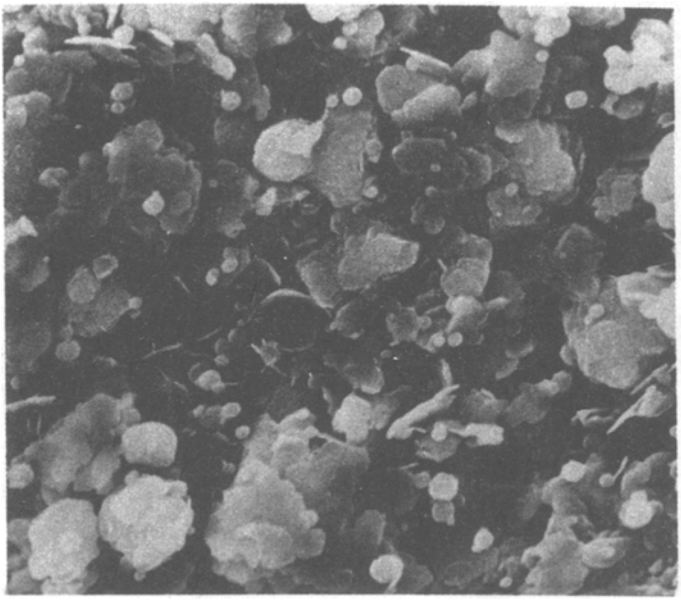

Fig. 6 SEM of C_3A paste hydrated 2 hours without addition, magn. 5400 ×

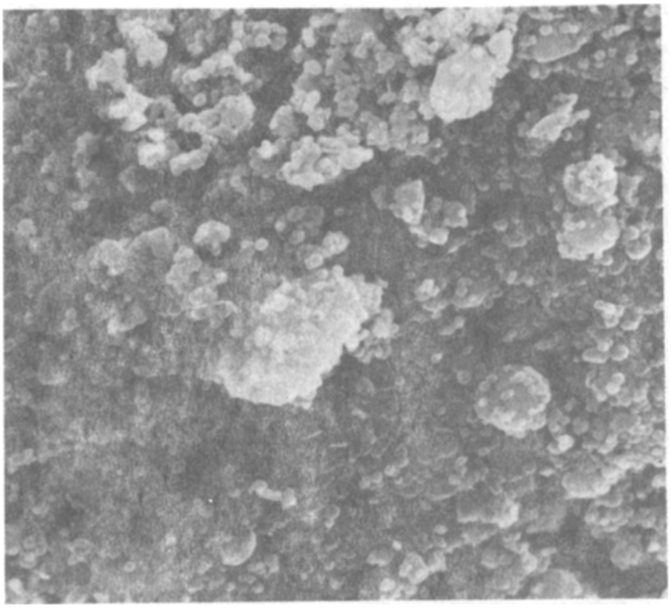

Fig. 7 SEM of C_3A paste hydrated 2 hours with addition of diethylene glycol, magn. 5400 ×

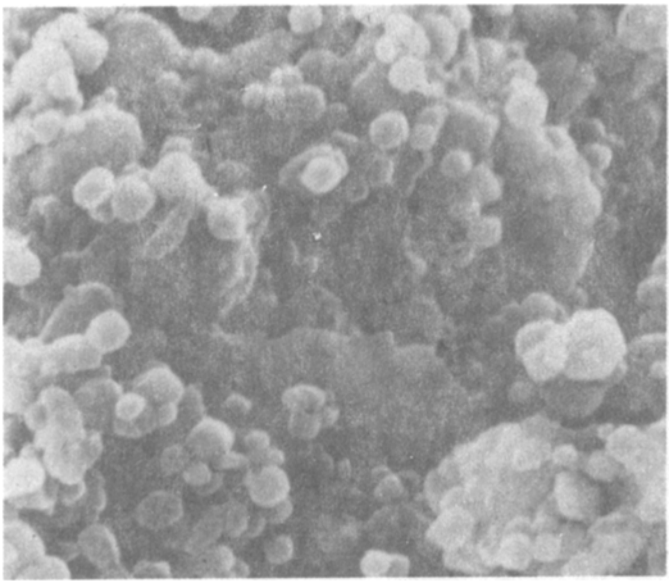

Fig. 8 SEM of C_3A paste hydrated 7 days with addition of diethylene glycol, magn. 20,000 ×

components. On the addition of diethylene glycol, the hydration reactions of tricalcium silicate are retarded especially in the first hydration phases.

The morphologic form of the hydrates and the low content of calcium hydroxide in C_3S pastes containing diethylene glycol suggest that diethylene glycol promotes the formation of CSH with a higher C/S ratio, prolongs the induction period and probably forms a complex with Ca ions.

The hydration of tricalcium aluminate was accelerated by the addition of diethylene glycol. The initially formed weak calcium-organic complex retards the early crystallization of hydration products, more anhydrous phase can be dissolved before the hydration barrier is formed, an initial increase of reactivity takes place and the induction period is shortened. Later, the C_3AH_6 produced probably reacts with diethylene glycol.

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Zusammenfassung — Der Einfluss von Diethylenglykol auf die Hydratation von Tricalciumsilicat- (C_3S) und Tricalciumaluminat- (C_3A) -Pasten wurde untersucht. Diethylenglykol verzögert die Hydratation des C_3S und beschleunigt die des C_3A.

In C_3S-Proben, die mit Diethylenglykol hydratisiert wurden, ist der Gehalt an $Ca(OH)_2$ geringer, die Induktionsperiode länger und die Bildung von Hydraten verzögert. In C_3A-Pasten wird in Gegenwart von Diethylenglykol die Bildung des hexagonalen Calciumaluminathydrats beschleunigt und seine Umwandlung in die kubische Form begünstigt.

Резюме — Изучено влияние диэтиленгликоля на параметры гидратации паст трикальцийсиликата и трикальцийалюмината. Диэтиленгликоль замедляет гидратацию трикальцийсиликата, но ускоряет гидратацию трикальций алюмината. Количество гидроокиси кальция, найденного в пастах трикальцийсиликата, обработанных диэтиленгликолем, было более низким, причем индукционный период увеличивался, а образование гидратов замедлялось. В пастах трикальцийалюмината гидратация этиленгликолем ускоряет образование гидратов алюмината с гексагональной структурой и способствует их превращению до кубической структуры.