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EFFECT OF CEMENT COMPOSITION ON THE EXPANSION OF HEAT-CURED CEMENT PASTES

I. Odler and Y. Chen
Technical University Clausthal,
Clausthal-Zellerfeld, Germany

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ABSTRACT

On 20 cement pastes made from cements of variable C_3A and SO_3 contents and cured at different curing conditions the effect of cement composition on the extent of expansion was studied. It appears that the extent of the generated expansion depends especially on the C_3A and SO_3 contents in cement, but not on the SO_3/C_3A ratio. The extent of expansion increases with the amount of water supplied to the cement paste from outside.

INTRODUCTION

There have been reported cases of delayed expansion and crack formation in concrete products that had been heat-cured at high temperatures, i.e. above about 70 °C. It has been suggested that this type of concrete damage is due to delayed formation of ettringite (AFt;$C_3A.3C\bar{S}.32H$) in the hydrated cement paste. This phase is not formed above about 70 °C and monosulfate (AFm- $C_3A.C\bar{S}.12H$) is formed instead. In the course of subsequent curing at ambient temperature the monosulfate is converted to ettringite in a reaction with calcium sulfate, bound within the C-S-H phase that had been formed in the hydration of tricalcium- and dicalcium silicate. This conversion of monosulfate into ettringite is believed to be responsible for the observed expansion and crack formation (1 - 9). It has also been found that an expansion of this type takes place only in concrete mixes made with quartz based aggregates, and not in those made with limestone or in neat cement pastes (10).

Expansion and damage of this type, though reported frequently in the literature, is not a phenomenon observed consistently, even at curing temperatures well within the range of ettringite unstability. There are indications that the occurence of this phenomenon depends also on the properties of the cement used. It has also been suggested that the expansion does not take place with blended cements that contain, in addition to portland cement clinker, granulated blast furnace slag, fly ash or a natural pozzolana (1,2,4,5). As to plain portland cement it has been suggested that expansion may be prevented either by the use of C_3A-free clinkers, or by restricting the SO_3/Al_2O_3 molar ratio in cement to below 0.55 (4,5).

In our experiments we studied the expansion and ettringite content in a series of paste specimens prepared from portland cements of varying C_3A and SO_3 contents and cured at different conditions. The main aim of the work was to study the effect of cement composition on the extent of expansion. Also studied was the relationship between the amount of ettringite formed and the degree of expansion.

EXPERIMENTAL

Four cements made from clinkers produced in the same plant were employed. Their compositions are given in Table I. The main differences between them were their C_3A and SO_3 contents. By varying these two parameters the following combinations became available:

low C_3A low SO_3 = cement No. 1
low C_3A high SO_3 = cement No. 2
high C_3A low SO_3 = cement No. 3
high C_3A high SO_3 = cement No. 4

TABLE I

Chemical and Phase Compositions (According to Bogue) of the Cements Studied (Mass Percent)

	No. 1	No. 2	No. 3	No. 4
CaO	63.7	62.8	63.8	62.9
Si_2O	21.3	20.8	20.2	19.8
Al_2O_3	4.7	4.3	5.5	5.3
Fe_2O_3	2.9	2.9	2.3	2.3
MgO	2.3	2.7	2.8	2.8
K_2O	1.0	0.7	0.9	0.8
Na_2O	0.2	0.4	0.4	0.3
SO_3	3.4	4.8	3.4	5.0
C_3S	52.1	50.7	55.3	52.6
C_2S	21.8	21.4	16.2	17.1
C_3A	7.6	6.6	10.6	10.2
C_4AF	8.7	8.7	7.0	6.9
$CaSO_4$	5.8	8.2	5.8	8.6

From the above cements, paste specimens of size 10x10x60 mm^3 were prepared with water-cement ratio of 0.40 and 0.50.

Figure 1 shows the curing regimes used. One set of test specimens was cured for the whole time at 20 ± 2 °C and served as control (curing regime 0). Two additional sets were first kept at 20±2 °C for 30 minutes and then heated either to 50 °C in one hour (curing regime a) or to 90 °C in two hours (curing regime b). The two last sets of specimens were similarly heat cured, but only after a precuring time of four hours (curing regimes c and d). After heat curing at maximum temperature for eight hours the samples were allowed to cool to room temperature. The heat curing regimes described above were maintained by placing steel molds filled with the paste and sealed in a plastic foil in a water bath at the given temperature. The heat curing regimes selected corresponded to conditions in which the maximum temperature was either within (regimes a and c) or outside (regimes b and d) the range of ettringite stability. Altogether two sets of samples consisting each of 6 test specimens were prepared for each cement, water/cement ratio and curing regime.

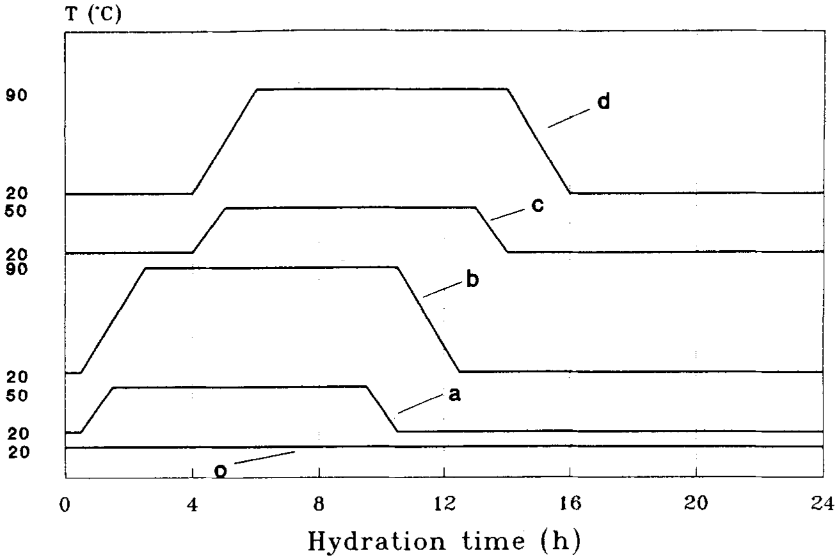


FIG. 1

Curing regimes

After demolding, the test specimens were first kept in humid air at 20±2 °C. After 3 months one half of them was placed under water, while the other half was kept further in air until testing.

The expansions of the test specimens were studied by measuring their lengths after different curing times (accuracy: 0.8 mm/m).

For determination of ettringite content, additional amounts of the pastes were sealed into small polyethylene bags and cured in a similar way as for the test specimens prepared for expansion studies. After different curing times the hydration of these samples was stopped by grinding the material in a porcelain mortar with excessive amounts of acetone, filtering it, washing it on the filter with additional amounts of acetone and diethyl ether and finally by drying the residue at 40 °C. Ettringite was determined on this residue by X-ray diffraction and by DTA. In both instances an ettringite preparation produced by hydration of pure tricalcium aluminate in a saturated aqueous calcium sulfate solution, was employed as reference.

RESULTS

Expansion

The test specimens cured at room temperature showed no distinct expansion up to 24 months of curing, regardless on cement composition. No expansion was observed either in any of the heat cured samples stored in air.

The expansions of the samples stored under water are summarized in Table II. Even here none of the pastes expanded significantly up to 12 months of curing. At even longer hydration times for pastes with w/c = 0.40 a distinct expansion, i.e. one above 10 mm/m, was observed only in samples made from the cement with highest C_3A and gypsum contents (No. 4) and cured at 90 °C. Such expansion was associated with cracking and bending of the test specimens.

TABLE II

Linear Expansions (mm/m) of Cement Pastes Cured for 90 Days in Humid Air and Subsequently under Water

Cement	w/c	Curing Regime	Curing Temp. (°C)	Period of Storage (Months)			
				6	12	18	24
No.1 C_3A= 7.6% SO_3= 3.4%	0.4	o	20	<+1	<+1	<+1	<+1
		a	50	+1.3	<+1	<+1	+1.2
		b	90	+2.3	+3.3	+2.0	+1.5
		c	50	<+1	-1.0	<+1	<+1
		d	90	<+1	<+1	+2.2	+2.2
	0.5	a	50		+6.6	+4.9	+5.7
		b	90		+4.9	+5.1	+2.9
No.2 C_3A= 6.6% SO_3= 4.8%	0.4	o	20	+3.8	+2.5	+2.5	+1.7
		a	50	+1.7	<+1	+1.0	+1.0
		b	90	<-1	<-1	<-1	<+1
		c	50	<+1	<+1	<+1	<+1
		d	90	<+1	<+1	<+1	+1.3
	0.5	a	50		+4.2	+3.7	+3.5
		b	90		+5.9	+4.6	+4.1
No.3 C_3A=10.6% SO_3= 3.4%	0.4	o	20	+2.3	+2.7	+2.8	+3.3
		a	50	<+1	<+1	<+1	<+1
		b	90	+2.8	+1.8	+1.3	+1.8
		c	50	<+1	<+1	<+1	+1.5
		d	90	+1.5	+1.7	+2.0	+1.8
	0.5	a	50		+5.0	+3.5	+4.6
		b	90		+7.5	+8.3	+6.1
No.4 C_3A=10.2% SO_3= 5.0%	0.4	o	20	<+1	+1.3	+1.2	+1.3
		a	50	+2.0	+1.8	+3.0	+1.8
		b	90	+1.3	+4.3	+13.8 *	+15.9 *
		c	50	-1.0	<-1	<-1	<-1
		d	90	<+1	<+1	+14.2 *	+17.3 *
	0.5	a	50		+3.7	+3.9	+4.2
		b	90		+3.0	+2.7	+18.9 *

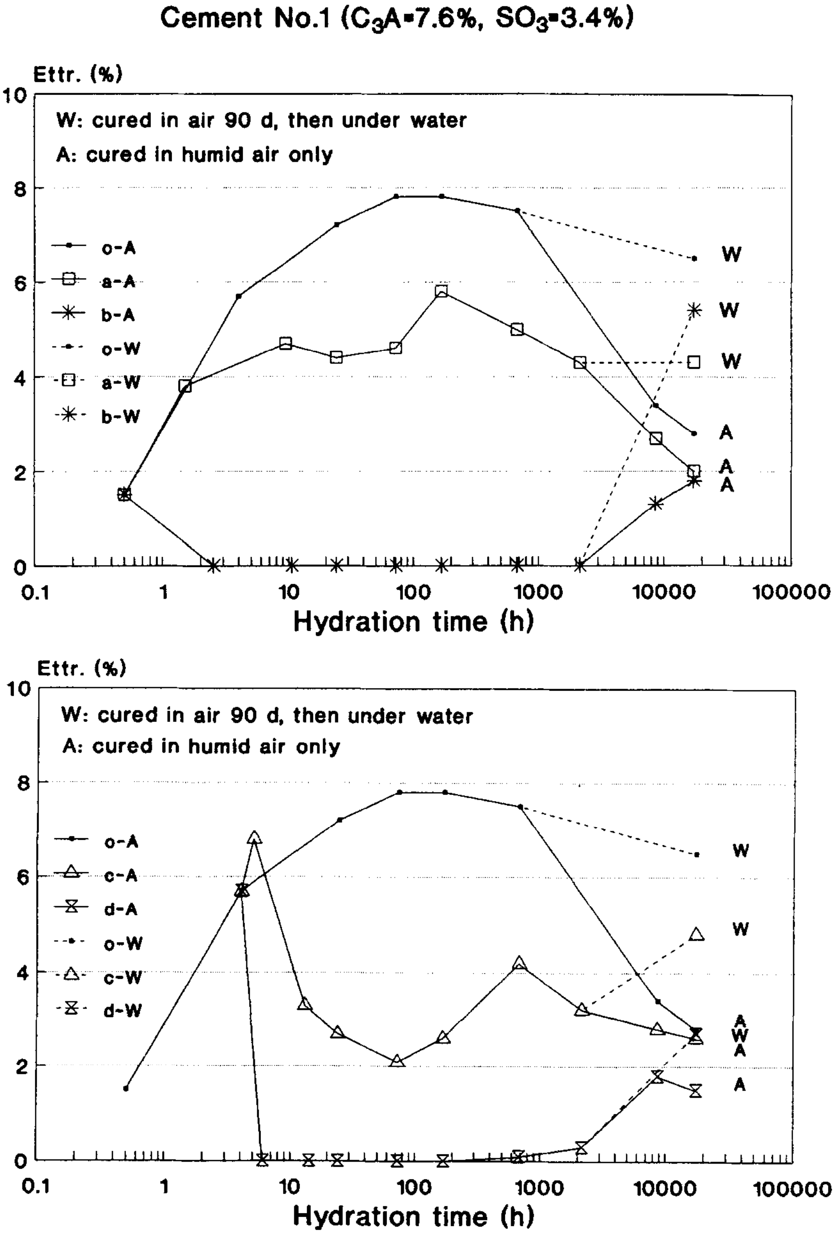
* = cracks

Pastes with w/c = 0.50 expanded more than those with w/c = 0.40. However even here the expansion after 12 months of hydration did not exceede 10 mm/m. No signs of unsoundness were apparent, regardless of cement composition or curing regime. After even longer hydration times samples made from cement No. 4 cured at 90 °C exhibited cracking as in the case of these made with w/c = 0.40.

Ettringite formation

The amounts of ettringite found after different hydration times are plotted in Fig. 2 - 5. The values are the averages of results found by DTA and X-ray diffraction. Those found after 24 months of hydration are summarized in Table III. From the latter, it is apparent that the results found by the two methods were rather similar.

In pastes cured entirely at 20 °C in humid air the ettringite content increased to a maximum and subsequently declined . The maximum ettringite content was higher for cements No. 2 and 4, with higher SO_3 contents than for cements No. 1 and 3. Within the range studied it was



Cement No.1 (C_3A=7.6%, SO_3=3.4%)

FIG. 2

Ettringite contents of pastes made from cement No. 1

independent of the C_3A content. Placing the pastes into water after 3 months of hydration resulted in a more moderate decline or even in a renewed increase in the amount of ettringite.

In samples cured at 50 °C (curing regimes a and c) the amounts of ettringite were, with a single exception, near but generally lower than those of the control pastes cured at 20 °C. In this case the final ettringite contents were higher for the cements with higher gypsum additions.

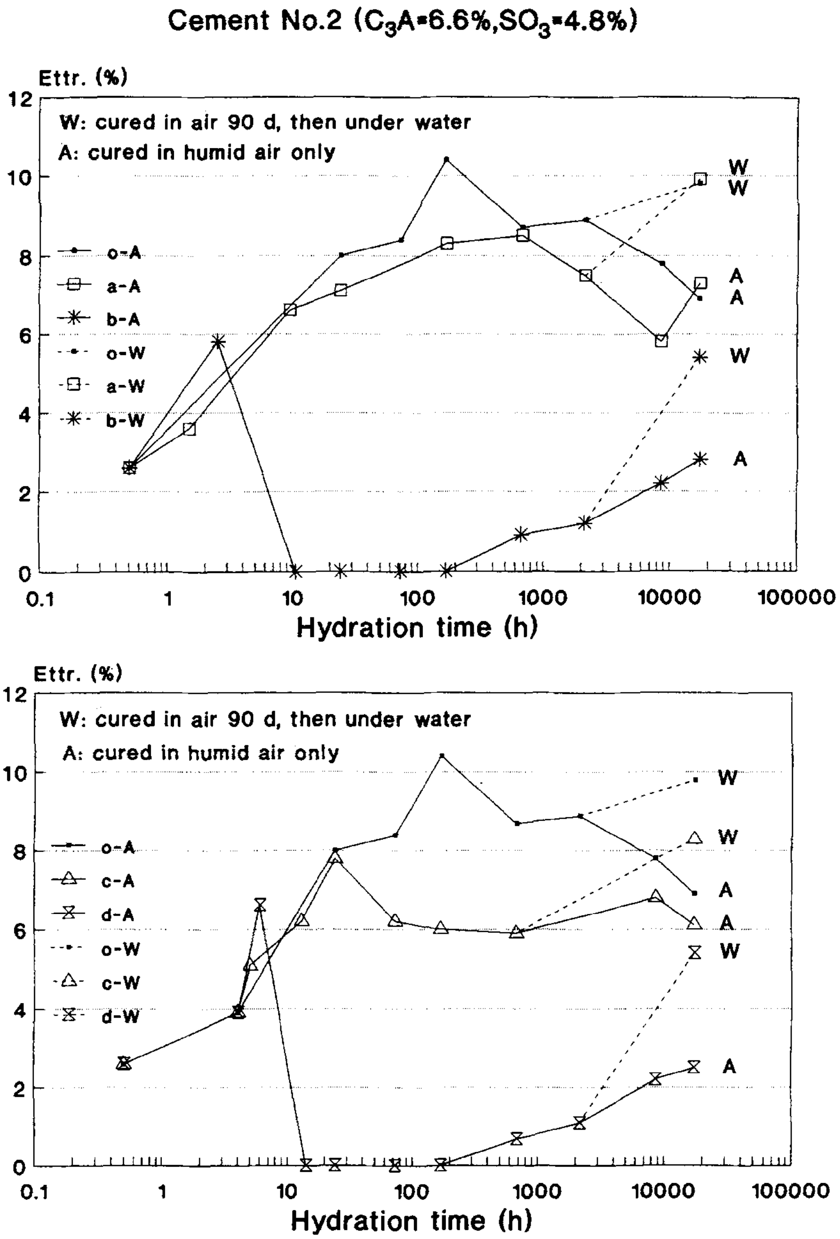


FIG. 3

Ettringite contents of pastes made from cement No. 2

In samples cured at 90 °C (curing regimes b and d) the ettringite formed during precuring at ambient temperature was rapidly decomposed as the curing temperature was increased to 90 °C. A renewed formation of ettringite was observed in all samples during subsequent storage at 20 °C. This renewed ettringite formation was markedly enhanced if the material was stored in water.

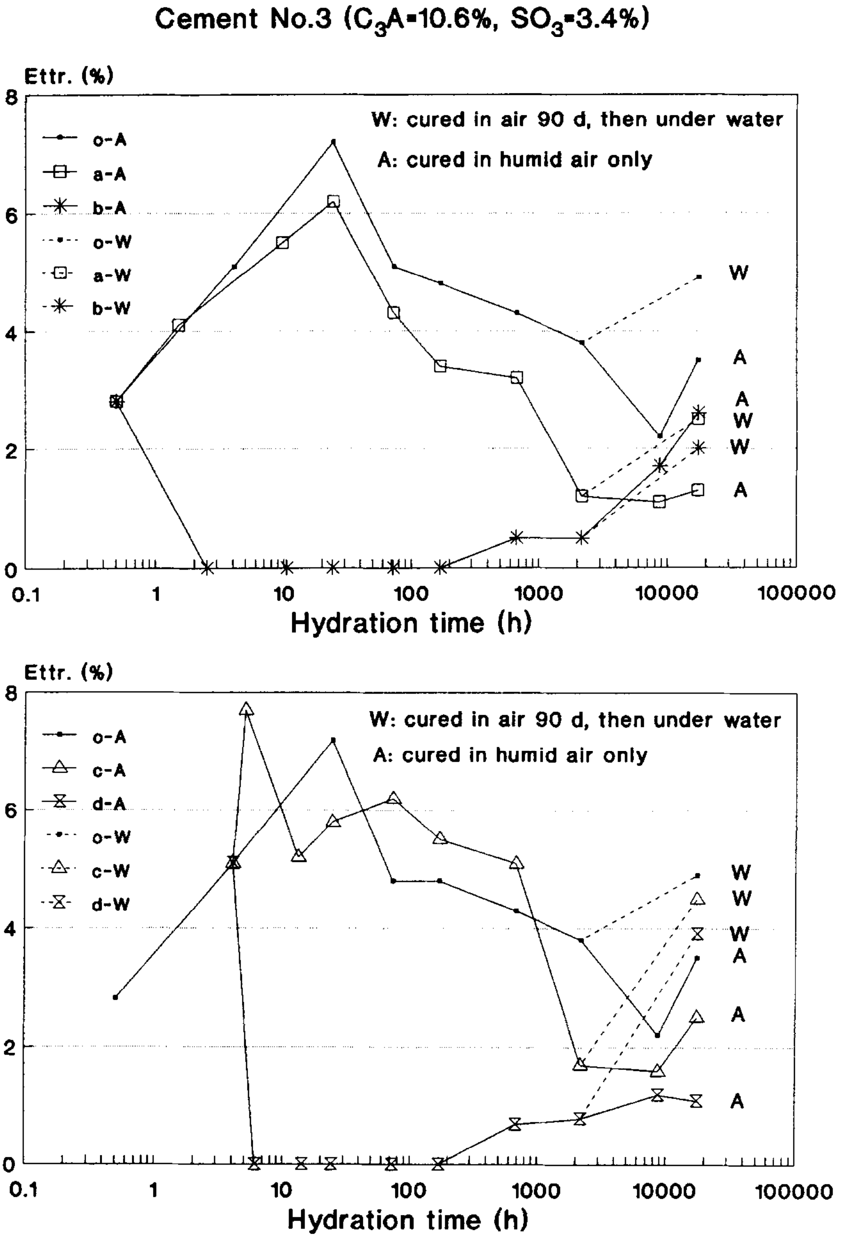


FIG. 4

Ettringite contents of pastes made from cement No. 3

DISCUSSION AND CONCLUSIONS

Our results confirm earlier reports on a delayed ettringite formation in cement pastes that had been heat cured at high temperatures. They show clearly that such ettringite formation progresses very slowly, yet may be stimulated by the supply of water from an external source.

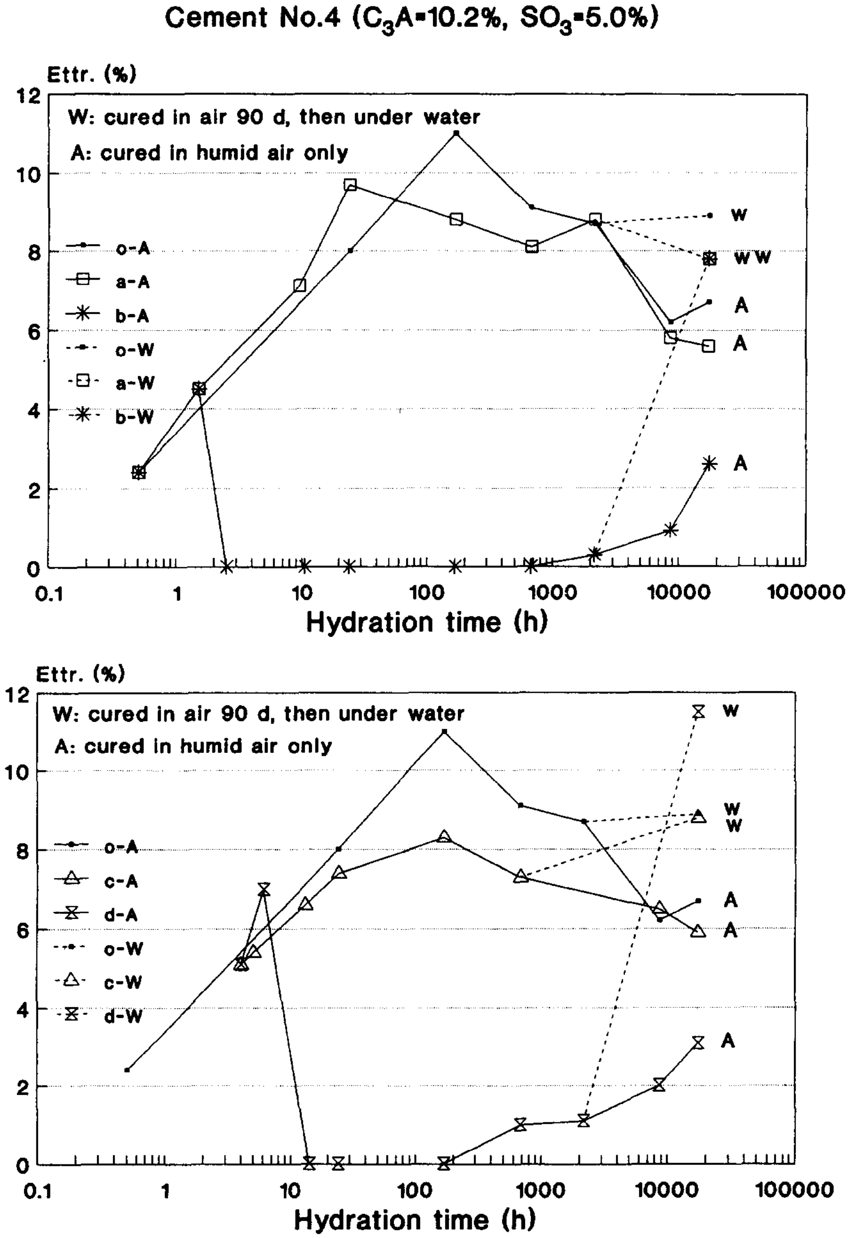


FIG. 5

Ettringite contents of pastes made from cement No. 4

TABLE III

Ettringite Content (%) of Cement Pastes after 720 Days of Curing

Cement	Curing Regime	Ettr.(in air)			Ettr.(under water)		
		DTA	XRD	av.	DTA	XRD	av.
No.1	o	2.6	2.9	2.8	7.5	5.4	6.5
	a	1.8	2.1	2.0	4.2	4.3	4.3
C_3A= 7.6%	b	1.7	1.9	1.8	5.3	5.5	5.4
SO_3= 3.4%	c	2.6	2.6	2.6	5.8	3.8	4.8
	d	0.9	2.1	1.5	2.9	2.5	2.7
No.2	o	8.3	5.5	6.9	10.8	8.8	9.8
	a	9.5	5.1	7.3	12.0	7.7	9.9
C_3A= 6.6%	b	2.7	2.9	2.8	5.5	5.3	5.4
SO_3= 4.8%	c	7.0	5.1	6.1	9.5	7.1	8.3
	d	2.8	2.1	2.5	6.9	3.9	5.4
No.3	o	3.1	3.8	3.5	5.3	4.5	4.9
	a	1.2	1.4	1.3	2.7	2.2	2.5
C_3A=10.6%	b	1.9	3.3	2.6	2.2	1.7	2.0
SO_3= 3.4%	c	2.7	2.2	2.5	4.8	4.1	4.5
	d	0.9	1.2	1.1	5.0	2.8	3.9
No.4	o	7.3	6.0	6.7	11.4	6.4	8.9
	a	5.6	5.6	5.6	7.9	7.7	7.8
C_3A=10.2%	b	2.4	2.8	2.6	9.2	6.4	7.8
SO_3= 5.0%	c	6.0	5.7	5.9	10.4	7.2	8.8
	d	3.3	2.8	3.1	13.5	9.5	11.5

Our results also confirm the occurence of substantial expansion and cracking associated with this delayed ettringite formation. It has to be stressed that all our experiments were performed on neat pastes and thus do not take into consideration events that may take place at the paste - aggregate interface. The great majority of the previous investigations were made on mortars or concretes. The present results show that both the reformation of ettringite after heat curing at a sufficiently high temperature, and the expansion that may be associated with it, can occur in neat pastes as well as in mortar or concrete, but that both occur more slowly than has typically been reported in the latter cases. The presence of a quartz, or other siliceous aggregate is thus not essential for these phenomena to take place.

From the present experimental data it appears that the extent of the expansion depends greatly on the composition of the cement and especially on its C_3A and SO_3 contents. Contrary to previous reports we were not able to find any effect of the SO_3/C_3A ratio on the extent of expansion. Instead, a critical expansion, associated with cracking and deformation, was observed in our experiments only in samples made from a cement with exceptionally high contents of both SO_3 and C_3A and thus with the greatest potential for ettringite formation.

There were indications that the extent of expansion increases with the amounts of water supplied to the cement paste from outside, as the amount of ettringite formed increases significantly with this variable.

Another factor that seems to have also an effect on the extent of expansion is the water/cement ratio employed in preparing the paste. The increased expansion seen in pastes with a higher w/c appears to be a consequence of the lower strength obtained under these conditions.

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