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On the Delayed Expansion of Heat Cured Portland Cement Pastes and Concretes

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Abstract

Under high temperature heat curing conditions the C_3A phase of Portland cement hydrates to yield monosulfate. The latter phase converts to ettringite during subsequent curing at ambient temperature, but only after an induction period of many months. This reaction may be associated with an expansion, but only with cements sufficiently high in both C_3A and SO_3. The amount of ettringite needed to cause expansion is distinctly lower than that needed to have this effect in cements with excessive SO_3 contents. © 1996 Elsevier Science Limited.

INTRODUCTION

The expansion of Portland cement pastes and concretes cured at ambient temperature due to the presence of excessive amounts of sulfates in the cement has been well established. It is generally believed that this phenomenon is due to an excessive formation of ettringite in the paste under these conditions.

In 1981 and subsequent years, Ludwig and co-workers reported cases of expansion and cracking in heat cured concrete at SO_3 levels that did not cause expansion at ambient temperature.[1–4] This phenomenon, previously not recognised, was later confirmed by a number of other investigators. It is widely agreed that the reason for such expansion is a delayed formation of ettringite in the hardened material. This takes place because, in the course of heat curing at temperatures above about 70°C, calcium aluminate monosulfate hydrate is formed as the sole product of hydration of tricalcium aluminate, even in the presence of excessive amounts of SO_3. After heat curing has been concluded and the temperature of the material drops, monosulfate may convert to calcium aluminate trisulfate hydrate (ettringite) in a reaction with calcium sulfate hitherto bound, probably by adsorption, in the C–S–H which is also formed.

An expansion of this kind is not a phenomenon observed consistently in heat cured concrete. In fact, in most instances heat curing does not affect the volume stability of hardened concrete noticeably and a distinct expansion, associated with cracking, has to be considered more as an exception than a rule.

It has been suggested that, to avoid excessive expansion, the SO_3/Al_2O_3 molar ratio of cements employed in concrete mixes to be heat cured be limited to values below 0·55,[3,4] or that blended cements be employed, containing granulated blast furnace slag, fly ash or natural pozzolana in addition to clinker and calcium sulfate.

In our own work we studied the effects of cement composition and curing conditions on the expansion of heat cured pastes, and the relationship between the amount of ettringite formed and the extent of expansion. For comparison, we included in our study expansion measurements on Portland cement pastes hydrated at ambient temperature.

RESULTS AND DISCUSSION

Expansion of Portland cement pastes at ambient temperature

Table 1 shows the ettringite contents and linear expansions of a series of cement pastes

Table 1. Ettringite contents and linear expansions of cement pastes after 365 days of curing at ambient temperature*

		WPC		*SRPC*	
SO_3 (%)	*Curing*	*Ettringite (%)*	*Expansion (mm/m)*	*Ettringite (%)*	*Expansion (mm/m)*
2·3	A	8	<1	10	<1
	W	13	<1	13	<1
4·7	A	17	48 c	13	<1
	W	28	79 c	13	<1
7·0	S	22	46	12	<1
	A	28	178 c	13	<1
	W	30	165 c	16	<1

*WPC = white Portland cement; SRPC = sulfate resistant Portland cement; A = curing in humid air; W = curing under water; S = curing in a sealed state; c = crack formation.

(w/c = 0·40, specimen size 10 × 10 × 60 mm) after one year of curing. The cements were made from either a white Portland clinker ($C_3A = 12\%$, $C_4AF = 0\%$) or a sulfate resistant Portland clinker ($C_3A = 0\%$, $C_4AF = 17\%$), with variable gypsum additions. All had a fineness of 300 $m^2\ kg^{-1}$ (Blaine). The test specimens were cured either completely sealed, or in air, or in water. It may be seen that a measurable expansion was detectable only in pastes made from the white clinker and then only at the higher gypsum additions, The expansion was distinctly higher for samples cured in humid air or in water than for one that was completely sealed and unable to pick up water from the environment while stored. The amounts of ettringite formed, determined by X-ray diffraction, were higher in the pastes made from the white Portland cement, except for those made with the lowest gypsum addition. It generally increased in the order sealed < air cured < water cured sample.

Table 2 shows the expansions of two pastes of white Portland cement with high contents of gypsum after different curing times. It may be seen that a measurable expansion was detectable within 7 days of curing and that the expansion process was virtually completed within the first 90–180 days.

Expansion of heat cured Portland cement pastes

The expansions taking place in heat cured cement pastes were studied using four ordinary Portland cements, all produced in the same plant and differing in their C_3A and SO_3 contents. By varying these two parameters the combinations shown in Table 3 became available.

All four cements had the same specific surface area (300 $m^2\ kg^{-1}$). Pastes made from them (w/c = 0·40, specimen size 10 × 10 × 60 mm) were either cured for the whole time at 20°C or heat cured. The heat curing was done for 8 h at temperatures of either 50°C or 90°C, with a heating rate of about 30–40 °C h^{-1}. Prior to the heat curing, the pastes were precured at ambient temperature for either 0·5 or 4 h. During the heat curing, the specimens were kept in completely sealed steel moulds. After cooling down, the demoulded test specimens were first kept in humid air at 20°C, exactly as for the control samples. After 3 months, half of

Table 2. Expansion after different curing times of pastes made from white Portland cement (mm/m)

	10% Gypsum		*15% Gypsum*	
Curing time (days)	*Cured in humid air*	*Cured under water*	*Cured in humid air*	*Cured under water*
7	5	8	8	15
28	17	25	18	48
90	45	70	102	160
180	46	74	175	160
365	48	79	178	165

the test specimens were transferred into water, while the rest were kept further in air until testing.

After 24 months none of the samples kept in air showed any measurable expansion. Data for samples stored in water are summarised in Table 4. It is obvious that a distinct expansion, associated with crack formation, was present only in samples made from the cement high in both C_3A and SO_3 and heat cured at 90°C. The time of precuring at ambient temperature prior to heat curing seems to have little effect on the extent of expansion.

Kinetics of expansion

Table 5 shows the progress of expansion of pastes made from cement No. 4. It appears that expansion due to heat curing got under way only after a significant delay of one year of subsequent curing at ambient temperature.

Table 3. C_3A and SO_3 contents of the cements

Cement No.	*C_3A*	*SO_3*
1	Low (7·6%)	Low (3·4%)
2	Low (6·6%)	High (4·8%)
3	High (10·6%)	Low (3·4%)
4	High (10·2%)	High (5·0%)

Delayed ettringite formation

The amounts of ettringite in the samples were determined both by DTA and by X-ray diffraction which gave results in reasonable mutual agreement. The average values from the two methods for the samples hydrated for 2 years are included in Table 4. The ettringite contents were generally higher in pastes made from cements of higher SO_3 contents but seem to be little dependent on the C_3A content. For a given cement, the differences between the ettringite contents of pastes hydrated only at ambient temperature, heat cured at 50°C or heat cured at 90°C are not great and seem not to be of a systematic nature. It is especially remarkable that the final ettringite contents of samples that exhibited significant expansion and cracking were similar to those of some other samples that did not expand. The final ettringite contents of samples cured entirely in air (not shown in Table 4) were distinctly lower than those found in the water cured materials.

A comparison with samples that expanded at ambient temperature due to an excessive SO_3 content also indicates that expansion of heat

Table 4. Ettringite contents and linear expansions of cement pastes cured at various temperatures followed by 24 months' storage in water

Cement No.	*C_3A (%)*	*SO_3 (%)*	*Temperature of heat curing (°C)*	*Time of precuring at 20°C (h)*	*Expansion (mm/m)*	*Ettringite content (%)*
1	7·6	3·4	20°		<1	6·5
			50°	0·5	2	4·6 } 4·7
			50°	4·0	<1	4·8
			90°	0·5	2	5·4 } 4·1
			90°	4·0	2·2	2·7
2	6·6	4·8	20°		2	9·8
			50°	0·5	<1	9·9 } 9·1
			50°	4·0	<1	8·3
			90°	0·5	<1	5·4 } 5·4
			90°	4·0	2	5·4
3	10·6	3·4	20°		3	4·9
			50°	0·5	<1	2·5 } 3·5
			50°	4·0	2	4·5
			90°	0·5	2	2·0 } 3·0
			90°	4·0	2	3·9
4	10·2	5·0	20°		1	8·9
			50°	0·5	2	7·8 } 8·3
			50°	4·0	<1	8·8
			90°	0·5	16c	7·8 } 9·8
			90°	4·0	17c	11·8

Table 5. Expansions of heat cured cement pastes and of a paste cured entirely at ambient temperature*

W/c ratio	0·5	0·4	0·4	0·4
Precuring time at 20°C (h)	0·5	0·5	4·0	-
Temperature of heat curing (°C)	90°	90°	90°	-
Expansion (mm/m) after subsequent curing in air at 20°C for 90 days followed by curing in water at 20°C for a time of:				
90 days	<1	1	<1	2
270 days	3	4	<1	2
450 days	3	14 c	14 c	2
630 days	19 c	16 c	17 c	2

Cement No. 4; C_3A, 10·2%, SO_3, 5·0%; specific surface area (Blaine), 300 m^2 kg^{-1}; c = Crack formation.

cured samples requires the formation of significantly lower amounts of ettringite.

Figure 1 shows the ettringite contents reached after different hydration times in pastes made from cement No. 4 and cured entirely at 20°C, heat cured at 50°C and heat cured at 90°C, in each case with a precuring time of 0·5 h. All three pastes were cured for the first 90 days in humid air and subsequently under water. In samples that were not heat cured, the ettringite content reached a maximum after about 7 days and declined moderately afterwards. The ettringite contents in samples heat cured at 50°C were not very different from those of samples cured entirely at ambient temperature, In contrast, for samples heat cured at 90°C, the ettringite contents decreased to zero in the course of heat curing. Renewed ettringite formation got under way only after several months of subsequent curing at ambient temperature. A delayed formation of ettringite was observed also in samples that were kept permanently in air, but the amounts of ettringite formed were distinctly lower.

CONCLUSIONS

It appears that an expansion of cement pastes and concretes that have been cured at high temperatures is due to a renewed and retarded formation of ettringite, which had decomposed and whose additional formation was prevented under conditions of heat curing. This phenomenon appears to be confined to mixes heat cured at temperatures above about 70°C, whereas with more moderate heat curing conditions the formation of ettringite in the paste seems to be not noticeably affected.

The data indicate that renewed ettringite formation, and with it an expansion of heat cured cements pastes and concretes, begins only after prolonged storage at ambient temperature. It is not obvious why the conversion of monosulfate

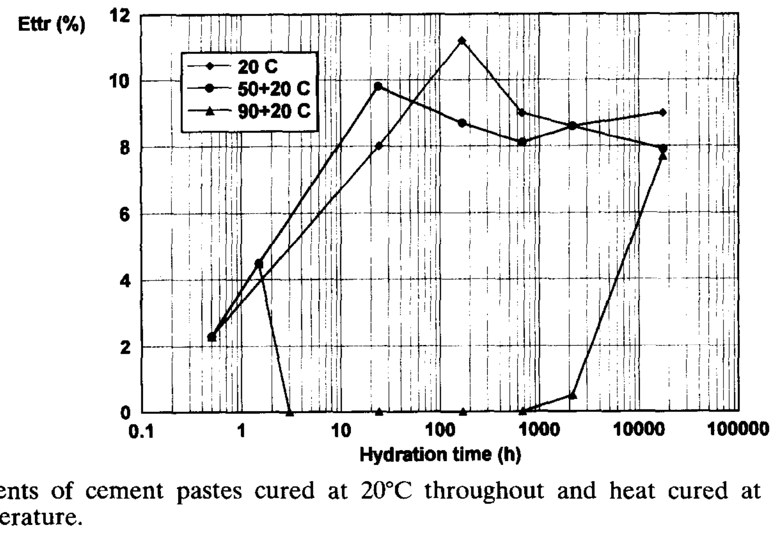

Fig. 1. Ettringite contents of cement pastes cured at 20°C throughout and heat cured at 50°C or 90°C followed by storage at ambient temperature.

that had been formed under heat curing conditions into the thermodynamically more stable ettringite requires such an exceptionally long induction period. It also appears that curing under water, rather than in humid air, distinctly accelerates this conversion process.

The amounts of ettringite found in pastes that exhibited expansion after heat curing at 90°C were not very different from those found in some pastes that were heat cured at 50°C, or entirely at ambient temperature, and which did not expand. This suggests that, in addition to the amount of ettringite formed, a particular mechanism of formation is essential for the expansion to take place. It appears that a delayed formation of ettringite in a mature paste by reaction between monosulfate formed as a primary hydration product and sulfate ions bound within the C–S–H is more effective in causing expansion than is the formation of the same amount of ettringite from tricalcium aluminate and gypsum in the initial stage of the hydration process.

All experience and observations made so far suggest that delayed expansion in heat cured concrete may be prevented by either or both of two methods. These are selection of a suitable cement, and not exceeding temperatures above which ettringite becomes unstable and thus cannot be formed.

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