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Investigations on cement expansion associated with ettringite formation

I. Odler *, J. Colán-Subauste

Technical University Clausthal, 38678 Clausthal-Zellerfeld, Germany

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Abstract

The formation of ettringite and the expansion associated with it were studied on pastes made from an Al-bearing compound, gypsum, and tricalcium silicate. There were significant differences in the rate at which ettringite was formed and in the capacity of the formed ettringite to generate expansion. In some systems ettringite formation was not associated with expansion. An uptake of water from the environment seems to be inessential for an expansion to take place, but intensifies its extent. © 1999 Elsevier Science Ltd. All rights reserved.

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Ettringite (AFt-phase, abbreviated $C_3A \cdot 3C\overline{S} \cdot 32H$) is formed in the hydration of a variety of inorganic binders. The formation of limited amounts of this phase may be considered acceptable; however, in some cements excessive amounts of formed ettringite may cause expansion and cracking of the hardened paste and must be avoided. On the other hand, in some expansive cements the formation of ettringite is employed to generate desired expansive stresses. It has also been recognized that a simple proportionality between the amount of formed ettringite and the extent of expansion does not exist, and in some cementitious systems even large amounts of this phase may cause only insignificant volume changes.

The mechanism of expansion caused by ettringite formation is not fully understood. It is most widely believed that the expansion is due to a topochemical formation of this phase and to an anisotropic growth of the formed ettringite crystals [1–10]. According to another theory, the expansion is due to an inbibition of water by ettringite crystals of colloidal dimensions, rather than by the formation of ettringite itself [11–13].

In the present paper we are reporting our data on the kinetics of ettringite formation and associated expansion of pastes made from tricalcium silicate in combination with different Al compounds and calcium sulfate. The main role of tricalcium silicate was to produce a coherent C-S-H matrix that must be present in the study of expansion phenomena. Moreover, calcium hydroxide, formed in the C_3S hydration together with the C-S-H phase, participated in some systems in the formation of ettringite. The aim of the work was: (1) to study the effect of the Al^{3+} source on expansion caused by ettringite formation; (2) to investigate the effect of water uptake from the environment on this phenomenon; and (3) to analyze the relationship between the amount of ettringite formed and the extent of expansion.

1. Experimental

1.1. Materials

Seven different Al-bearing starting materials were employed as sources of Al^{3+}:Monocalcium aluminate (abbreviated CA), tricalcium aluminate (abbreviated C_3A), tetracalcium trialuminate sulfate (abbreviated $C_4A_3\overline{S}$), and tetracalcium aluminate ferrite (abbreviated C_4AF) were synthesized by burning precompacted mixes of an appropriate composition made from $CaCO_3$, Al_2O_3, $CaSO_4$, and Fe_2O_3 in an electric furnace at temperatures needed to reduce the free CaO content below 0.5 wt.%.

Monosulfate (AFm-phase, abbreviated $C_3A \cdot C\overline{S} \cdot 12H$) was synthesized by shaking a water suspension of Al_2O_3, $CaSO_4 \cdot 2H_2O$, and $Ca(OH)_2$ with a 1:1:3 molar ratio in a closed container for 144 h at 110–120°C. The reaction product was filtered, washed with methanol, and dried in air at ambient temperature. The preparation contained approximately 77% of monosulfate. The rest were small amounts of the starting materials and ettringite.

A glass of the composition CaO, 45 wt.%; Al_2O_3, 35 wt.%; and SiO_2, 20 wt.% (designated CAS-glass, or CAS) was produced by heating the starting mix in a Pt dish in an electric furnace to 1630°C and quenching the obtained melt in an excess of water. The aluminum sulfate [$Al_2(SO_4)_3$, abbreviated $A\overline{S}_3$] and gypsum ($CaSO_4 \cdot 2H_2O$, abbreviated $C\overline{S}H_2$) used were commercial products. Tricalcium silicate

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* Corresponding author. Address correspondence to 16 Olde Village Drive, Winchester, MA 01890, USA. Tel.: 781-721-7773; Fax: 781-721-7773.

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(abbreviated C_3S) was synthesized by repeated burning of the pertinent $CaCO_3 + SiO_2$ blend to 1550°C.

Finally, ettringite used as a standard in the quantitative determination of this phase in the hydrated experimental pastes was synthesized by stirring a suspension of 0.2 mol C3A and 0.6 mol gypsum in 1 L of water for 72 h. The obtained material was filtered, washed with acetone and ethyl ether, and dried in air at ambient temperature.

All materials, with the exception of monosulfate and ettringite, which were available in highly dispersed form, were ground to a specific surface area of 300 ± 10 m^2/kg (Blaine) prior to being used in the experimental work.

1.2. Mix preparations and curing of test specimens

Experimental mixes were prepared by blending each of the Al compounds together with gypsum in an Al_2O_3/SO_3 molar ratio of 1:3. The amounts of these constituents were selected to yield 30 wt.% of ettringite (related to the whole paste) upon complete hydration. The rest of the mix consisted of tricalcium silicate and water, which added in amounts corresponding to a water-solid ratio of 0.40.

The mixes were designated according to the Al compound used in their preparation. From each of the mixes test specimens 10 × 10 × 60 mm were produced. After setting and demolding they were stored until testing either in dry air (over silica gel), in water vapor saturated air, or in lime-saturated water at 20°C. The chemical reactions shown in Eq. (1) through Eq. (6) took place in the pastes in the course of hydration:

$$CA + 3\ C\bar{S}H_2 + 2\ CH + 24\ H \rightarrow C3A \cdot 3C\bar{S} \cdot 32H \quad (1)$$

$$C_3A + 3\ C\bar{S}H_2 + 26\ H \rightarrow C_3A \cdot 3C\bar{S} \cdot 32H \quad (2)$$

$$C_4A_3\bar{S} + 8\ C\bar{S}H_2 + 6\ CH + 74\ H \rightarrow 3\ C_3A \cdot 3C\bar{S} \cdot 32H \quad (3)$$

$$C_4A\bar{S}H_{12} + 2\ C\bar{S}H_2 + 16\ H \rightarrow C_3A \cdot 3C\bar{S} \cdot 32H \quad (4)$$

$$C_4AF + 6\ C\bar{S}H_2 + 2\ CH + 50\ H \rightarrow 2\ C_3(A_{0,5},F_{0,5}) \cdot 3C\bar{S} \cdot 32H \quad (5)$$

$$A\bar{S}_3 + 6\ CH + 26\ H \rightarrow C_3A \cdot 3C\bar{S} \cdot 32H \quad (6)$$

1.3. Testing

The longitudinal changes and masses of the test specimens were determined after different hydration times up to 1 year of hydration, or until they disintegrated due to excessive expansion. To stop hydration and to remove the nonreacted water, the pastes hydrated for different periods of time were ground in a porcelain mortar with excessive amounts of acetone and then filtered. The residue was washed on the filter with additional amounts of acetone and ethyl ether and finally dried in air. The final product was employed for quantitative determination of ettringite by differential thermal analysis (DTA).

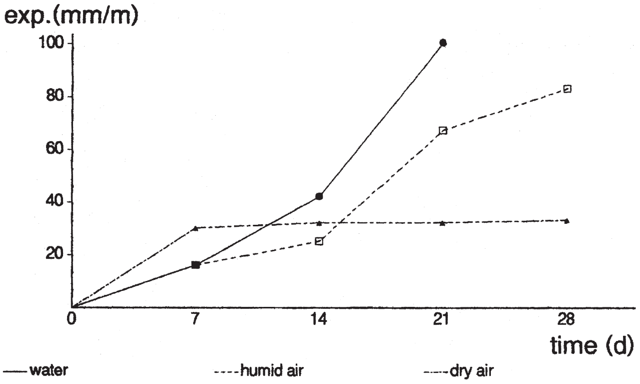

Fig. 1. Expansion of paste CA.

2. Results

2.1. Expansion

The expansion data (average values of three test specimens) for pastes produced with CA, C_3A, C_4A3S, AFm, and C_4AF are summarized in Figs. 1–5.

A comparison of results found on test specimens that were cured underwater reveals great differences both with respect to the kinetics of the expansion process and the overall expansion. Specimens made with CA, C_4A_3S, and AFm expanded very quickly and disintegrated within less than 1 month due to excessive expansion. The paste made with C_3A also exhibited significant expansion, but the expansion process progressed more slowly; the specimens disintegrated after about 6 months of curing. The samples C_4AF expanded even more slowly and a marked crack formation became apparent only after 1 year. Finally, test specimens made with aluminum sulfate and the CAS-glass did not exhibit expansion even after one year of curing.

Figs. 1–5 also show the effect of curing conditions on expansion. Generally, pastes cured in humid air expanded similarly to those cured underwater, albeit more slowly. All test specimens disintegrated within less than 1 year, except those made with C4AF, aluminum sulfate, and CAS-glass.

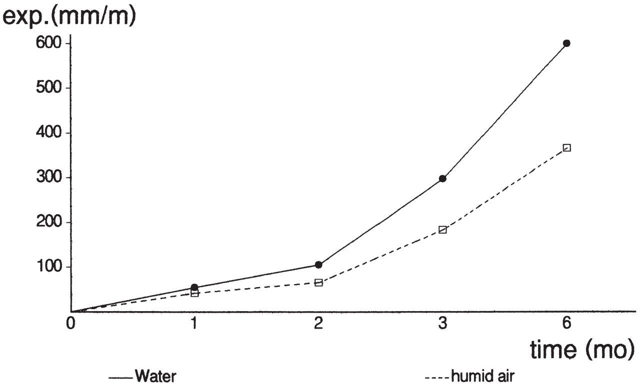

Fig. 2. Expansion of paste C_3A.

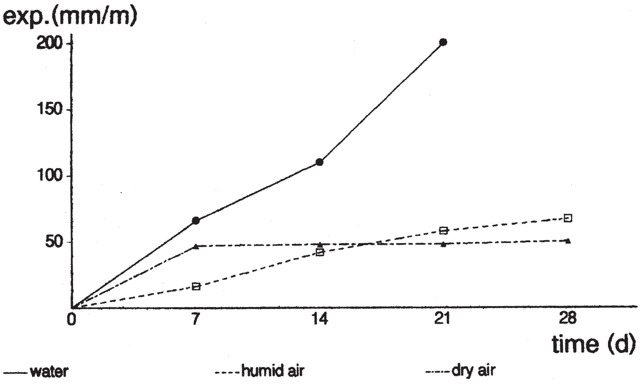

Fig. 3. Expansion of paste C_4A_3S.

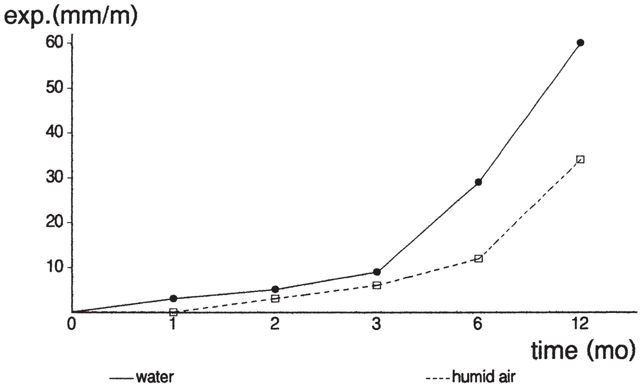

Fig. 5. Expansion of past C_4AF.

Only two pastes, those made with CA and C_4A_3S, exhibited a distinct, though reduced expansion if cured in dry air. The expansion took place within the first week of curing. Expectedly, all pastes cured underwater exhibited an increase in mass associated with a water uptake from the environment. The extent of the water uptake was roughly proportional to the expansion taking place. The mass changes of samples that were cured in humid air were also positive, but lower than those found in water-cured specimens. On the other hand, samples cured in dry air exhibited a distinct mass loss due to a loss of pore water under these conditions.

2.2. Ettringite formation

Figs. 6 and 7 show the kinetics of ettringite formation in the studied samples under humid air and water curing conditions. The rate at which ettringite was formed differed significantly in different pastes. The fastest formation of ettringite took place in the paste made with aluminum sulfate where the reaction was virtually completed within 1 day after mixing. A fast ettringite formation also took place in pastes made with C_4A_3S, CA, and AFm. The reaction was distinctly slower in the paste made with C_3A and even slower in that made with C_4AF. In the paste made with the CAS-glass, distinct amounts of ettringite were formed within the first few days, but the formation of this phase slowed down significantly after that.

Pastes cured underwater generally hydrated faster than those cured in humid air but the differences were not too great. In contrast, the hydration process in test specimens cured in dry air virtually stopped within a few days due to a loss of a significant fraction of free water under these conditions.

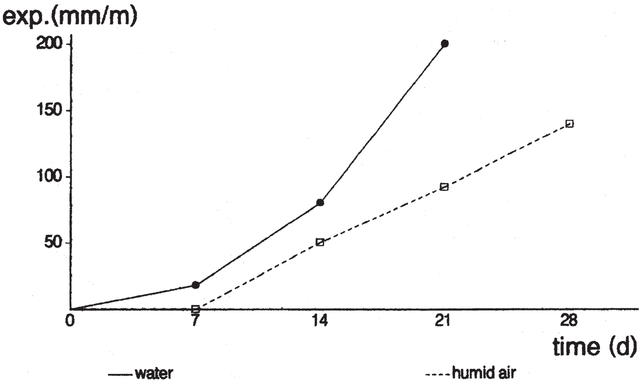

Fig. 4. Expansion of paste AFm.

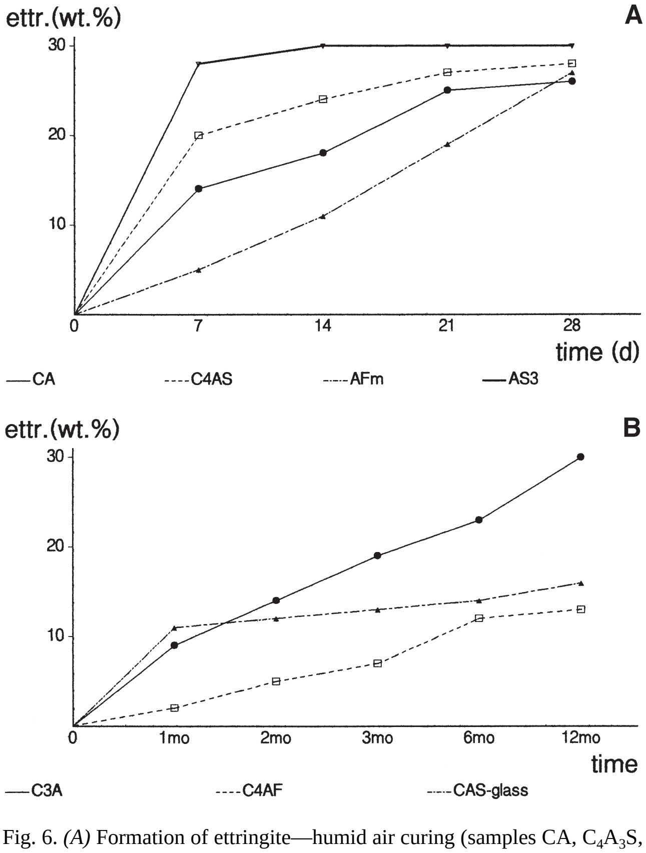

Fig. 6. *(A)* Formation of ettringite—humid air curing (samples CA, C_4A_3S, AFm, and AS_3). *(B)* Formation of ettringite—humid air curing (samples C_3A, C_4AF, and CAS).

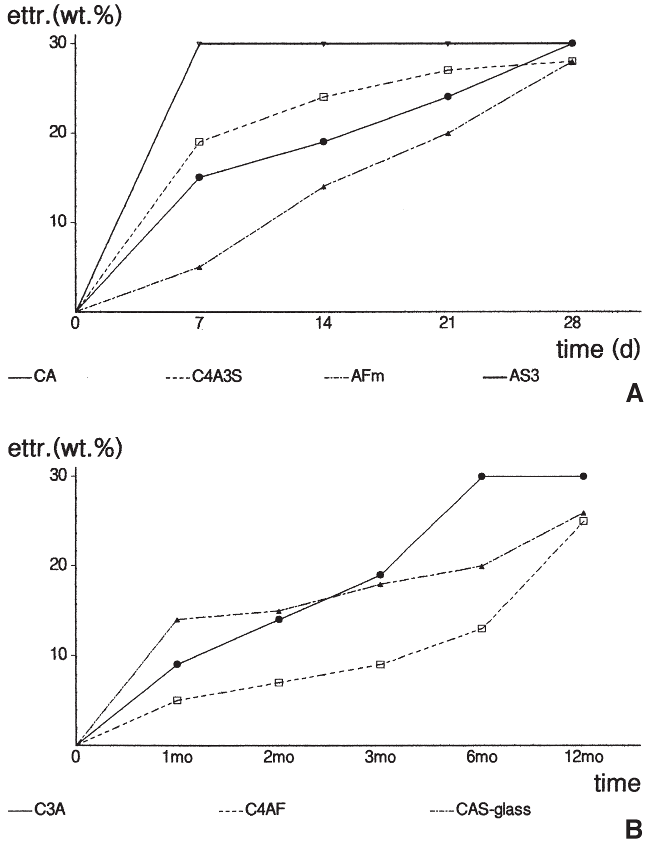

Fig. 7. *(A)* Formation of ettringite—water curing (samples CA, C_4A_3S, AFm, and AS_3). *(B)* Formation of ettringite—water curing (samples C_3A, C_4AF, and CAS).

3. Discussion

The determinations of the ettringite content in pastes hydrated for different periods of time revealed significant differences in the rate at which this phase was formed. Not surprisingly, the fastest formation of ettringite took place in the paste made with aluminum sulfate. This was apparently due to the high dissolution rate and high solubility of this compound in water. Under these conditions, the liquid phase quickly becomes saturated with Al^{3+} and SO_4^{2} ions and the precipitation of ettringite is controlled only by the rate at which calcium hydroxide is released in the hydration of the present tricalcium silicate. In all remaining pastes the rate of ettringite formation appeared to be controlled by the rate of dissolution of the Al compound involved and the different rates of ettringite formation appear to reflect the existing differences in this respect.

There were no indications of the presence of an induction period in the formation of ettringite in any of the pastes studied.

Figs. 8 and 9 show the expansion of the studied pastes as a function of the amount of ettringite formed. One can see that the capacity of ettringite to cause expansion was not uniform and that different amounts of ettringite were needed to produce a given degree of expansion in pastes made with different Al compounds. These differences in the capacity of the ettringite to cause expansion probably reflect the existing differences in how this phase is formed in pastes made with different Al sources.

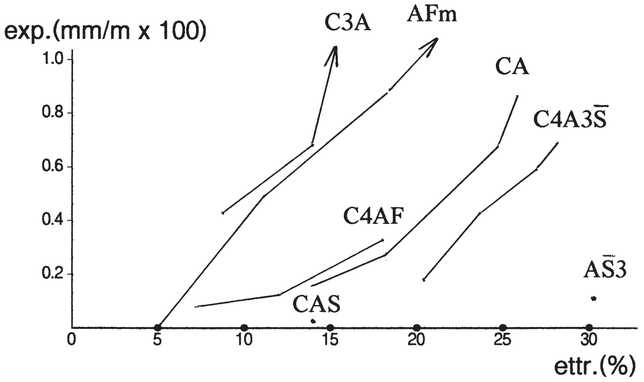

Fig. 8. Expansion as function of the amount of ettringite formed—humid air curing.

The results obtained with the paste that contained C4AF indicate that the reduced expansion of pastes made with cements that contain C4AF as the main Al-bearing phase is due to a slow formation of ettringite (AFt), rather than to a reduced capacity of the iron-containing AFt-phase to generate expansion.

As to the absence of any expansion in pastes made with aluminum sulfate, two possible explanations can be offered: Due to its high solubility, aluminum sulfate becomes readily dissolved in the liquid phase and ettringite is produced by a random precipitation from the liquid, rather than in a topochemical process. Under these conditions, the ettringite crystals do not exhibit the oriented growth needed for an expansion to take place. A second factor that may be involved is the fact that most, if not all, ettringite was produced prior to setting (i.e., at a stage when the plasticity of the paste is still preserved and any internal stresses may be eliminated by plastic deformation of the material).

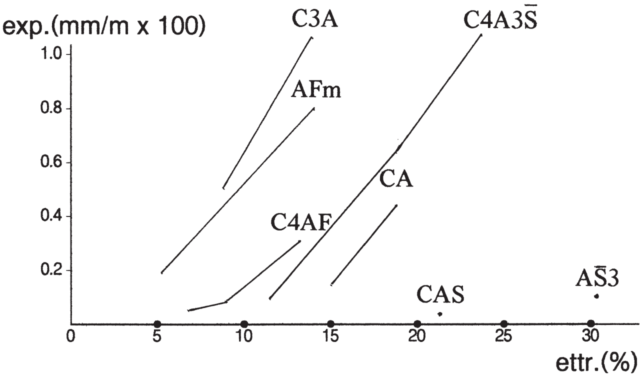

Fig. 9. Expansion as function of the amount of ettringite formed—water curing.

The absence of any expansion in pastes made with the CAS-glass is not obvious. Based on scanning electron microscopy observations on similar pastes produced, however, just from CAS-glass and gypsum it was suggested that the absence of expansion is due to an exclusive through-solution formation of ettringite in such systems [10]. Another factor that must be also taken into consideration is the fact that most of ettringite in the studied paste was formed within the initial stage of hydration, probably prior to setting, and a significant fraction of the CAS-glass remained nonhydrated even after 1 year of hydration.

A comparison of the expansion taking place in humid air and water-cured samples revealed that at equal ettringite levels the expansion was greater in the latter ones. Thus it appears that the enhanced water uptake under these conditions stimulates the expansion of the hardened paste. Since the expansion under both conditions was accompanied with an uptake of water from the environment, it appears likely that swelling phenomena were involved in the expansion process. Results obtained on test specimens cured in dry air revealed, however, that an uptake of water is not essential for the expansion to take place, and that some cementitious systems may expand even while losing water by evaporation.

4. Conclusions

1. The rate of ettringite formation in different cementitious systems may vary greatly depending on the phase serving as the source of Al^{3+}. There are indications that in most instances the rate of dissolution of the Al-bearing phase is the factor that controls the overall rate of reaction.
2. The capacity of ettringite to cause expansion differs greatly in pastes made with different Al compounds serving as source of Al^{3+} ions. These differences appear to reflect the existing differences in the way ettringite is formed in the particular cementitious system. It is being suggested that, at otherwise constant conditions, the expansion increases with increasing fraction of ettringite formed topochemically and exhibiting oriented growth.
3. The extent of ettringite-related expansion depends on the conditions of curing. It increases with increasing amounts of water taken up from the environment while ettringite is formed, indicating the participation of swelling phenomena in the expansion process. However, in some, but not all, cementitious systems an expansion may take place even at a stage when the paste loses water by evaporation.

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