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Review

Delayed ettringite formation☆

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Abstract

Delayed ettringite formation (DEF) can damage concrete that has experienced a temperature above about 70°C. Claims that slow release of sulfate from the clinker can have a similar effect in concrete not thus heated are unsupported. Chemical and microstructural aspects of DEF are reviewed. Expansion results from formation of ettringite crystals of submicrometre size in the paste, the larger crystals readily observed in cracks and voids being recrystallisation products. The rate and ultimate extent of expansion are influenced by factors of three types: chemistry, which determines how much ettringite can be formed; paste microstructure, which determines the stresses produced by its formation; and concrete or mortar microstructure, which determines the response of the material to those stresses. Alkali present before the end of the heat treatment can increase expansion, but when present subsequently, it decreases expansion by inhibiting ettringite formation. Leaching therefore promotes expansion.

Keywords: Delayed ettringite formation; Thermal treatment; Microstructure; Alkalis; Leaching

1. Introduction

Delayed ettringite formation (DEF) may be defined as the formation of ettringite in a cementitious material by a process that begins after hardening is substantially complete and in which none of the sulfate comes from outside the cement paste. It is known in some cases to have caused damage in materials that have experienced temperatures above about 70°C. It has been claimed that DEF has caused damage also in materials that have not been at such temperatures, but as will be seen, these claims are not well founded if one excludes the obvious case of cements containing excessive proportions of total SO_3.

Various cases of damage in field concretes have been attributed wholly, or more often partly, to DEF. Most were precast products made by elevated-temperature curing [1–4]. Some were mass concretes, in which the temperature was believed to have risen excessively from the heat of hydration [5]. In most of the cases in which siliceous aggregates were used, there was also extensive damage from alkali–silica reaction (ASR).

2. Can DEF damage materials that have not experienced an elevated temperature?

It has been claimed that DEF can cause damage in concrete that has not experienced an elevated temperature [6–8]. This was attributed to excessive contents of SO_3 in the clinker or, more precisely, to the presence of that SO_3 in phases from which it was only slowly released. The conclusion was based on studies of field concretes. No supporting evidence from laboratory studies made under controlled conditions or from examinations of the allegedly offending cements or clinkers was given.

One might ask what phases in a cement clinker could contain sulfate that is only released slowly. It was suggested that these were anhydrite and the silicate phases [6]. Rarely, anhydrite occurs in high-SO_3 clinkers low in alkali, but it reacts relatively quickly [9,10]. Belite reacts slowly, but the amounts of SO_3 substituting in belite are at most a few tenths of a percent on the mass of cement and are moreover balanced by substitution of Al_2O_3, so that if a sulfoalumi-

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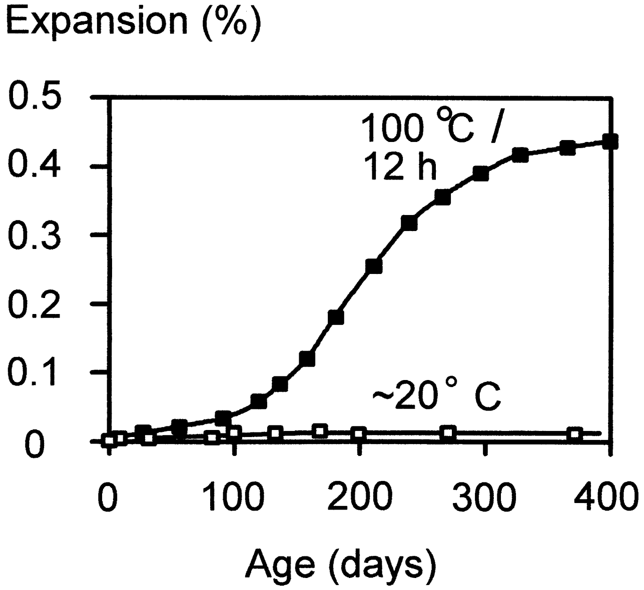


Fig. 1. Linear expansion data for a mortar cured at ~20°C and at 100°C followed by storage in water at ordinary temperature. Adapted from Yang et al. [15].

nate phase is formed at all, it is more likely to be monosulfate than ettringite [11]. Neither experimental data [11] nor normative calculations [12] favours the view that either excessive contents or the distribution of clinker SO_3 is a likely cause of damage from DEF in materials that have not been subjected to an elevated temperature.

Various investigators have made parallel studies of expansion in mortars or concretes cured at ordinary and elevated temperatures [13–18]. Fig. 1 shows typical results. The mortar cured at an elevated temperature expanded markedly and that cured at about 20°C did not. Many similar results have been reported, even for cements containing more than 5% of total SO_3 [16].

3. Ettringite in cement paste and concrete

It is often said that ettringite forms in the early stage of cement hydration but is later replaced by monosulfate. This is true up to a point, but with many cements, as Copeland et al. [19] noted many years ago that ettringite persists indefinitely. Small crystals are inherently unstable relative to larger ones because of their greater surface areas, and it follows that ettringite formed as small crystals in a cement paste tends to recrystallise in any voids or cracks that may exist in a mortar or concrete. It follows that the presence of relatively large ettringite crystals, of the kinds readily seen by petrography or SEM, does not necessarily indicate distress. We have discussed this more fully elsewhere [20]. Erlin [21] noted that the presence of ettringite or other phases in bands at aggregate boundaries shows only that the paste has expanded and that in order to find why it has expanded, additional evidence is needed. Stark et al. [22] concluded that the presence of large ettringite crystals in cracks is usually a consequence of the cracks and not a cause.

4. Expansion from DEF

The pioneer work of Ghorab et al. [23] and of Heinz and Ludwig [24,25], confirmed by many others, showed that there are two necessary but not sufficient conditions for expansion to occur from DEF. First, the internal temperature of the material must be above ~70°C for a sufficient length of time; and second, after its return to ordinary temperature, the material must be kept wet or moist, intermittently or permanently. Expansion typically follows a S-shaped curve (Fig. 1). For 40 × 40 × 160 mm mortar prisms cured at 80–100°C and subsequently stored in water, expansion typically becomes significant after a few months and is substantially complete within 1 or 2 years. It is slower if storage is in moist air. Because of the small size of the specimens, free access of water, and absence of restraint, laboratory studies probably represent a worst case scenario in relation to typical field concretes, for which expansion or cracking may be presumed to occur much more slowly.

Laboratory studies show some other characteristic features. Expansion is influenced by the nature and size grading of the aggregate [23,26–28]; it is very slow in mortars made with limestone sand [17,26,28] and also in neat pastes [29] but faster with quartz aggregates. It spreads inwards from external surfaces and is faster for thin discs than for normal prisms [15,28,30]. Expansion is favoured by preexisting weaknesses of all kinds, notably including ASR. From a study of mortars made with a limestone aggregate with and without a reactive siliceous admixture, Diamond and Ong [31] concluded that where ASR and DEF occur together, the ASR reaction begins before that of the DEF and indeed during the heat treatment itself and that it can cause damage, which may later be exacerbated by DEF.

5. Chemistry of DEF

It has often been supposed that ettringite is intrinsically unstable in a cement paste above about 70°C, but if enough sulfate is present, it can exist in a cement paste at temperatures at least up to 90°C [24,25,32,33]. The reason why ettringite so often disappears at this or lower temperatures is that the C-S-H and the pore solution compete with it for sulfate [34,35]. This tendency increases with the pH. In order to obtain results in a reasonable time, most laboratory studies have been made at 80–100°C. Typically, after curing for a few hours at these temperatures, X-ray diffraction (XRD), NMR, and other techniques show a poorly crystalline AFm phase approximating to monosulfate and a little hydrogarnet but no detectable ettringite. The AFm phase is not always detectable by XRD. Rarely, a little ettringite can be detected.

By the end of the heat treatment, substantial fractions of both the Al_2O_3 and the SO_3 have entered the C-S-H [14,15,18,36–38]. Most of the Al is firmly bound, and NMR evidence shows that most of it substitutes in the structure for Si [39]. A little may enter interlayer sites [40,41]. The sulfate is very loosely bound and has been described as adsorbed [42–44]. Analyses of the pore solution squeezed out under pressure have given widely varying results, even for apparently similar cements and curing condition [18,45–47]. The highest value reported is ~200 mmol/l [45]. It has been suggested, originally by Wieker and Herr [45], that the pore solution is the major store for sulfate in the heated material other than monosulfate, but calculations based on the probable amounts and compositions of the pore solution and the C-S-H show that it is much less important in this respect than the C-S-H.

When the material is subsequently stored at ordinary temperature, most of the Al that has entered the C-S-H stays there. Al present in hydrogarnet is also firmly bound [48,49]. Some Al_2O_3 may be provided by continuing hydration of the clinker phases, but the main reactants are C-S-H, monosulfate, and pore solution. These phases are mixed on a submicrometre scale [36], and the reaction can only occur by dissolution and precipitation. The reactants produce the necessary species:

C−S−H	provides	$Ca^{2+}, SO_4^{2-}, OH^-, H_2O$
Monosulfate	provides	$Ca^{2+}, SO_4^{2-}, OH^-, Al(OH)_4^-, H_2O$
Pore solution	provides	H_2O, SO_4^{2-}

These react to form ettringite, according to Eq. (1):

$$6Ca^{2+} + 2Al(OH)_4^- + 4OH^- + 3SO_4^{2-} + 26H_2O \rightarrow Ca_6[Al(OH)_6]_2{\cdot}(SO_4)_2{\cdot}26H_2O \quad (1)$$

The concentration of the aluminate ion in the solution is extremely low. Most of the ettringite is therefore likely to be formed close to the main source of this constituent, which is the monosulfate.

6. Microstructural changes

We shall use the term outer product for hydration product formed in space originally occupied by water and outer C-S-H gel more specifically for those parts of it that consist of C-S-H alone or mixed with other phases on a submicrometre scale. Fig. 2A shows some recent SEM X-ray microanalyses of the outer C-S-H gel in a mortar directly after curing at 90°C and after subsequent wet storage [18,50]. No significant expansion occurred during this storage. Each point represents an analysis of a region in the order of a micrometre across in each direction. Those obtained directly after the heat treatment correspond to C-S-H containing some S and Al, in some cases alone and in others mixed in various proportions with monosulfate. The outer product also included larger crystals of monosulfate, which are outside the scope of Fig. 2A.

For the material examined after storage, most of the analyses correspond to C-S-H with a lower S/Ca ratio. Some correspond to mixtures with phases containing little or no sulfate, such as monocarbonate or hydrogarnet. The analyses in Fig. 2A provide no positive evidence of ettringite, though clusters of ettringite crystals, outside the scope of Fig. 2A, were observed in hollow shells, pores, and air voids.

Fig. 2B shows similar results obtained using another cement. In this case, substantial expansion occurred during storage after the heat treatment. Two differences from the results for the nonexpansive mortar may be noted. First, the S/Ca ratio of the C-S-H directly after the heat treatment

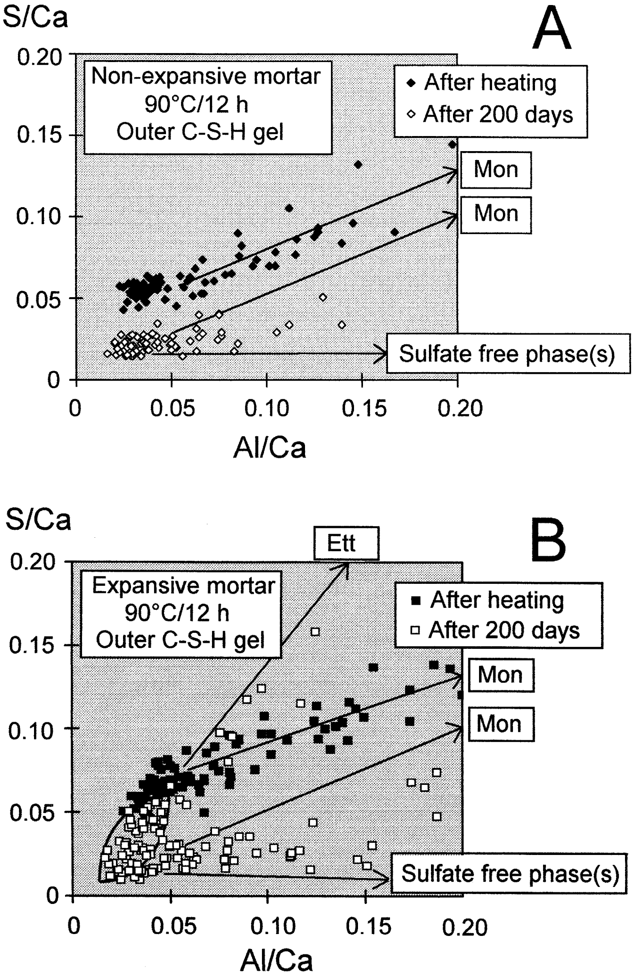


Fig. 2. S/Ca atom ratios vs. Al/Ca atom ratios for the outer C-S-H gel in two mortars, in each case directly after heating at 90°C and after a subsequent 200-day storage in water at ordinary temperature. Mortar B expanded during storage; Mortar A did not. Mon = monosulfate; Ett = ettringite (Famy [18]).

is ~0.07, which is significantly higher than the value of ~0.05 found in the nonexpansive mortar. Second, in the material examined after storage, many of the analyses indicate close mixtures of C-S-H with ettringite. The analyses in the lower part of the ringed area (S/Ca ~0.02) correspond to C-S-H alone, and those in the upper part (S/Ca ~0.05) to mixtures of C-S-H with small proportions of ettringite. Some other analyses correspond to mixtures of C-S-H with higher proportions of ettringite. As with the nonexpansive mortar, ettringite was also present as crystals or groups of crystals large enough for separate analysis. These were present in cavities and cracks within the paste and at aggregate interfaces and outside the scope of Fig. 2B.

XRD shows that the ettringite begins to form in an expanding material within days of the end of the heat treatment [15,36]. At first, all of it is present in the outer C-S-H gel and in small cavities of up to 10 μm dimensions, but later, it is also observed in cracks at aggregate boundaries and running through the paste. The formation of ettringite at aggregate interfaces was first described by Heinz and Ludwig [24] and has subsequently been observed by many investigators.

7. The seat of expansion: paste or aggregate interfaces?

Two main hypotheses have been proposed to explain the mechanism of expansion. One view is that expansion is caused by the growth of the relatively large crystals that form at aggregate interfaces and elsewhere [7,15,23,28]. The other is that it is caused [51], or at least begins [52], with the growth of the much smaller crystals formed within the paste.

Microstructural arguments have been put forward in support of both of these views. Johansen et al. [51] observed cracks surrounding aggregate particles, which contained ettringite, and found that if due account was taken of stereology, the widths of the cracks were proportional to the sizes of the aggregate particles. They showed that this relation can only reasonably be explained by supposing that the paste expands uniformly and isotropically. They considered that this produced the cracks and that the ettringite within them was purely a recrystallisation product. In agreement with this view, Famy [18] found that the initial effect at aggregate interfaces was usually the formation of empty gaps and that this was later followed by that of wider rims containing ettringite and calcium hydroxide. The ettringite rims were only observed after significant expansion had occurred.

There is general agreement that cracks form at aggregate boundaries and that they contain ettringite, but Diamond [7], and later Yang et al. [15,28], found a more complex picture. The cracks did not, in general, go right round the aggregate particles, their widths were not closely related to the sizes of the particles, and ettringite was also present in cracks that had formed in the paste. This was regarded as supporting the view that expansion is caused by growth of the ettringite crystals in the cracks.

It would not be profitable to discuss whose observations were right. One must assume that both are right for the specimens, or regions of specimens, that were examined. Equally, it is unlikely that markedly different mechanisms operate in very similar materials. A probable explanation is that expansion results wholly or mainly from processes taking place within the paste but is not usually uniform or isotropic. In fact, one would not expect expansion of the paste to have these characteristics, except perhaps in localised regions. There are many reasons for this. They include, among others, variations in the strength of the paste–aggregate bond and in the shapes, sizes, and distributions of particles at all levels, local variations in the rates of reactions, heterogeneity in the distribution of hydration products due to the differing sizes and compositions of the clinker grains, and the effects of reinforcement and of gravity. Even if the expansive forces operating within the paste are uniform and isotropic, the restraints on expansion are not. Cracks may therefore be expected to form not only at aggregate interfaces but also within the paste, and the cracks around aggregates will be neither continuous nor of uniform width.

8. Physical chemistry of crystal growth

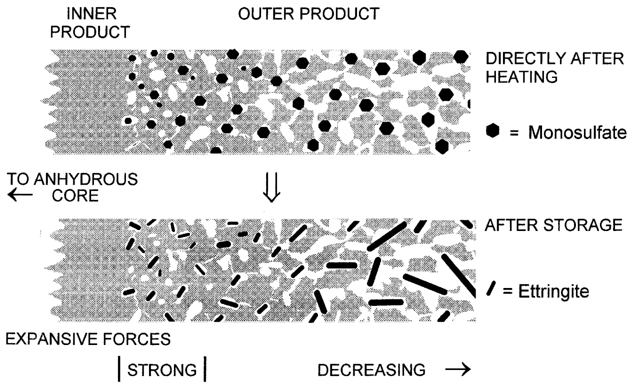
Scherer [53] has discussed the physical chemistry of crystal growth in porous materials. The following points may be noted.

- The driving force for growth is provided by supersaturation, and the hydrostatic pressure that is needed to stop growth increases with the degree of supersaturation. The maximum stress that can be exerted on the surroundings depends on this pressure and on the geometry of the crystal and its surroundings.
- A crystal will not grow where it has to exert pressure if the constituent species can equally well be deposited in a place where this is not necessary. Johansen et al. [51] earlier noted the importance of this in the present context.
- For a crystal growing in a pore, if certain equilibrium conditions are satisfied, a substantial pressure can arise at the pore wall only if the pore radius is below ~100 nm. It is uncertain whether these conditions would be satisfied in the case of an ettringite crystal growing in close proximity to a source of aluminate ions. If they are not, substantial pressures could arise from the growth of larger crystals.
- Growth in a single pore is unlikely to cause damage because the volume affected by the stress is too small. The strength of a mortar or concrete is controlled by flaws, some tens or hundreds of micrometres in size, and the damaging stresses must occur over regions many micrometres in size.

These considerations suggest that the highest expansive pressures will arise where the supersaturation is high and the crystals are formed in relatively isolated regions, which provide minimal possibilities of deposition in alternative sites. The regions also need to be closely spaced over regions of at least 10 μm dimensions. These conditions are most likely to exist in small, poorly connected pores containing or close to sources of the necessary ionic species and especially of $Al(OH)_4^-$.

9. A suggested expansion mechanism

The microstructural evidence shows that monosulfate is intimately mixed with C-S-H at the end of the heat treatment and that under conditions giving rise to expansion, the ettringite subsequently formed is also closely intermixed with C-S-H. This evidence, combined with the conclusion that substantial pressures from crystal growth are most likely to be generated if this occurs in confined spaces at high supersaturation, suggests the mechanism depicted in Fig. 3. Fig. 3 is schematic and not drawn to scale. The uppermost diagram represents part of the microstructure immediately after the heat treatment. The hexagons represent monosulfate crystals and the shaded areas all other solid phases. In a paste cured at an elevated temperature, the inner product around or replacing each cement grain is itself surrounded by a shell of outer product, which is relatively dense [54]. With increasing distance away from the inner product, the texture of the outer product becomes more open. The conditions likely to produce high growth pressures are maximised in the dense shells of outer product surrounding the inner product and to a lessening extent with distance away from the inner product. The lower diagram in Fig. 3 represents the situation after storage. The monosulfate has reacted and has been replaced by ettringite.



NOT TO SCALE. The length of the section is ~5 μm, and the smallest crystals are <100 nm in maximum dimension.

Fig. 3. Schematic diagram illustrating the suggested mechanism for expansion of the paste in a mortar expanding due to DEF. The shaded areas represent all solid phases other than monosulfate and ettringite. Blank areas represent pores.

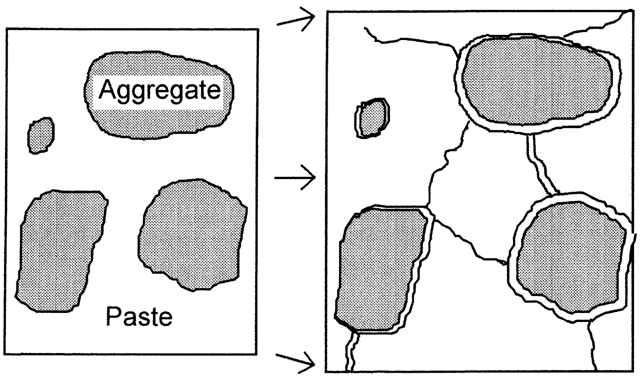


Fig. 4. Schematic diagram illustrating the suggested mechanism of expansion of a mortar or concrete through DEF. Nonuniform expansion of the paste produces cracks in the paste and at aggregate interfaces. Ettringite and portlandite recrystallise in these cracks without contributing significantly to the expansion.

Fig. 4 shows the microstructure at a much lower magnification. It is assumed that expansion of the paste produces cracks both in the paste and at aggregate interfaces. Ettringite, and also calcium hydroxide, recrystallises in these cracks but this does not generate any significant expansive pressures. Especially in a saturated paste, the degree of supersaturation in the cracks is probably low and the cracks are large, thereby offering ample alternative sites in which the ettringite can crystallise.

If a material damaged by DEF is reheated and again stored under moist conditions at ordinary temperature, further expansion and cracking occur [18,23]. In this situation, ettringite is deposited in the cracks at aggregate interfaces and elsewhere during the first period of storage. During the second heating, it is partly replaced in these locations by monosulfate. Because of the presence of the monosulfate, and in contrast to the situation during the first period of storage, high growth pressures could perhaps arise in these cracks when ettringite is reformed.

10. Factors governing expansion

Whether expansion occurs during storage after the heat treatment, and so its rate and ultimate extent, depends on factors of three kinds. These are

1. Chemistry, which determines the amount of ettringite formed;
2. Paste microstructure, which determines the stresses that can result from its formation; and
3. Concrete or mortar microstructure, which determines how the material responds to those stresses.

We shall consider each of these in turn.

11. Effect on expansion of the quantity of ettringite formed

Caution is needed in assessing the results of quantitative determinations of ettringite by either XRD or thermal methods because neither may respond adequately to the small and possibly imperfect crystals responsible for expansion. XRD determinations [13,14,15,18] show a broad tendency for expansion to increase with ettringite content but no general relation. Recent work [18] confirms that curing and storage conditions markedly affect the expansion associated with the formation of a given amount of ettringite. The absence of any general relation is to be expected if the proposed mechanism is correct, since the quantity of ettringite formed is only one of the factors affecting expansion, the effects of which may be obscured or swamped by the microstructural factors mentioned above.

One would expect that any relationship between expansion and the amount of ettringite would be with that formed during storage rather than with that present at the end of the given storage period. The two are not necessarily the same as some ettringite can be present at the end of the heat treatment. Fig. 5 shows trends in the amounts of ettringite formed during storage for cements containing differing amounts of Al_2O_3 and SO_3, calculated using the rather fragmentary data available in the literature. It is essential to take into account that substantial fractions of the Al_2O_3 and SO_3 are not available for forming sulfoaluminate phases. Much of the Al_2O_3 is present in other phases, such as C-S-H, unreacted ferrite, or ferrite hydration products, and the C-S-H also contains some of the SO_3. The contours represent amounts of ettringite formed during storage, increasing in the direction of the arrow. There are no numbers on the contours, for two reasons. One is that the data and uncertainties in the calculations do not justify it. The other is that many other variables affect the results and any such numbers could be valid only for the particular values of these variables that were assumed. Only the general form of the curves, therefore, can be significant.

The curves imply that if the ettringite forms in such a way as to cause expansion, there are various pessima. If there is no SO_3, there can be no ettringite. If there is too much, ettringite and not monosulfate will be present at the end of the heat treatment. If there is no Al_2O_3, there can again be no ettringite, and if there is too much, monosulfate and not ettringite will be present after storage. The pessimum SO_3 is likely to increase with the content of Al_2O_3; this produces a pessimum in the SO_3/Al_2O_3 ratio. Studies of specific groups of cement compositions have indicated the existence of all these pessima [13,16,30,55], but these cannot reliably be generalised to all cements or curing cycles.

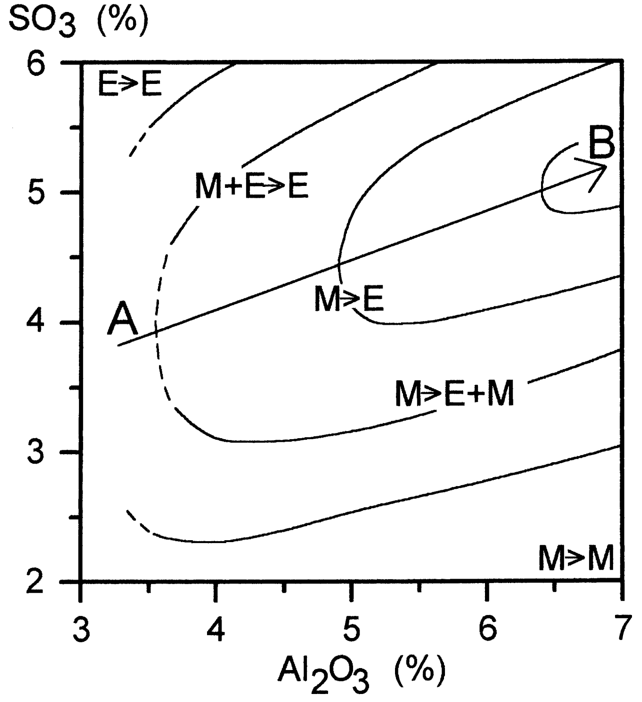


Fig. 5. Schematic diagram showing probable trends in the amounts of ettringite formed after cooling, assuming that variables other than the contents of Al_2O_3 and SO_3 in the cement are as far as possible kept constant. Contours represent amounts of ettringite formed during storage, increasing in the direction of the arrow AB. Sulfoaluminate phases present before and after cooling are shown by M (monosulfate) and E (ettringite).

12. Factors influencing the amount of Al_2O_3 available for forming sulfoaluminate phases

Inspection of Fig. 5 suggests possible explanations of the effects of some other variables. Probably the large majority of Portland cements have compositions on the high Al_2O_3, low SO_3 side of the pessimum locus, AB. For these cements, anything that binds Al_2O_3 will tend to increase ettringite formation, unless it binds so much that the effective Al_2O_3 content moves across to the other side of the pessimum. For compositions on the other side of the pessimum locus, binding of Al_2O_3 will have the opposite effect.

Several variables affect the amount of Al_2O_3 available for forming sulfoaluminate phases.

•*MgO content.* Binding of Al_2O_3 in a hydrotalcite-type phase may explain the observed tendency for expansion to increase with MgO content [56,57], though hydration of periclase may also contribute.

•*Al_2O_3/Fe_2O_3 ratio.* Expansion from DEF is insignificant with sulfate-resisting Portland cements [23,57]. This may be because much of the Al_2O_3 and Fe_2O_3 in the ferrite phase enter hydrogarnet- or hydrotalcite-type phases on hydration [19,58].

•*Curing temperature and time.* Expansion increases with curing temperature up to 100°C and with curing times up to ~3 days [25,59] but is lessened or totally suppressed if the curing time is extended to 7–10 days [18,59]. The increases could be partly due to increased hydrogarnet formation. However, one study showed a significant increase in hydrogarnet after prolonged curing [60], but another showed only a slight increase [18].

•*Additions of slag, trass, or fly ash*. These can decrease expansion [16,23]. This could be due, at least in part, to increase in the quantity of Al_2O_3 available for sulfoaluminate formation.

•*CO_2*. This binds Al_2O_3 through formation of carboaluminate phases. Carbonation has been considered to play an essential role in DEF [61], but evidence that it is a universal requirement is lacking.

13. Effect of paste microstructure on expansion

As noted earlier, the expansion associated with the formation of a given amount of ettringite is influenced by the microstructure of the material in which it is deposited. Several aspects may be considered more fully.

1. The expansion is lessened or eliminated if the material is plastic and easily deformed. This explains why substantial amounts of ettringite can be formed during the early hydration of cement at ordinary temperatures without causing significant expansion. It is not directly relevant to expansion from DEF, as in this case, the material has hardened before the ettringite formation begins.

2. Expansion is affected by the amount of pore space available. As Glasser et al. [35] noted, some of the ettringite produced through DEF is deposited in freely available space and does not contribute to expansion. For this reason among others, one would not expect that expansion would depend simply on the amount of ettringite produced.

3. Expansion also depends on the quality of the pore space, for the reason discussed in Sections 8 and 9. A given amount of ettringite will produce more expansion if the pores in which it is deposited are small and poorly connected than if they are large and more highly connected.

If these assumptions are correct, one would expect the expansion from DEF to increase with the degree of hydration at the end of the heat treatment, since this decreases the volume, size, and connectivity of the capillary pores. The degree of hydration also correlates with the compressive and tensile strengths. One would therefore expect that factors increasing the strength at the end of the heat treatment would also tend to increase expansion from DEF.

As Kelham [57] noted, this hypothesis is consistent with the experimental data. Increases in alite content or fineness and decrease in water/cement ratio all tend to increase the ultimate expansion [17,59]. As noted earlier, increases in curing time or temperature within normal limits also increase expansion. Increase in curing temperature may alter the microstructure by increasing not only the degree of hydration but also the extent to which the outer product is concentrated into shells immediately surrounding the inner product. This might be expected to further increase the expansion associated with the formation of a given amount of ettringite.

Increased contents of SO_3 tend to increase early strength, especially if they are accompanied by high contents of alkali. These effects may contribute to high expansion. This is discussed further in Section 16. The SO_3 content may thus influence expansion both by its effect on the stoichiometry and by its effect on the microstructure.

The relations between the rate and the ultimate extent of expansion are probably complex. On the one hand, increased hydration by the end of the heat treatment decreases the permeability of the paste and of the mortar or concrete as a whole. This may explain why, although ultimate expansions from DEF are high for materials of low water/cement ratio (e.g. 0.375), the rates of expansion in such materials can be very low [59]. On the other hand, a low rate of expansion may increase the extent to which the expansive forces are relieved by creep and thereby decrease the ultimate expansion.

14. Effect of concrete or mortar microstructure on expansion

The concrete or mortar microstructure determines how the material responds to the stresses produced by ettringite formation. Expansion from DEF of an undamaged, neat paste is very slow [29]. Evidently, the material is strong enough to resist the stresses caused by ettringite formation to an extent that greatly retards the reaction and the resulting expansion. It may even limit the extent to which the reaction can proceed. This is also the case in a material made with a limestone aggregate [17,26,28,31], presumably because of the strength of the paste–aggregate bond. In mortars or concretes made with quartz aggregates, the paste–aggregate bond is inherently weaker than with limestone, and the formation of gaps around the quartz particles during prolonged autoclaving of aerated concretes [62] suggests the possibility that even under milder conditions, it is further weakened by heat treatment. A weaker bond allows the reaction and expansion to proceed more quickly.

Anything that weakens the material will lower its ability to resist expansion. It has been known for many years that in order to obtain satisfactory strengths in concrete cured at elevated temperature, it is necessary to be careful with such variables as heating and cooling rates and precuring times [63–66]. If these are not well chosen, microcracks can form because of thermal stresses. This has long been considered important for its effect on strength, but it also renders the concrete more liable to all kinds of damaging processes, of which DEF is only one. It will favour DEF both because it lets water in more easily and because it weakens the paste–aggregate bonds. Other effects that produce microcracks, such as ASR [2,31], freezing and thawing [67,68], or mechanical damage [69], can promote DEF in the same way.

15. Effect of the storage medium on expansion

Famy [18] and Famy et al. [70] confirmed earlier observations that the rate and ultimate extent of expansion from DEF are slower for storage in moist air than for storage in water and also showed that storage in alkali hydroxide solutions greatly retards or eliminates expansion. Fig. 6 shows some observations made on a mortar that had been cured at 90°C. Expansion was relatively fast and extensive if the subsequent storage was in water, slower and less extensive if it was in moist air, and slower still if it was in a solution of KOH simulating the pore solution. If this KOH solution was replaced after 300 days by water, the expansion speeded up and approached the value it would have reached had it been in water all the time. In a more concentrated KOH solution, expansion was negligible. During storage in water, much of the alkali cation content was leached out, the charge being balanced mainly by loss of hydroxyl.

The authors explained these results by the fact that alkali inhibits the formation of ettringite during storage, the sulfate tending to remain in the C-S-H, monosulfate, and pore solution. During storage in water, the fall in the pH of the pore solution caused by leaching favours loss of sulfate from the C-S-H and the consequent replacement of monosulfate by ettringite. Leaching also occurs, though to a lesser extent, in near saturated air of fluctuating relative humidity. If the storage solution contains alkali hydroxide, leaching is reduced to an extent that increases with the concentration. An increased rate of leaching could partly or wholly explain observations that small or thin specimens expand faster than larger ones.

Brown and Bothe [34] pointed out that ASR lowers the pH of the pore solution. They considered that this would favour ettringite formation, mainly because of the increase in Ca^{2+} concentration resulting from the equilibrium with $Ca(OH)_2$.

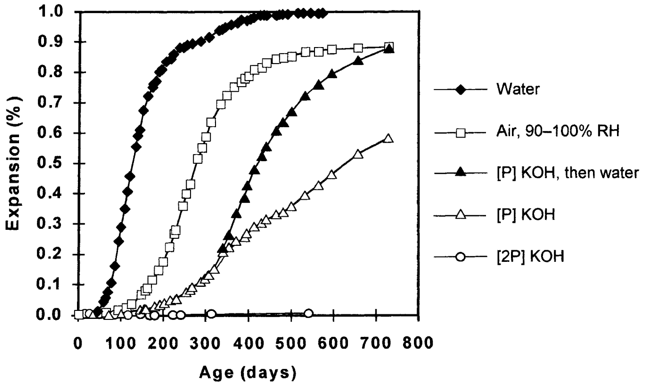


Fig. 6. Expansions of mortars cured for 12 h at 90°C and subsequently stored at ordinary temperature in various media. [P] KOH = simulated pore solution (460 mmol/l KOH); [2P] KOH = 920 mmol/l KOH. Adapted from Famy [18].

16. Effects of KOH or K_2SO_4 in the initial mix

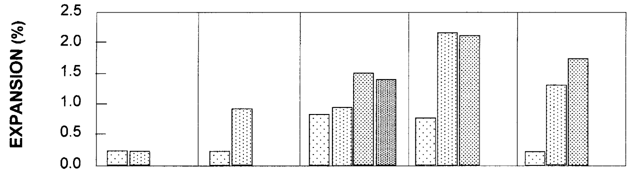
An early study indicated that expansion was likely to increase with the alkali content of the cement [45], but later work on a wide range of cements showed a correlation coefficient with equivalent Na_2O that decreased with age from +.63 at 100 days to only +.35 at 800 days [59]. The cements considered in these studies differed not only in alkali contents but also in many other variables. More reliable conclusions can probably be obtained by comparing cements in which, as far as possible, the only variations are in alkali content.

Fig. 7 gives data for groups of cements within which the only differences arise from additions of an alkali hydroxide or substitution of part of the gypsum by an alkali sulfate. As Kelham [57] noted, K_2SO_4 has the same effect as KOH, provided that in the latter case additional calcium sulfate is present so that both the K_2O and the SO_3 contents are the same. The vertical lines separate data for a given clinker and a given SO_3 content, and within each of these groups, the data are for alkali contents that increase from left to right. For cements high in SO_3, expansion is favoured by high alkali contents, but in the case where the cement has a low SO_3 cement, alkali has no significant effect.

Two considerations indicate that any effect produced by alkali in the initial mix must be due to something happening before the end of the heat treatment. One is that the effect, if any, is the opposite of that produced by alkali present during storage. The other is that under the conditions to which the data relate, alkali present in the initial mix was lost by leaching during storage.

At least two mechanisms could explain the observations. The first is based on those of Wieker and Herr [45] and Glasser et al. [35], modified to take account of incorporation of sulfate in the C-S-H. It could apply only in cases where, at the lower alkali content considered, ettringite is present at the end of the heat treatment. This occurs if the SO_3 content is above the pessimum (Fig. 5). Under any conditions, high pH favours the presence of monosulfate rather than ettringite, with relatively high contents of sulfate in the C-S-H and pore solution. If this situation exists during storage, it inhibits expansion, as was shown in Section 15. If it occurs during the heat treatment, the lowered content of ettringite increases the amount that can form during storage and thus also the possibility of increased expansion.

The second mechanism is based on the fact that increased alkali content, especially if combined with high SO_3 content, tends to increase the rate of alite hydration at early ages. As with other effects that increase hydration at early ages, discussed in Section 13, this could increase the



Clinker	F	F	C	A	C
SO_3	2.9	3.9	4.2	5.1	5.3
Na_2O_E	0.4 1.2	0.4 1.2	0.38 0.78 0.56 1.18	0.58 1.23 1.20	0.38 1.23 1.18
Addition*	None KOH	None K_2SO_4	None KOH KOH KOH	None K_2SO_4 KOH	None KOH K_2SO_4
Reference	Famy [18]		Kelham [57]		

* In addition to calcium sulfate

Fig. 7. Effects on expansion from DEF of additions of KOH or K_2SO_4 to the initial mix. The vertical divisions delineate groups of mortars made with the same clinker and the same content of total SO_3, and within each group, the content of equivalent Na_2O ($Na_2O+0.66K_2O$) increases from left to right.

expansion produced by the formation of a given amount of ettringite during storage.

These mechanisms are not mutually exclusive. The existing data are inadequate to establish their relative importance, and further work is required.

17. Conclusions

The studies reviewed in this paper show that temperature is a critical factor in relation to DEF. Expansion from this cause does not occur if the temperature within the mortar or concrete has not exceeded ~70°C. The formation of ettringite after the heat treatment does not necessarily produce expansion. The studies also indicate the need to bear in mind the following points in relation to published and future work.

- The observations emphasize the need for caution in extrapolating from laboratory tests to field conditions. In the present case, the effects of leaching, or absence of it, and also of ASR, are very important. Conversely, one must probably be even more cautious in trying to establish basic chemistry from field evidence, because this rarely if ever presents all the necessary facts and field situations are generally more complicated than at first appears.
- The traditional method of studying expansion, in which bars of mortar or concrete made with many different cements are placed in the same large tank, is unsound. Each sample should be placed in an individual container and not only the expansion but also the solution composition and anything else relevant should be monitored. It is also necessary when setting up the experiment to consider such things as whether or not to exclude CO_2, or to maintain the solution composition constant and if so at what values, and whether to include specimens of varying shapes and sizes.
- It is unprofitable to work on a range of cements, varying in many parameters, and to analyse the data by some such statistical technique as regression. Although this approach has yielded some useful results, those relating to the effects of alkali yielded no clear picture. The reasons for this are apparent from the results summarised in this paper. It is essential, in so far as this is possible, to study the effects of varying one variable while holding all others constant, as has now been done in the case of alkali.
- It is equally unwise to generalise from the results of studies on a narrow range of cements. Many different parameters, some of which are not readily quantifiable, influence expansion, and the effects of changes in one variable may depend on the values of the others. It is necessary to study the effects of one variable at a time, but such studies must be made on a wide range of cements. The approach outlined in this and the preceding paragraph entails a great deal of work but may be the only way by which reliable conclusions can be obtained.

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