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The Role of Sulfate Mineralogy and Cure Temperature in Delayed Ettringite Formation

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Abstract

Warm-cured cement pastes tend to become expansive during service at normal ambient temperatures. Evidence that delayed ettringite formation is responsible is critically reviewed and it is concluded that ettringite is partially or completely destabilised during thermal cure. These features are corroborated and quantified by thermodynamic calculations. Reformation of ettringite at ambient temperature has potential for expansion but other associated reactions could also contribute. The relevant chemical and mineralogical balances are reviewed. Some tentative suggestions are given to avoid or minimise delayed ettringite formation but it is emphasised that further focused research is required to quantify the causes of expansion and formulate suitable protocols to avoid dimensional instability. © 1996 Elsevier Science Limited.

INTRODUCTION

Ettringite is a normal and apparently innocuous constituent of hydrated Portland cement. Indeed, the average content of ettringite in modern Portland cements may have increased in recent decades, as more sulfate is added in order to control set times of clinkers high in alite and to improve early strengths.

Calcium sulfoaluminate additives are also widely used to enhance the early-age ettringite content. Used correctly, the expansive tendency of the ettringite thus formed counteracts the normal contraction of fresh cement paste as autogenous shrinkage occurs. Moreover, ettringite formation may make a positive contribution to early strength.

Even major increases in ettringite contents are not necessarily deleterious. Thus, commercial belite–calcium sulfoaluminate cements, containing 8–9% SO_3, are dimensionally stable when formulated as pastes, mortars and concretes. These cements, widely used in China, have been characterized[1] and their hydration products described.[2] Yan and Odler[3] report formulation data for other ranges of strong, dimensionally stable, ettringite-rich cements. Although in some minds the terms *ettringite* and *expansive* are synonymous, these examples show that this association is not necessarily correct.

On the other hand, there is no doubt that under some circumstances, yet to be defined, ettringite formation can be expansive. Mather[4] measured the restrained pressure generated from ettringite-forming reactants. The mechanical pressures thus generated exceeded 350 MPa, much greater than the strengths of well-made, well-cured concrete.

Since ettringite formation is, of itself, not necessarily expansive, the focus of research has — correctly — been directed towards late ettringite formation. In this context, *late* refers to ettringite which develops in a cement matrix subsequent to its initial set and hardening. The potential for expansion is most likely to be apparent in this period. One well-known cause of delayed ettringite formation resulting in expansion is caused by uptake of sulfate from external sources, e.g. by sulfate-rich water reacting with cement. In this instance, the cement furnishes two of the components necessary to form ettringite — Ca and Al — while the other

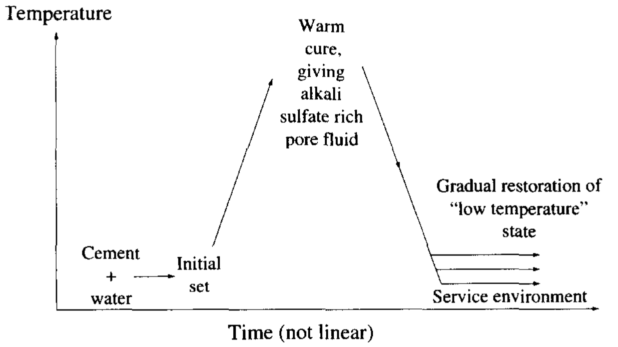

Fig. 1. Thermal regimes in warm-cured cement concretes.

two, SO_4^2 and H_2O, are furnished from external sources. However, this is not the focus of the present contribution, which instead deals with isochemical formation of ettringite. Isochemical ettringite is that which is formed when the system bulk composition remains constant but where spontaneous mineralogical changes nevertheless result in more ettringite being formed. These spontaneous changes may arise as a consequence of thermal cycling. Figure 1 shows a typical cycle.

MODELLING STUDIES

The chemistry and mineralogy of ettringite formation were reviewed by Damidot and Glasser.[5–7] They assembled thermodynamic data for the relevant solids and calculated phase equilibria in the $CaO–Al_2O_3–SO_3–H_2O$ system, initially for 25°C. Since extensive experimental studies have been made of this system, it was possible to compare calculated and experimental data at many points. Given the uncertainties in experimental studies (relatively few data points, uncertainty about the attainment of equilibrium, etc.) as well as uncertainties in calculation (mainly limited by the accuracy of the underlying data) very good agreement between data sets was obtained. However, a very significant advantage of computer-based schemes is that calculations can be done for any specific compositions and temperatures within the envelope of the database. On the other hand, the interpretation of experimental data — usually presented in tabular form or as complex phase diagrams, in which three (or more) dimensions are compressed into two — is often imprecise. Experimental studies, it will be recalled, are typically conducted only on selected isopleths and isotherms and extrapolation between data sets tends to be a judgmental process.

The modelling studies described above were extended to temperatures other than 25°C and also, to alkali-containing systems. Calculations were made up to 85°C using sodium as the model alkali.

A frequently-raised objection to computational schemes is that concentrations have increasingly to be replaced by activities. The alkali of cement pastes concentrates in the aqueous phase (in set cement, the aqueous phase comprises the pore fluid), with the result that its mean ionic strength increases with increasing alkali concentration: under these conditions activity corrections are needed. The problem need not be approached by computation. For example, Taylor[8] gives semi-empirical formulae with which to calculate alkali balances. However, computational methods have also advanced and the necessary corrections for activities can be achieved by using either the Pitzer approach, or by the extended Debye–Hückel treatments, both of which gave satisfactory results at least up to ≈1M total alkali, judging by comparison between calculated and experimental data. Thus, thermodynamic modelling is a flexible and versatile technique with which to solve specific problems concerning chemical and mineralogical balances.

Höglund,[9] was, to the writer's knowledge, the first to make a preliminary approach to delayed ettringite formation by means of calculation. He made an analysis of the reaction between cement and sulfate-containing ground water, but also performed some isochemical calculations, comparing ambient with elevated temperatures. Figure 2 shows the basis of his calculations. He found that the minimum pore fluid sulfate content necessary to stabilize ettringite was very dependent on temperature, noting that '...above 50°C, ettringite is not formed at sulphate concentrations up to 5×10^{-4} mol per litre (sulfate). At a temperature of 5°C, ettringite is formed already at a sulphate concentration of 2×10^{-7} mol per litre'. The results do not mean that ettringite will inevitably form at the stated concentrations — the solubility data are specifically for aqueous solutions which coexist also with solid AFm and $Ca(OH)_2$ — or that if ettringite does form, a significant quantity will necessarily crystallise. Nevertheless the calculations were performed on an assemblage

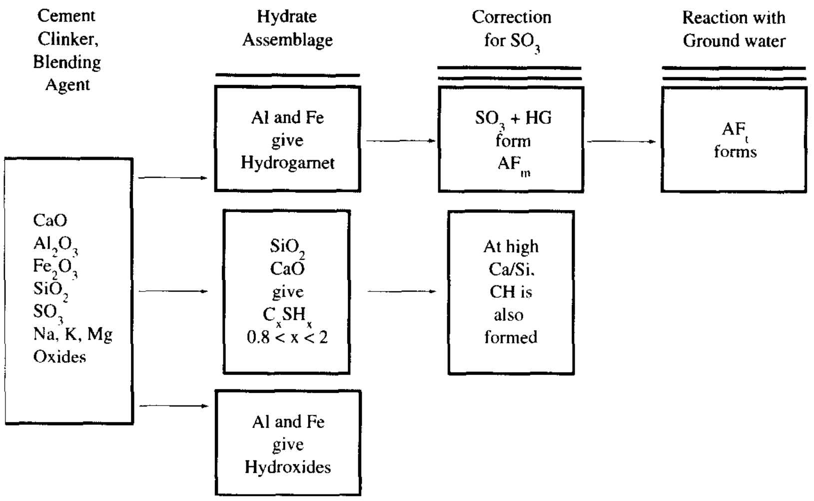

Fig. 2. Hierarchy of hydration and reaction, after Höglund.[9]

which occurs in real cements and the trend for ettringite solubility to increase rapidly with rising temperature is a noteworthy conclusion of this study.

Damidot and Glasser[5–7] reviewed the available experimental data, mainly those of Jones[10,11] and d'Ans and Eick.[12] Calculation using the PHREEQ code reproduced essentially the same features as were found experimentally although previous experimental studies of the influence of sodium on ettringite stability and solubilities were somewhat limited in scope owing to the complexity of the system. Comparison of existing data with a limited number of new experimental determinations and the results of calculations was made: agreement between experimental and calculated data was good at low ionic strengths but less so at higher strengths. The minimum solubility of ettringite coexisting with $Ca(OH)_2$ and C_3AH_6 at 25°C was calculated to give a pore fluid 0.034 mM in sulfate at 25°C. Interpolation of Höglund's calculations, presented in graphical form, gives a comparable value. Both sets of calculations confirm the experimental observations that as the alkali contents of cement pore fluids increase, ettringite solubility also increases.

Temperature plays a very important role in controlling phase stability and solubility amongst the sulfate phases. Ettringite itself remains stable up to ≈ 100°C, that is, throughout the normal range of warm-curing conditions. Nevertheless, its increasing solubility with rising temperature may result in its disappearance, or near disappearance, from many warm-cured pastes at temperatures below 100°C. Note that the disappearance of ettringite from a selected composition does not imply that it is unstable in the absolute thermodynamic sense, i.e. that it must disappear from all compositions.

To determine the extent to which the components of ettringite dissolve and to perform calculations relevant to the secondary ettringite problem, some boundary conditions need to be fixed. Table 1 presents relevant calculated solubility data, assuming that $Ca(OH)_2$ and C_3AH_6 are present and that both coexist with ettringite. If calcium monosulfoaluminate is instead substituted for C_3AH_6, the 25°C values do not change significantly ($\pm 10\%$). This arises because calcium monosulfoaluminate becomes a stable phase above 40°C and is therefore only slightly metastable with respect to the set of solid decomposition products used in the 25°C calculation; calculations made for higher temperature do assume the presence of AFm. Of course the amounts of phases are sensitive to mass balances and I return to this point subsequently.

At 50° and especially at 85°C, the soluble sulfate component of the pore fluid increases rapidly, even more so as the alkali concentration increases. Calcium solubilities, on the other hand, are only slightly affected: Al is somewhat solubilized by increasing alkali contents as well as by temperature but overall, the solubility of Al relative to that of SO_4 remains low. For example, at 85°C with 500 mM Na dissolved in the pore fluid, the aqueous molar ratios of SO_4:Ca:Al in the pore fluid are calculated to be approximately 90:6:1. These ratios are far removed from those of ettringite, indicating the incongruency of dissolution.

Table 1. Calculated solubilities of ettringite in phase mixtures (mM/l)

A. Coexistence of the phases: AFt, $Ca(OH)_2$ and C_3AH_6			
25° [Na] =	SO_4	Ca	Al
0	0·015	22·0	0·010
250	0·384	1·98	0·060
500	1·98	0·99	0·122
1000	11·22	0·44	0·189
B. Coexistence of the phases AFt, $Ca(OH)_2$ and AFm			
50°C [Na] =	SO_4	Ca	Al
0	0·042	16·0	0·042
250	17·94	1·35	0·103
500	66·93	0·841	0·155
1000	222	0·547	0·199
85°C [Na] =	SO_4	Ca	Al
0	0·41	11·33	0·016
250	76·7	2·48	0·283
500	184	2·06	0·354
1000	421	1·70	0·377

The practical significance is that phase-pure ettringite, which dissolves congruently at 20°C (or nearly so) becomes increasingly soluble, but incongruently soluble, in the pore fluid of warm cured cements. Sulfate is the most soluble of its components and this leads to a redistribution of the other components, mainly amongst solids and to a lesser extent aqueous phase, with the result that pore fluid is likely to increase in amount as water is liberated and, also, to store much of the sulfate of a typical OPC system. Conversely, as the pore fluid cools, its potential for reforming ettringite by direct precipitation from the aqueous phase is limited by the relatively low solubilities of Ca and Al. Nevertheless, its soluble sulfate must decrease: in order to reform ettringite, sulfate in the pore fluid must react with cement solids which contain the necessary Ca and Al. Water may also need to migrate to these sites.

The delayed ettringite which reforms as the temperature returns to ambient is, of course, the theme of this paper. Glasser *et al.*[13] calculated the potential for delayed ettringite formation using a mass balance scheme based on the ability of the system to store soluble sulfate during the high temperature cure as is shown in Fig. 1. It was concluded that during warm cure the storage capacity of pore fluid, especially if alkalis were also present, was sufficient to dissolve enough sulfate to achieve a significant increase in the molar volume of solids upon restoration of the lower temperature equilibrium. Analysis disclosed that the choice of lower temperature, 0–25°C, was not nearly as crucial to the overall solid volume change as was the upper temperature. Calculations of molar volume changes, undertaken for a number of representative clinkers, predicted a pessimum SO_3 content: that is, for each clinker, the expansion potential was predicted to pass through a maximum at a particular SO_3 content.

SULFATE IN THE PORE FLUIDS OF WARM-CURED CEMENTS

As a test of these calculations, four commercial cements were subjected to different cure regimes. These were cast as cylinders to permit pore fluid expression. One data set, from samples set and cured at a constant 20°C, was intended as a control. Other cylinders were given brief (6–24 h) cure at elevated temperatures (55–100°C) as soon as practicable after demoulding. The pore fluid compositions were followed, commencing a few days after the conclusion of warm cure and thereafter for up to ≈180 days at 20°C. All four cements had similar alkali contents, so the variation of pore fluid alkali contents was not large.

Interpretation of the data is incomplete but it was apparent that despite precautions against drying out, a few cylinders lost water, as shown by post-cure measurements of their evaporable water contents. Excluding the suspect samples, the cement pore fluid compositions divide into four groups with respect to their sulfate contents. The first group is representative of controls continuously maintained at 20°C and had pore fluid SO_4^{2-} contents which remained essentially constant, in the range 8–15 mM. The other data sets could be classified according to pore fluid sulfate contents into one or other of three groups. One group had pore fluid sulfate contents which returned within 2–3 days to post-warm cure values, comparable to those of controls (8–15 mM sulfate). A second group of pore fluids remained anomalously high in sulfate, 15–50 mM, and moreover this high concentration persisted at least up to 120–180 days post warm cure, Finally, a third group of samples had high sulfate contents in the immediate post-warm cure stage, 50–100 mM, but which decreased slowly over the duration of observations, up to ≈160 days. If, as appears likely, the return to 'normal' pore fluid sulfate contents results from abstraction of pore fluid sulfate to form ettringite, the rate at which secondary ettringite forms must vary markedly from one cement to another.

DISCUSSION

Warm curing of Portland cement compositions may occur as an indirect consequence of self-heating in large masses or more directly, when used to accelerate curing. However, warm curing may induce dimensional instability and it is important to define an envelope of acceptable cure conditions which avoid problems. A general explanation for the expansion seems to be reasonably well established, Scrivener and Taylor[14] have examined the microstructures of pastes which have undergone delayed ettringite expansion and observed that ettringite crystallized in pores within the paste in the post warm-cure phase. But they held that this recrystallisation did not of itself cause distress and could not be the cause of expansion, which they instead attributed to expansion of the paste.

Table 2. Distribution of sulfate in hydrated pastes

Major sites	
AFt	How close is composition to theoretical? Does significant substitution of silicate, carbonate and hydroxide for SO_4 affect composition and stability?
AFm	Does significant substitution of OH^- for SO_4^{2-} occur and is the extent of substitution temperature dependent?
Minor sites	
C–S–H	Is sulfate in C–S–H a real substitutent or is it occluded as AFm, etc.? How does temperaure affect substitution and occlusion?

Glasser *et al.*[13] suggested that paste expansion arises as a consequence of sulfate redistribution. They noted that pore fluid present at high temperature cure should extract and concentrate much of the alkali present in cement and that soluble alkalis, together with temperature, enabled much of the total sulfate originally present in the clinker and hydrate solids, to dissolve in the pore fluid. Upon cooling to ambient, ettringite reformed partly by sulfate diffusion into pores, giving rise to ettringite precipitation where pore fluid met solids. They accepted Scrivener and Taylor's[14] explanation that ettringite precipitated in pores was innocuous and suggested that the sulfate also diffused into denser regions of the paste where, upon contacting sources of Ca and Al, ettringite precipitated. The latter mechanism was, in their view, the principal cause of expansion: formation of low density ettringite within relatively dense, pore-free regions of the paste.

Recent unpublished studies of real cements described here show that this overall explanation is probably right but that the detailed process of ettringite-induced expansion is more complex than was at first supposed. Table 2 highlights some of these problems which relate to sulfate distribution. The calculations tend to use ideal formulae but both AFt and AFm phases may depart significantly from their ideal compositions. Reports of sulfate incorporation in C–S–H neglected in the calculations, are especially of concern. It is likely that some of the sulfate found in C–S–H by microanalysis is, in fact, held in the form of occluded AFm. Nevertheless Odler[15] has found significant sulfate to be sorbed by C–S–H. These observations on sulfate balances are based on cements cured at ≈20°C. During warm cure, when much C–S–H is formed at elevated temperatures, the extent of sulfate inclusion and its inclusion mechanisms — structural incorporation or occlusion, or both — are not known. These sulfate balances could affect the amount of ettringite formed as a consequence of a given thermal cycle. There is also direct evidence that different cements behave differently with respect to their post warm-cure chemistries. Thus, in the post warm-cure phase, sulfate concentrations are, as predicted, found to decrease but not necessarily to the expected steady-state levels (8–16 mM, depending on alkali content) in 6 months. One possibility consistent with persistently higher sulfate concentrations is for anhydrite and/or gypsum to precipitate during warm cure, leaving it to sustain high pore fluid sulfate solubilities at ambient. Eventually, this postulated sulfate should dissolve, react with Al and reprecipitate as ettringite, AFm, or both. However, this theory remains unproven and a search for precipitated calcium sulfate in fresh, warm-cured product is underway.

Meantime, further analysis of the mechanism discloses several other deficiencies in our understanding of the problem: see Table 2.

What content of unreacted clinker phases remains at the end of the warm cure cycle? Any residual clinker will presumably hydrate eventually. Normally, the process of continued hydration would not be expansive. But warm cure may, in some unanticipated way, change the nature of the diffusion barriers inhibiting migration of water to residual clinker such that its continued hydration becomes expansive.

Does warm cure alter the AFm phase such that its readjustment to ambient is expansive? Scrivener and Taylor[14] note the apparently low hydration state of the AFm produced in warm cures. Presumably rehydration will eventually occur in moist environments. This process, occurring within an already hardened gel, may be expansive. In this hypothesis, ettringite would appear to be blamed unfairly for causing expansion; the return of AFm to a more normal hydration state might instead be responsible.

The sulfate content of C–S–H gel is unknown. Analysis of normal C–S–H reveals sulfate as a constituent, but is this sulfate present as an occluded second phase or phases, e.g. AFm, or AFt or mixtures thereof? Or is it genuinely incorporated into the ill-defined C–S–H structure as Odler[15] found? If it is genuinely incorporated, what is the temperature dependence of sulfate incorporation and how rapidly reversible is the process of sulphate sorption and desorption? Answers to these questions would help define the role of C–S–H as a potential host for exchange reactions involving sulfate.

Can ettringite precursor exist in amorphous form and if so, is its subsequent conversion to crystalline ettringite expansive? The theories expounded by Mehta[16] about 'amorphous ettringite' seem to have been overlooked. In this hypothesis, ettringite might become amorphised by brief high temperature cure, with loss of structural water, but subsequently uptake of water by imbibition in amorphous material, or by recrystallisation at ≈20°C, or by some combination of these processes, could result in expansion.

Some combinations of the above theories may be operative. It should be recalled in this context that we can often predict with a fair degree of accuracy the chemical and mineralogical response of cements to changing temperature but that the physical consequences, e.g. the quantitative correlation between the dimensional change resulting from a particular mineralogical reaction or reactions is more difficult to predict.

What guidance can be given? At present, the best guidance would appear to be threefold. Firstly, limit the maximum alkali content of cement. This can be done by using low alkali cement but more subtle variations might be acceptable. For example, it might be acceptable to use a cement of higher alkali content provided the alkali were to be released slowly, in the postwarm cure stage. Secondly, the lowest practicable warm cure temperature should be used. Finally, limits could be placed on one of the other components in cement which could potentially form ettringite. Since it is impractical to limit calcium in a Portland cement, any additional chemical limits must fall on alumina, or on sulfate, or both. In this context, it should be recalled that Glasser *et al.*[13] have predicted that for expansion based on ettringite reformation, a pessimum SO_3 content existed for each clinker and for the peak temperature of each thermal cycle. The consequence of limiting the water content, as occurs in some high strength formulations, might be considered.

In conclusion, as research proceeds it should be possible to prove conclusively whether secondary ettringite is responsible for the observed expansion and, if so, to refine calculations of its expansive potential. Once this objective is attained, it should be possible to design thermal cure regimes for different Portland cement types which remain dimensionally stable during and after thermally-accelerated cures.

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