Cement and Concrete Composites 18 (1996) 205–215

0958-9465/96/$15.00

PII: S0958-9465(96)00017-0

Delayed Ettringite Formation — Processes and Problems

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(Received 12 January 1996)

Abstract

The scope of the delayed ettringite formation (DEF) problem is reviewed. Based on the experience of the writer and others, DEF is to be expected in both steam cured and non-steam cured concrete. The microstructural details appear identical. The common association with alkali–silica reactions is explored, and explained in terms of both prior cracking providing space for ettringite and in terms of the reduction in alkali hydroxide concentration in the pore solution attendant on ASR. The controversy concerning basic DEF mechanism between proponents of 'homogenous paste expansion' and 'crystal pressure' is explored. In the writer's opinion the microstructural evidence is not compatible with homogeneous expansion, but is a distinct consequence of crystal pressure developed by ettringite. The thermodynamic analysis that limits expansive pressure in terms of the degree of supersaturation that can be supported may be applicable to ettringite in air voids, but is inapplicable to ettringite in cracks. Fracture mechanics considerations predict local stress concentrations at the crack tips that are many times those that can be generated in open spaces. An apparent example of such effects in opening up space between mica lamellae in steam cured concrete by ettringite deposition is provided. © 1996 Elsevier Science Limited.

INTRODUCTION

It is apparent from the commissioning of this special issue of this journal and from the large number of papers on the subject in recent years that delayed ettringite formation (DEF) has become a topic of major significance to the international concrete technical community. However, there appears to be some lack of familiarity and perspective concerning certain DEF occurrences, and perhaps an insufficient appreciation of certain microstructural features. Also there are major differences of opinion with regard to the expansion mechanism or mechanisms that need to be aired and reconciled, if possible. The writer hopes that this paper will contribute to the clarification and resolution of these concerns. He thanks Professor Taylor, the Guest Editor of this issue, for the opportunity to present it.

SCOPE OF THE DEF PROBLEM

Cracking and deterioration of concrete associated with, and stemming primarily from, delayed ettringite formation is *not*, as some authors appear to suggest, a problem confined to steam cured concrete that has been subjected to curing at excessive temperatures. Field reports of damage associated with DEF in *non*-steam cured concrete, have been presented in the literature for some time; examples include Refs 1–4. In these particular reports the DEF-induced damage was associated with ASR, but this is not necessarily the case. The writer has personal experience of 'classical' DEF not associated with ASR occurring in non-steamed cured concretes.

DEF is a growing problem in practice; Hime[5] has indicated that his firm has a considerable number of field cases under current investigation in the United States, many of them being in non-steam cured concretes.

There is also a somewhat well founded suspicion that a wide range of highway pavements in the midwestern United States are undergoing deterioration at least partly induced by DEF; see for example Ref. 6.

Pioneering laboratory studies on heat-induced DEF were carried out by Heinz and Ludwig.[7] Cases of DEF in non-steam cured paste were studied by Odler and Gasser.[8]

Occurrences of DEF in steam cured concretes, especially in steam cured railway sleepers, have been repeatedly reported. In many of these occurrences, there is strong evidence of simultaneous, or at least concurrent ASR.[9–12] Interestingly, in the first major reported occurrence of railway sleeper DEF[13] ASR was not mentioned at all, but subsequently Shayan and Quick[14] showed conclusively that ASR was a major cause of the deterioration.

Diamond and Ong[15] have shown that high temperature steam curing itself can induce immediate ASR for some reactive aggregates, and that a further acceleration of ASR takes place in steam cured mortar after cooling and exposure to moist conditions. DEF is facilitated under these conditions, and it was found that by 6 months 50% more ettringite was present in the mortars undergoing ASR than in companion mortars steam cured in an identical fashion but lacking alkali reactive aggregate.

The effectiveness of prior ASR-induced cracking in stimulating the development of DEF has been noted by the present writer in forensic investigations, and similar conclusions have been reported by Oberholster *et al.*[10] and by Shayan and Quick[14] among others. Some evidence exists also that DEF may be facilitated by the prior cracking induced by freezing and thawing.[16]

In laboratory studies Fu *et al.*[17] re-affirmed the effectiveness of prior cracking in promoting DEF distress, and suggested that nucleation of delayed ettringite takes place preferentially in crack tip zones. The significance of this concept will be discussed later.

In addition to the promotion of DEF by ASR-induced cracking, various workers have raised the possibility of a chemical relationship between ASR and DEF. For example, Brown and Bothe[18] suggested that ettringite formation is retarded in the presence of pore solutions that have high concentrations of alkali hydroxide, such are produced with high alkali cements. Since ASR progressively reduces the alkali hydroxide concentration, they postulated that such reduction may trigger ettringite formation. In particular such an effect might occur at selected locations of more depressed alkali hydroxide concentrations, i.e. near alkali-reacting aggregates.

The relationship between chemical characteristics of the cement used and the development of DEF symptoms is of course not accidental. Specifically, many of the DEF occurrences reported in the literature, and others investigated by the writer, have been associated with cements of high sulfate content (4–5% SO_3). Not uncommonly these cements have high clinker sulfate contents as well.

In this connection a certain historical perspective is appropriate. In 1948, as a portion of the PCA long-time study of cement performance, Lerch and Ford[19] compiled analyses of representative American cements and of the clinkers from which they were produced. Clinker SO_3 contents at that time were typically less than 0.5% and total cement sulfate contents rarely exceeded 2%. In contrast, cements with total sulfate levels of 4–5%, incorporating clinker sulfate levels of 3% or more are not unknown in current practice. The potential for DEF is thus much greater than it was in the era of lower sulfate levels.

CHARACTERISTIC SYMPTOMS OF DEF

DEF is clearly an expansive process, marked by enlargement of the affected concrete members and by the development of gross cracking. As would be expected, the macroscopic crack pattern is controlled to a considerable extent by the geometry of the restraint system and by superincumbent loads. Cracking in railroad sleepers tends to be primarily parallel to the long axis, that is, parallel to the direction of the prestressing cables; it is normally most severe at the ends of the sleepers, i.e. in regions where prestress is not effective. DEF often induces loss of prestress across the sleeper, and after failure of the steel–concrete bond and cracking in the vicinity of the steel, water may penetrate and corrosion of the steel often occurs.

Concretes undergoing DEF suffer a general loss in dynamic elastic modulus, even if sampled in apparently sound areas between visible cracks. Measured values may drop to as low as 1.5 GPa, i.e. about one-third the normal modulus of unaffected concrete. In extreme cases, the concrete becomes crumbly and soft, and it is evident that the effectiveness of the cement paste binder has been destroyed.

MICROSTRUCTURAL FEATURES ASSOCIATED WITH DEF

The microstructural features characteristically associated with DEF have been described by many investigators, including the present writer and his colleagues.[20] These are best illustrated in backscatter SEM, although optical microscopy can also provide useful information. It should be stressed that in the writer's experience, identical microstructural features have been found in steam-curing induced DEF and in DEF where the concrete was not steam cured.

Figure 1 shows a low magnification SEM depicting the usual microscopic crack pattern developed in DEF. The concrete here was steam cured. Features include (a) a 'rim' or 'bond' crack surrounding many sand grains (and coarse aggregate pieces), forming an intrinsic part of an interconnected network crack pattern extending across the paste. The sizes of uncracked blocks of paste between the crack meshes vary; here they are roughly 300 μm.

Figure 2 shows the corresponding crack pattern (at slightly higher magnification) of a concrete undergoing DEF that had *not* been steam cured. The characteristics of the response are obviously identical in both cases.

In the usual occurrences of DEF the rim cracks and much of the lengths of paste crack are lined with ettringite oriented perpendicularly to the aggregate surface. Figure 3 shows a typical illustration, with the arrows pointing to the ettringite-filled rim crack. The blocky appearance of the ettringite in this mode of examination does not necessarily imply an aberrant crystal habit; examination at high magnification, especially in secondary mode SEM indicates that the individual crystals are mostly high aspect ratio elongated needle or rods, somewhat fused together.

The width of the rim crack in Fig. 3 is about 20 μm, which is fairly typical; such widths generally range up to 40 μm in most DEF examples examined by the writer. It should be noted that crack widths may vary from place to place around the perimeter of individual aggregate grains. It is also not uncommon to see only partial rim cracks. Aggregate grains are often

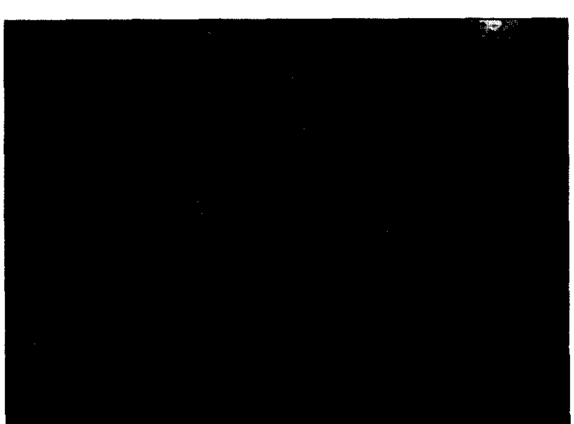

Fig. 1. Charactreristic crack pattern and other microstructural features in a DEF-affected steam cured concrete.

Fig. 2. Charactreristic crack pattern and other microstructural features in a DEF-affected non-steam cured concrete.

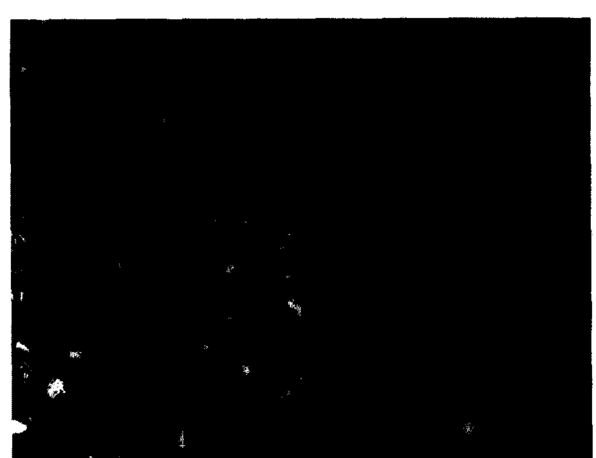

Fig. 3. Characteristic ettringite-filled rim crack around a coarse aggregate grain.

found where the rim crack extends only around part of the grain, the rest of the grain retaining close paste–aggregate contact.

The ettringite in the rim zone seen in Fig. 3 does not appear to quite fill the space, but it should be recalled that ettringite shrinks due to loss of water during the drying associated with sample preparation and with exposure to the high vacuum of the SEM. The blocky appearance of these deposits likely results from that shrinkage.

An EDS analysis was made at the spot in the ettringite filled rim crack indicated, just above the center of the micrograph. The analysis indicates that these ettringite crystals, like most such deposits, are almost stoichiometric ettringite. The specific analysis here was 52.6% CaO, 9.8% Al_2O_3 and 35.5% SO_3 on a dry basis. The dry-basis stoichiometric percentages are 49.6% CaO, 15.0% Al_2O_3 and 35.4% SO_3. Small amounts of SiO_2 and of K_2O (about 0.2% each) were also detected.

Figure 4 shows a similar ettringite deposit, this time filling a crack across the cement paste rather than a rim crack around an aggregate particle. Note that other crack branches are empty. The dark gray aggregate particle in the upper left region shows a partial perimeter rim crack filled with ettringite. Note that the right hand, generally vertical section of the perimeter shows clear paste–aggregate contact, with the bond intact.

Many workers have observed ettringite deposits in air voids, either as linings or sometimes as apparently complete fillings. The upper right hand corner of Fig. 2 contains an example of a lining; here several bright crystals of CH are present as well. Completely filled air voids, might presumably lose their effectiveness in preventing freezing damage in subsequent freezing and thawing exposure, but it is rare that all of the air voids are filled.

The existence of DEF-induced ettringite deposition in cracks and air voids is well appreciated by those concerned with the subject. What is not is the degree to which ettringite deposits *within* the space previously occupied by the cement paste. Ettringite deposits take various forms, but are commonly (but not always) morphologically detectable by the shrinkage and cracking features discussed earlier.

Figure 5 shows such a deposit, about 60 mm long, in the lower left corner. Interestingly, there are no filled rim cracks around the aggregate particles in this concrete.

Figure 6 shows a pair of smaller ettringite deposits, circled, on opposite sides of the very bright sand grain.

The deposits in Figs 5 and 6, while not spectacularly obvious, are reasonably noticeable to a careful observer. Ettringite may also be deposited within the paste as more or less single grain inclusions of the order of 5 mm or so that are not so easily detected. Figure 7 shows such individual single-grain ettringite inclusion in paste. Each of the hand-circled areas has been checked by EDS and its identity confirmed. It is usual to find that EDS analyses for such individual grains are highly deficient in sulfate as compared to normal ettringite composition, but they show reasonable Al_2O_3 contents for ettringite, typically 12–15%.

Fig. 4. Ettringite-filled paste crack and ettringite filled rim crack developed only part way around the periphery of a sand grain.

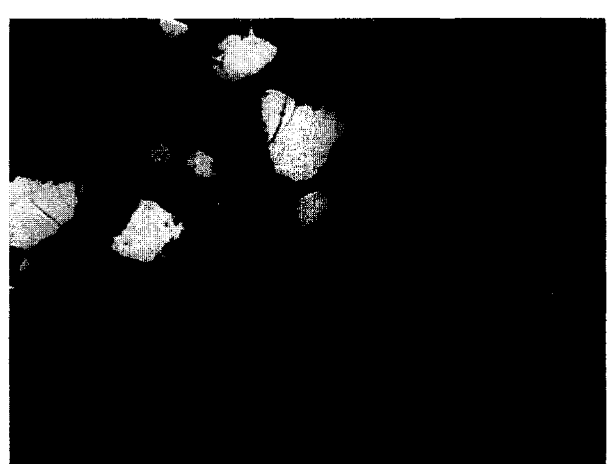

Fig. 5. Ettringite deposit within space formerly occupied by cement paste.

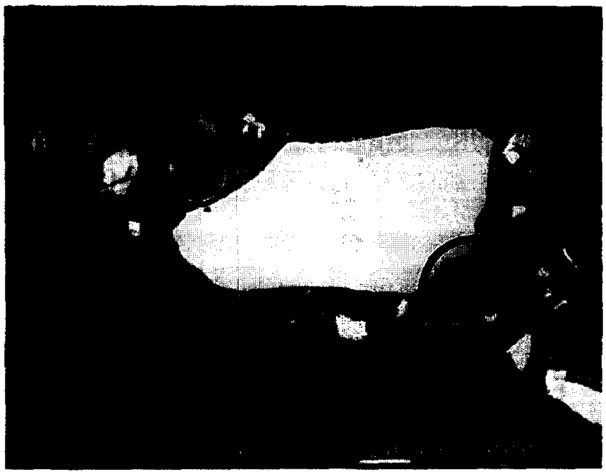

Fig. 6. Smaller but distinct ettringite deposits on opposite sides of a sand grain.

Ettringite (and monosulfate) are also thought to occur in minute crystals closely intermixed with and occupying space within individual inner product or 'hydrated phenograin' C–S–H deposits in ordinary cement pastes. Such closely intermixed minute crystals can apparently be found using TEM but are not detectable at the relatively low magnifications possible in backscatter SEM.

MECHANISMS OF DEF EXPANSION AND CRACKING

General considerations

It is widely appreciated that exposure to of concrete to temperatures of the order of 70°C for several hours in steam curing destroys the normal ettringite that has previously been deposited, and that after cooling and for some period of days or weeks thereafter no crystalline aluminosulfate hydrate component can be detected. Subsequently ettringite begins to form, and progressive deposition of ettringite is in some fashion the basis for DEF-induced distress. In non-steam cured concrete, because of excessive sulfate or slow availability of C_3A or some kinetic factor, ettringite may continue to form long after the time that ettringite formation is normally complete.

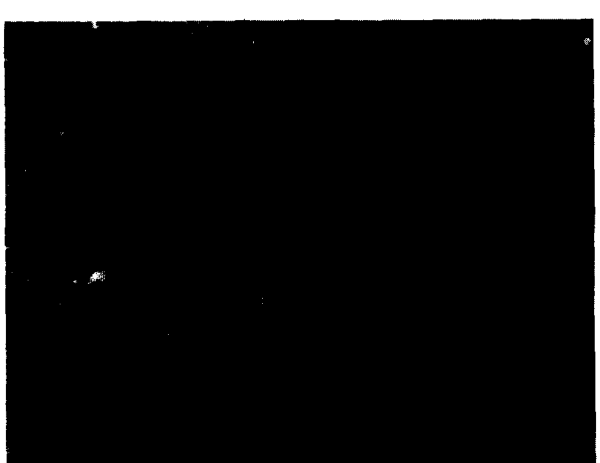

Fig. 7. Inconspicuous single ettringite crystals deposited in a nest within cement paste.

That the formation of large amounts of ettringite in cement pastes and concretes can be expected to induce expansion (and cracking, if unrestrained) has been known for many years. Successful and well-established commercial products such as shrinkage compensated cements and expansive cements that derive their expansive properties from such massive ettringite formation are well known.

The magnitude of these expansions can be very great. Odler and Gasser[8] measured linear paste expansions of more than 175% in one year for never-heated pastes made of a susceptible clinker plus excessive gypsum addition (15%). For 10% gypsum the expansion observed was more than 40%. For a 'normal' gypsum content (5%) the expansion was 0.9%, about the same as the expansion induced by steam curing and underwater storage in the studies reported by Lewis *et al.*[21] Odler and Gasser[8] monitored the ettringite content of their pastes, and unlike Lewis *et al.*[21] noted a general correlation between expansion and the amount of ettringite formed.

Nevertheless, in the case of DEF associated with steam curing, the specific mechanism or mechanisms at work are, to say the least, highly controversial. If anything, intensive investigations carried out over the last few years have heightened, rather than ameliorated the controversy.

On the one hand, highly respected investigators such as Scrivener and Taylor,[22] Johansen *et al.*[23] and others have maintained that the basis for the DEF effect in steam-cured concrete is a uniform and homogeneous paste expansion taking place sometime subsequent to the start of post steam curing exposure. According to the picture proposed by Johansen *et al.*[23] this postulated uniform paste expansion results in rim cracks opening up around aggregates (which do not expand). The rim cracks are subsequently filled in by recrystallized ettringite, but crystallization pressure exerted by the ettringite is not deemed to either initiate or widen the rim cracks. Rather, the recrystallized ettringite infilling is deemed to be mechanically passive, and is considered to play no part in the expansion and cracking of the concrete. Similarly, deposition of ettringite in paste cracks and in air voids and other open spaces are considered to be benign.

These authors generally do not refer to the various cases of distress produced after various delays in *non*-steam cured concretes as illustrations of DEF. In the present writer's experience non-steam concrete showing such distress can display symptoms and microstructures identical to those developed in steam cured concretes, and are also examples of 'DEF'.

In contrast to the 'homogeneous paste expansion' view, other investigators (including the present writer) contend that the expansion and cracking characteristic of DEF are the consequences of crystal pressure exerted by the growing ettringite crystals on their surroundings. Proponents of this view consider that ettringite deposited in rims surrounding aggregate grains, and ettringite deposited in cracks as contributing to the overall expansion, through crack development and propagation.

A critique of the 'homogeneous paste expansion' hypothesis

The mechanism of the postulated 'homogeneous expansion' following steam curing was originally described in rather vague terms by Johansen *et al.*,[23] who suggested that 'the delayed ettringite formation may involve *in situ* reactions between C_3A and C_4AF in homogeneously distributed unhydrated, or not completely hydrated, cement particles and calcium aluminate hydrates with SO_4^{2-} ions in the pore liquid and CSH.'

More recently, Scrivener and Taylor[22] indicated that the earliest ettringite found after steam curing and exposure to a wet environment appeared to be microcrystalline ettringite closely intermixed with inner product CSH; only later were ettringite crystals found that were distinguishable by SEM. The concept was hinted at that the development of closely-intermixed ettringite might in some way be responsible for the homogeneous expansion postulated by various authors.

This idea was further elucidated by Lewis *et al.*[21] They found that after heat treatment and subsequent exposure, but prior to expansion taking place, the C–S–H compositions analyzed by EDS suggested the presence of closely-mixed microcrystalline ettringite with the CSH; during expansion the compositions of the closely-mixed sulfoaluminate appeared to shift to lower sulfate contents. At the end of the expansion process the analyses of the C–S–H gel indicated that the gel was intermixed only with monosulfate, although ettringite not closely intermixed with C–S–H gel continued to exist. Subsequently Lewis and Scrivener[24] suggested that the change-over from closely intermixed ettringite to closely intermixed monosulfate liberated sulfate ions to the pore solution. They also suggested that the time of this change-over was important; the longer this process was postponed during the underwater storage, apparently the greater the ultimate expansion might be.

The idea that ettringite closely intermixed with the C–S–H is associated with homogeneous expansion was further developed by Glasser *et al.*[25] On the basis of investigations of thermodynamic stability at various temperatures in the $CaO–Al_2O_3–CaSO_4–Na_2O–H_2O$ system. They suggested the following sequence may occur in steam cured pastes: first, that pore solution sulfate contents increase substantially at steam curing temperatures (especially with high alkali cements), that the subsequent cooling leads to supersaturation of the pore fluid with respect to ettringite, and that this supersaturation results in massive ettringite precipitation. However, they viewed this ettringite precipitation as innocuous, and argued that the expansion itself derives from nucleation of ettringite *within the pre-existing monosulfate crystals* closely intermixed within inner product CSH.

Unfortunately, the sequence of events postulated by Glasser *et al.* seems to be in direct contradiction to the direct pore solution evidence of Ong.[26] Ong examined pore solutions expressed from steam cured cement pastes, and also determined the ettringite contents of those pastes by DSC at intervals. Determinations were made during the steam curing cycle itself (to 95°C), and subsequently during room temperature exposure at 100% RH.

In conflict with the predictions by Glasser *et al.*,[25] but in conformity with the experimental results of Brown and Bothe,[18] no evidence of monosulfate was detected by DSC at any stage.

Furthermore, the pore solution results did not appear to be as Glasser *et al.*[25] had predicted. It was clear that the pore solution sulfate concentrations did *not* increase substantially at steam curing temperatures. For a normal alkali cement, the maximum sulfate concentration that was reached during the steam curing cycle was only about 0.2N, and this was reached during the early ramping up of the heating cycle, *before* the destruction of the early ettringite. The pore solution sulfate content then actually dropped slightly (to 0.18N) as heating progressed. When the maximum temperature had been reached and all early ettringite had been destroyed, the sulfate concentration in the pore solution had actually dropped to about 0.13N. This concentration was maintained through the cooling part of the steam curing cycle and did not change appreciably for many weeks of room temperature exposure at 100% RH.

Parallel experiments were also carried out on a high alkali cement paste. In conformity with the predictions of Glasser *et al.*[25] and in line with normal expectations, the sulfate concentrations were indeed significantly higher at all stages. However, again, no increase in sulfate concentration was noted as the temperature reached the hot part of the steam curing cycle concomitant with the destruction of the ettringite.

Nor was there any evidence of 'massive precipitation of ettringite from solution' on cooling for either paste. No ettringite was detected for at least 28 days in either case, and the development of 'delayed' ettringite was just that — delayed. It occurred only slowly and progressively over months of exposure. Solution sulfate concentrations were stable for periods of months after cooling, while the slow precipitation of ettringite (and the consequent expansion) were occurring.

These results will be submitted for publication elsewhere.

An idea frequently cited in support of the homogeneous expansion following steam curing hypothesis is the observation reported by Johansen *et al.*[23] that for an experimental mortar the width of the gap around aggregate grains is proportional to the size of the grain. It appears to the writer that this is a considerable oversimplification. In the affected concretes he has examined, most rim cracks are between 10 and 30 mm across, and within this limited range do not appear to vary appreciably with the size of the aggregate.

Further to the point, the postulated homogeneous expansion of the paste appears to be quite incompatible with three obvious features of the microstructure of DEF-affected concretes. First, as pointed out specifically for Fig. 3, and visible also in Figs 1 and 2, for many aggregate grains the rim crack does not go all the way around the aggregate, but only part-way around. Can it be argued that paste expanded homogeneously on one side of the aggregate particle but not on the other?

Secondly, as is visible in most fields examined by the present writer, some aggregate particles in a given field of view have rim cracks; others simply do not have rim cracks at all. Can this be consistent with the effects of homogeneous paste expansion?

The third point is most important. Figure 8 is reproduced from Johansen *et al.*,[27] and is used by these authors to illustrate the basic concepts of the postulated effect of the homogeneous expansion, i.e. that 'peripheral gaps around the particles are created when the matrix is expanding relative to the particles.'

The present writer invites comparison of this figure with the actual crack pattern of Figs 1 and 2 of the present paper, or indeed with the crack pattern exhibited in the optical micrograph of DEF-affected concrete shown as Fig. 2 of the same Johansen *et al.* paper. In such micrographs it is seen that the rim cracks are in fact portions of a continuous crack network running across the paste, as well as around *some* aggregate grains, *partly* around others, and entirely missing from the perimeter of still others. In contrast, the pattern of cracking observed seems readily compatible with the idea

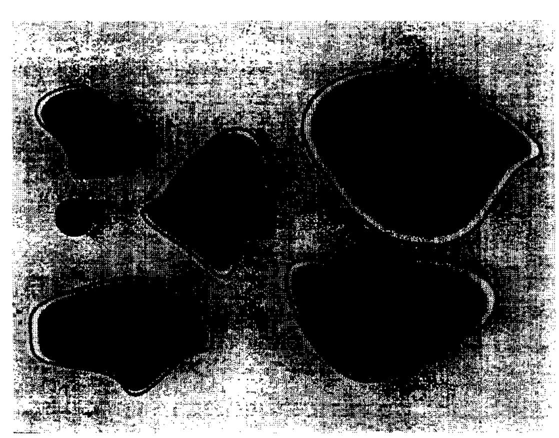

Fig. 8. Schematic illustration of concept of effect of homogeneous paste expansion, after Johansen *et al.*[27]

of inhomogeneous, locally varying expansion associated with ettringite deposition in weak areas or in pre-existing cracks — i.e. the 'crystal pressure' hypothesis.

The 'ettringite crystal pressure' hypothesis

Simply stated, this hypothesis maintains that expansion and cracking found in DEF is the obvious and necessary result of growth of macroscopic ettringite crystals in restricted spaces, the growing crystals exerting expansive stresses against the restraint offered by the pre-existing microstructural elements. Under this hypothesis most of the ettringite crystals depicted in the micrographs shown in this paper would be expected to participate in this process; the only obvious exception would be ettringite deposited as incomplete linings in partly filled air voids or other open spaces.

That expansive pressures of enormous magnitude can be developed by crystal growth is proven every day with the highly successful use of so called 'silent explosives'. These materials, produced as specialty products by various cement companies, depend on crystal pressure exerted by CaO hydrating to $Ca(OH)_2$. In practice holes are drilled within hard rock boulders or other masses that need to be broken up. Products containing free lime and water are used to fill the holes, and the holes are fitted with strong plugs. The 'silent explosive' then produces expansive stresses by crystal pressure sufficient to break up the rock mass, without the necessity of employing dynamite or other explosives.

Proponents of the homogeneous expansion hypothesis have tended to reject crystal pressure partly on the grounds of thermodynamic analysis. This usually takes the form of the well-known thermodynamic argument that the pressure that can be developed is limited by the degree of supersaturation with respect to the growing crystals, and it is maintained that the needed degree of supersaturation cannot be produced by the ettringite formed under the conditions existing in DEF.

The supersaturation argument has been addressed by several workers. Taylor[28] calculated that for a reasonable degree of supersaturation (2.4), and assuming isotropic behavior, the pressure that can be exerted is only 3 MPa. However, results of others, notably Ping and Beaudoin[29,30] and, very recently, Deng Min and Tang Mingshu[31] are not in accord with these calculations. Deng and Tang calculated that crystallization pressures of ettringite in portland cement paste at 1 day could reach levels in excess of 55MPa, certainly far more than is needed to generate the expansion and cracking observed in DEF.

However, the writer believes that thermodynamic calculations based on overall average pressures miss the point. Concrete is a quasi-brittle material. As such, the concepts of fracture mechanics apply. In much simplified form, fracture mechanics suggests that any tensile stress exerted near the tip of a crack is magnified by a stress intensity factor that depends on the length of the crack and by the geometry of the crack tip. A common formulation, found in most current undergraduate engineering materials texts, is given as eqn (1):

$$K_t = s_m/s_o = 2(a/r_t)^{1/2} \tag{1}$$

where

K_t is the stress concentration or stress amplification factor at the tip of the crack

s_m is the maximum stress, that is the stress exerted at the tip of the crack

s_o is the applied tensile stress

a is half the length of the crack, and

r_t is the radius of curvature of the crack tip.

In the analysis, the stress may result from external applied stresses or from pressures generated by crystals growing within the crack.

Cracks in concrete are normally very long with respect to the radius of curvature of the crack tip, which is typically very sharp; accordingly the stress concentration factor is extremely large. Thus, only modest thermodynamically calculated overall pressures developed by crystal growth within cracks are needed to translate to extremely large stresses at the crack tips. Progressive extension and widening of the cracks is thus a predictable consequence, even under modest degrees of supersaturation.

Johansen *et al.*[27] have raised an interesting point in opposition to the crystal pressure hypothesis. They called attention to the fact that cracks are not typically seen radiating out from air voids filled with ettringite, and noted that if crystal pressure were at play, such filled voids would behave like expanding particles; thus, cracks radiating from into the surrounding paste should be observed. In point of fact, the geometry of spherical voids is such the stress intensity factor developed for cracks does not operate. Accordingly, stresses generated against the surrounding paste are limited to thermodynamically calculated pressure, which depends on the supersaturation attained.

A much more sophisticated analysis incorporating both fracture mechanics and thermodynamic considerations was recently provided by Fu *et al.*[17] Based on free energy considerations, it was shown that ettringite nucleation will take place preferentially in cracks, a conclusion well supported by experience. More to the point, according to this analysis, nuclei should first form near the tips of the cracks, where the lowest free energy conditions exist. After nucleation the driving force of any continued supersaturation then results in the growth of these ettringite crystals and subsequent propagation and opening of the crack. The local expansive stresses at the crack tip clearly reflect a very large stress intensity factor.

One final graphic argument might be adduced from the writer's experience. He offers Fig. 9 as evidence that ettringite precipitation exerts expansive force and results in expansion. The micrograph was taken from a steam cured concrete in which mica constitutes a minor component of the aggregate. Layers of ettringite are seen to have been deposited between the lamellae of the mica, apparently forcing them apart and inducing obvious expansion in the direction normal to the layers. Examples similar to Fig. 9 have been seen in both steam cured and not steam cured concretes undergoing DEF.

Fig. 9. Illustration of ettringite deposits seemingly producing separation of mica lamellae by crystal pressure in a DEF-affected steam cured concrete.

CONCLUSIONS

The arguments elucidated have ranged over a variety of topics and approaches, indicating the complexity of the DEF problem. They may be summarized as follows:

Concretes undergoing DEF following steam curing, and concretes undergoing DEF associated with excess sulfate or other factors that were not steam cured seem to show similar crack patterns and microstructural features, despite the difference in history. The fact that in steam curing much or all of the early ettringite is destroyed and must be constituted anew does not appear to change the pattern of cracking and ettringite deposition that ensues.

Concepts that maintain that DEF following steam curing reflects a special 'homogeneous expansion' in the paste by virtue of which nonshrinking aggregates develop empty rim cracks proportional to their size, only later to be filled in by ettringite deposits, seem not to be reflected by close examination of real concretes. Rather than developing a system of isolated empty rim cracks, it appears that the rim cracks do not go all the way around some aggregate particles, and are entirely absent from others in the same field. Furthermore the writer's experience suggests that the claimed relationship of crack width with aggregate size may not hold generally.

The observed crack pattern is that of a network with component crack segments running partly along aggregate peripheries (rim cracks), but generally connecting through segments running through the cement paste (paste cracks). The pattern appears to reflect local and inhomogeneous crack propagation rather than general and homogeneous paste expansion.

The association of DEF with prior cracking induced by ASR, by freezing, or even by shrinkage is not accidental but may be fundamental to the DEF processes. While the overall stresses that can be thermodynamically calculated to result from ettringite precipitation are limited by the limited degree of supersaturation sustainable in the pore solution, free energy considerations appear to preferentially promote ettringite precipitation near crack tips. In any event stress intensity factors associated with fracture mechanics considerations should grossly magnify the mechanical effects of ettringite crystallizing in cracks.

The common association between ASR and

DEF may reflect chemical factors in addition to the crack-inducing effect of ASR. The reduction in alkali hydroxide concentration attendant on ASR may also serve to promote ettringite precipitation.

The practical consequences of DEF are more various and more complex that simple expansion. Loss of prestress in prestressed railway sleepers followed by debonding and subsequent corrosion are important factors in the DEF effects on sleepers. In any affected concrete the crack network induces a severe loss in dynamic elastic modulus, which has important structural implications. Filling up of fine air voids by ettringite may interfere with frost resistance.

In the last analysis, the spate of modern DEF problems stems from high contents of sulfate in many modern cements. These may involve high levels of intergound calcium sulfate, but in the writer's experience they may also reflect high (and often variable) clinker sulfate contents. In such cases, the need to add sufficient interground sulfate to assure normal setting behavior and strength gain thus can result in high total sulfate contents.

ACKNOWLEDGEMENTS

The writer is pleased to acknowledge the contributions of several former associates at Purdue University, including Shaode Ong, Yuting Wang, and David Bonen. The work was supported by the National Science Foundation Center for Advanced Cement Based Materials.

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