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The relevance of laboratory studies on delayed ettringite formation to DEF in field concretes

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Abstract

Many laboratory studies of delayed ettringite formation (DEF) have been conducted on thin mortar bar specimens, heat treated, and then immersed in water. Under these conditions, rapid diffusion of alkali hydroxide into the surrounding water occurs and necessarily reduces the alkali hydroxide concentration of the mortar pore solution. Results reported recently by Famy indicate that the DEF process is triggered as a consequence of such leaching. When it is prevented by immersion into alkali hydroxide solution instead of water DEF expansion is delayed or prevented entirely. Results reported by Zhang indicate that 51-mm mortar cubes behave differently than more leaching-susceptible mortar bars when exposed to the same wet environment. Mortars that show severe DEF as mortar bars remain almost free of DEF symptoms if they are stored as cubes, even after 900 days. Attention is called to the fact that DEF in concrete is found commonly in thick concrete members where the possibility of leaching is remote. For such concrete, the reduction in internal alkali hydroxide concentration that occurs with ASR can substitute for the effect of leaching. It is postulated that without effective reduction of alkali hydroxide concentration by one or the other process, DEF remains latent. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Laboratory studies of delayed ettringite formation (DEF) by Heinz and Ludwig [1] involved "model experiments" in which mortar bars previously exposed to high temperatures were immersed in water, and the consequent expansion was monitored. A large number of similar laboratory studies ensued, recent examples of which include those of Lawrence et al. [2], Kelham [3], Fu et al. [4], Scrivener and Lewis [5], and Yang et al. [6], among others.

These studies generally were carried out with a view toward defining the common chemical characteristics of DEF-susceptible cements, toward determining the effects of pre-curing time and of the temperature reached during the preliminary heat treatments, and especially, toward attempting to elucidate the mechanisms responsible for the DEF effects. The latter remain controversial.

In these studies, it was implicitly assumed that the DEF processes taking place under the experimental conditions imposed were sufficiently like those occurring in field concrete for the findings of the laboratory studies to be relevant to the field occurrences.

In most such DEF studies there has been little or no explicit recognition of the fact that pore solution components, especially alkali hydroxide, are inevitably diffused from the specimens into the surrounding water. This reduces the internal pH and perhaps the sulfate content of the specimens in an uncontrolled fashion.

The present writer has been concerned for some years with the effects of leaching on mortar bars, especially as applied to ASR studies. Several kinds of exposure have been tried, in which mortar bar specimens were not immersed in water, but instead were placed in moist environments maintained at 100% RH. In one method, the bars were suspended a few centimeters above a free water surface in flat "shoe-box" containers, the whole assemblage being maintained in a fog room maintained at constant temperature. While essentially 100% RH is in fact maintained, it was found that, due to local temperature fluctuations, condensation of water occurs more or less continuously on the upper surfaces of the specimens. The water thus condensed percolates through the bars, and over

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time removes a substantial portion of the alkali hydroxide, and other ions from the pore solutions of the specimens.

Data were obtained by Ong [7] for this mode of exposure of suspension over water of ASTM standard mortar bars $25 \times 25 \times 280$ mm in size. For mortar made with a low-alkali cement enhanced with KOH to a total alkali content of 1% $Na_2O_{equiv.}$, about 20% of the potassium was leached into the reservoir water by 1 month, and about 40% by 9 months, with the sodium ions being leached out even more rapidly. The OH^- content found in the reservoir water was essentially equivalent to the sum of the leached alkali ion contents, indicating that the alkali was leached out as alkali hydroxide. This kind of moist exposure is thus not free from the leaching effects produced by immersion of the specimens in water, although the rate of leaching is undoubtedly slower.

In subsequent studies, a different moist exposure procedure patterned after that described by Hooton [8] was used. The mortar bars were individually encapsulated in a heat-sealed plastic sleeve, each containing only a few milliliters of water, with the assemblage kept in a fog room. This method successfully ensured 100% RH exposure while almost completely eliminating leaching.

It seems to the writer that the relevance of laboratory DEF studies, especially of immersed samples, to DEF as it occurs in field concrete should not be taken for granted. Most of the reported field DEF occurrences are in structures of comparatively thick cross-sections, where the possibility of significant leaching of ions from the pore solution of the interior of the concrete is quite remote.

The present contribution was stimulated by certain laboratory results provided in two recent PhD theses, by Famy [9] and by Zhang [10] that contain portions that bear on this question. It should be indicated that neither author made a specific point of questioning the relevance of their laboratory results to field DEF behavior.

2. Pertinent experimental results reported by Famy [9]

Famy [9] studied the DEF responses of mortars prepared as relatively small, thin bars $16 \times 16 \times 160$ mm in size. After preliminary heat treatment at 90°C, the specimens were immersed in distilled water for up to 2 1/2 years. Under these conditions, her most DEF-susceptible mortar began rapid expansion in as little as 2 months. The expansion reached about 1% by about 300 days, and thereafter ceased. Famy also carried out trials with companion mortar bars that were not immersed, but rather were exposed above a free water surface in a manner similar to that previously described. With this exposure, the expansion of the specimens was considerably delayed, but eventually reached almost the same value as found for the immersed specimens.

Famy specifically measured the leaching of alkali ions from specimens exposed under both exposure conditions. Leaching was extremely rapid for the immersed specimens; after only 10 days they had lost 80% of their potassium and 60% of their sodium ion content. More than 95% of the potassium ion content was lost by 4 months. The alkali loss from the specimens suspended over water was less rapid, but eventually almost as complete; by 10 months, 85% of the potassium and 80% of the sodium ions were found to be leached out of the specimens.

Famy then carried out several perceptive experiments in which replicate specimens were immersed in KOH solutions rather than water, thus minimizing or preventing the leaching of K^+ ions. When immersed in KOH solution of the same K^+ ion concentration as that present in the pore solution of the mortar bars at 16 h, the expansion experienced was at least significantly delayed, and may have been prevented. Her “Mortar B,” which in water started to expand at about 2 months, showed no significant expansion in the KOH solution at the time of last recording (700 days). Her “Mortar D,” the fastest expanding mortar in water, exhibited some expansion in the KOH solution, but this expansion started much later and progressed much more slowly than in water. Substituting LiOH of equal OH^- ion concentration for the KOH had precisely the same expansion-inhibiting effect. Immersing “Mortar D” specimens in a very strong KOH solution (0.92 N) resulted in no expansion at all by 300 days, the latest measured time recorded in Famy’s thesis. The specimens have continued to be studied, and at last measurement have been immersed for 540 days with no expansion yet recorded [11].

Famy indicated that the content of ettringite developed in the mortars over time depended on the rate of alkali leaching into the storage solution. Immersion into storage solutions high in KOH delays the formation of ettringite “due to a slow leaching of potassium hydroxide from the pore solution, which will maintain high ettringite solubility.”

3. Pertinent experimental results reported by Zhang [10]

Zhang [10] carried out DEF experiments differing somewhat from those of Famy [9]. His specimens were of two kinds: ASTM standard $25 \times 25 \times 280$ mm mortar bars, thicker and larger than those used by Famy, and mortar cubes 51 mm on a side. Expansions were measured only on the bars, but observations were kept on the occurrence of cracking and other visible DEF symptoms on the cubes as well. All of the specimens were suspended over water rather than being immersed in water.

Under these conditions the DEF-induced expansions in susceptible mortar bars were generally less than those reported by Famy [9], and did not start until about 8 months had elapsed. The rates of expansion were slower as well, with many mortar bar specimens still expanding as late as 2 1/2 years.

Of particular concern in the present context are results observed by Zhang [10] for the mortar cubes, which, like the mortar bars, were suspended above a free water surface in a

100% RH environment. Actually, it was found that the level of the water in the containers used for the cubes gradually rose, and after some hundreds of days the bottoms of some of the cubes were found to be in contact with the water. Despite this contact with water, the cubes prepared from the same mortars that had cracked and expanded extensively starting at about 8 months as bars, mostly showed almost no indication of DEF-induced deterioration even after 2 1/2 years. One set showed some cracking along the bottom surface that had come into contact with water; the remainder showed only minimal cracks starting to develop along the bottom corners.

Thus, the extent of development of DEF symptoms depended on the configuration of the specimen, presumably as it influenced the leaching process. The cubes had a minimum section thickness twice that of the standard bars, and had much less area of surface exposed to leaching.

That such leaching is required for the development of DEF in laboratory studies is consistent with a variety of prior observations reported in the literature. For example, the data of Heinz and Ludwig [1] include, without comment, an extraordinary difference in the expansion characteristics of PZ 55 mortar bars, depending on specimen thickness. *Thin* mortar bars (10 × 40 × 160 mm) immersed in water expanded rapidly, starting at about 14 days, and reaching 0.8% expansion by 4 months. *Thick* mortar bars (40 × 40 × 160 mm) of the same mortar mix required 400 days to show the first signs of expansion, and expanded only minimally (0.2%) by the end of the experiment at 830 days. Obviously, the increase in minimum dimension by a factor of four would drastically increase the time required for leaching.

The question of long-delayed and minimal expansions for mortars of low water:cement ratios, low enough that the mortars would be only slowly permeable, is also relevant. Heinz and Ludwig [1] found that immersed w:c 0.4 bars showed only long-delayed and minimal expansion; similar bars of higher w:c (0.45, 0.5, and 0.7) all expanded much more rapidly, to similar levels of about 0.8%. Lawrence [12] reported similar findings in research undertaken at BCA. Immersed specimens of w:c ratio of 0.375 "were much less inclined to expand" than similar specimens of w:c ratio of 0.45, and "began to expand very slowly after a very long induction period." Such behavior is obviously consistent with the anticipated effect of reduced leaching of alkali and hydroxide ions out of the relatively impermeable specimens of low w:c ratio.

4. Mechanism of the leaching effect in triggering expansion

A number of workers, for example Brown and Bothe [13], have called attention to the relative difficulty of ettringite formation and retention in solid form in the presence of high concentrations of alkali hydroxide. It is obvious that the significant effect of leaching in its action as a precursor to DEF-induced expansion is the severe reduction in internal alkali hydroxide concentration, leading to the reduced pH condition favorable for the precipitation of ettringite. The reduced internal pH may also trigger the desorption of sulfate previously sorbed in the C-S-H gel, as indicated, for example, by Divet and Randriambololona [14]. Neither effect takes place if the alkali hydroxide, for whatever reason, does not leach out of the mortars.

5. Postulate: leaching as the "triggering effect" for the development of DEF symptoms in laboratory mortar bar experiments

On the basis of the evidence summarized above, the present writer postulates that in laboratory studies of DEF as described previously, leaching of alkali hydroxide from the pore solutions within the mortar specimens is *required* as a trigger for the sequence of responses that result in DEF-derived expansions and other symptoms of distress. Without the leaching, the development of DEF will be long delayed, reduced in magnitude, or prevented entirely. The importance of the specimen configuration, the storage conditions, and other factors that influence leaching is therefore manifest.

6. Relevance of laboratory mortar bar results to development of DEF in field concrete

DEF-induced damage has been reported for a variety of concrete structures in the field. Many reports (for example, Refs. [15–17]) exist of such damage in railway ties or sleepers. More scattered reports have described DEF symptoms in thick highway pavements [18], and in structures such as massive box-beams designed for concrete bridges [19]. Generally speaking, most such DEF-affected concrete structures or structural members are at least 200 mm in their smallest dimension. The possibility that such field structures could undergo leaching to the extent that appears to be necessary to develop DEF in laboratory mortar bars appears to be exceedingly remote.

One is thus faced with the conclusion that the usual type of laboratory DEF study using mortar bars immersed in water produces results that depend on an arbitrarily imposed condition (leaching) that is not normally found with field occurrences of DEF.

There is an obvious alternative to the leaching mechanism for the reduction in alkali hydroxide concentration of the pore solution. As pointed out specifically by Brown and Bothe [13], alkali silica reaction is the common process that reduces the alkali hydroxide concentration of the pore solution in bulk concrete. Carbonation, which almost universal, does so as well, but only near the surface.

The occurrence of ASR along with DEF in the field, documented in many papers (for example, Refs. [16,20,21]), is thus readily explainable. ASR can be seen as the functional field concrete equivalent to leaching in laboratory mortar bars, in that during ASR the alkali hydroxide concentration of the pore solution is reduced. In ASR, the alkali hydroxide is not physically removed, but it is sequestered within a separate ASR gel phase.

The lack of the necessity of leaching in cases where DEF is associated with ASR is eminently and conclusively exemplified in the observations of Meland et al. [22]. These authors examined cores taken from the crest of a dam in Norway, surely a perfect example of a massive structure not subject to leaching. They found massive deposits of ettringite, indicated as being due to DEF, in the vicinity of alkali-reacting aggregates.

The present writer thus postulates that in field concrete lacking either the leaching effect or the pH-lowering effect associated with ASR, the potential massive formation of ettringite that drives DEF-induced deterioration ordinarily remains latent. Conversely, ASR, if present, provides the pH-reducing effect necessary for the massive development of ettringite.

The implications of this formulation with respect to laboratory DEF research are obvious. Such things as mix design of the mortar, the dimensions of the immersed specimens, and the volume of water in which the specimens are immersed, all influence the relative rate of leaching, and thus the rate at which the DEF process is triggered. These experimental features are arbitrary and may be changed at will by the investigator. Furthermore, the leaching process does not produce an internal environment within the mortars that is identical to the internal environment of DEF-affected concrete in the field. Thus, the predictive value of the results of such experiments with respect to the relative field DEF susceptibility of concretes made from different cements or subjected to different pre-treatments in the laboratory may be open to question.

These considerations should be of concern to investigators, and especially to those charged with devising standards and specifications relating to DEF.

7. Conclusions

1. Evidence developed by others is cited to indicate that DEF-susceptible mortars exposed as conventional thin mortar bar specimens immersed in water undergo extensive leaching, resulting in rapid removal by leaching of alkali hydroxide from the pore solution. Such leaching is seen as a general prerequisite for the characteristic symptoms of DEF to develop in these specimens, assuming that the chemical characteristics and prior treatment are appropriate for DEF to occur. Conversely, similar mortars configured or exposed in such a way that leaching does not take place (or is only minimally possible) do not develop DEF symptoms or develop them only marginally and after very long delays.
2. An equivalent but not identical triggering effect can take place within field concrete structures if and when ASR occurs. ASR also acts to reduce internal alkali hydroxide concentration. For DEF-susceptible concretes in thick sections leaching is not operative, and it is postulated that DEF ordinarily remains latent unless this ASR-induced “equivalent” mechanism becomes operative.
3. In the common mode of laboratory DEF study of immersed specimens, mix design factors, specimen dimensions, and the volume of water in which the specimens are immersed jointly control the rate of leaching, and consequently influence the rate and extent of development of DEF symptoms. Since these parameters are the results of arbitrary choices by the investigator, conclusions drawn from laboratory studies where leaching triggers DEF may not be applicable to predictions of DEF susceptibility of field concretes.

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