

Delayed Ettringite Formation — A Concern for Precast Concrete?



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Mr. Hime joined Wiss, Janney, Elstner Associates, Inc., Northbrook, Illinois, in 1984. The Erlin, Hime Associates Division was created to give WJE added expertise in materials sciences. Mr. Hime, an expert in building materials behavior, has been active in the concrete industry for more than 44 years. He is the author of more than 50 publications relating to chemical analyses of cement systems, failure analyses, concrete properties, corrosion, and cement burns.

Internal sulfate attack on precast concrete products has been investigated by the author. The cause for these failures has been identified as delayed ettringite attack, a process whereby the normal formation of ettringite in plastic portland cement concrete is either delayed or is formed and then decomposed, only to destructively reform in the hardened concrete after months or years of exposure to water. Reasons for the apparent newness of the phenomenon, and methods for preventing it, are given on the basis of investigations of incidences during the past several years.

Durability failures of precast concrete products have generally been few. Most have been due to freeze-thaw damage or alkali-silica reaction. Because the causes of such failures have been thoroughly investigated and remedies have been discovered (air-entrainment, low-alkali cement, and nonreactive aggregates), distress due to these mechanisms is now rare.

Beginning in the early 1980s, a new distress mechanism was reported to have caused destructive cracking of concrete sleepers (railway ties) in Europe. This same mechanism is believed by the author to have not only caused distress to a specific group of ties in the United States, but also to other precast concrete products.

The mechanism was originally termed "secondary ettringite forma-

tion," but because that phrase has another meaning to most petrographers, the more definitive term "delayed ettringite formation," or simply DEF, was coined. DEF is the development of ettringite within the cement paste system of concrete *after* the concrete has hardened. The result is expansion, but a mechanism for it has not been agreed upon by experts. The end result is cracking of the concrete.

The ettringite in DEF should not be confused with either normal or secondary ettringite. The former is that which is produced by the normal hydration of portland cement and is developed before the concrete attains such rigidity as to be unable to accommodate expansive growth. The latter is generally that which occurs to portland cement concrete that has been so extensively exposed to water that



Fig. 1. Precast, prestressed railway tie evidencing DEF induced cracking after several years in service.



Fig. 2. Precast parking garage wall evidencing DEF induced cracking about 8 years after installation.

some of the ettringite has dissolved and harmlessly reprecipitated in air voids or on crack surfaces.

Although destructive development of ettringite in hardened concrete can also occur simply because of the presence of excessive amounts of sulfate (e.g., from gypsum in the aggregate or due to a gypsum or gypsum plaster addition to the mix), this internal sulfate attack will not be considered to be DEF by the author.

DEF was described in 1982 and 1987 by Heinz and Ludwig,^{1,2} and

since then has been so extensively investigated that reviews by Lawrence³ and Day⁴ have included dozens of references.

The general theory expressed by most investigators has been that DEF is caused by excessive heat curing, and thus decomposition of the ettringite (calcium sulfoaluminate hydrate, or $C_3A \cdot 3CaSO_4 \cdot 32H_2O$ in cement chemistry terminology) that is produced in portland cement systems during the first several minutes of hydration. Subsequently, if the concrete is

exposed to substantial amounts of water for months or years, ettringite re-forms, leading to destructive expansive forces that crack the concrete members.

The conditions for the decomposition of the normal ettringite in concrete have not been well established. Curing temperatures as low as 158°F (70°C) were found by Heinz and Ludwig to be sufficient for certain compositions of portland cement, primarily as relating to its sulfate and tricalcium aluminate contents. Others have suggested the minimum temperature may be even lower, and German specifications limit the maximum temperature to 140°F (60°C).⁵ However, in the United States at least, many precasters have cured their products at temperatures well above this minimum with no deleterious effect.

Our studies of failed railway ties on the East Coast (see Fig. 1) disclosed that a second cause for DEF may be as important as overheating during curing.⁶ Ties produced on Fridays, when steam curing was not employed, also failed. The cause of this failure was judged to be the inclusion of relatively large concentrations of sulfur in the clinker phase of the cement.

Historically, clinker sulfate levels have been well below 1 percent. However, changes in clinker production processes in some cement plants have recently led to sulfur contents, calculated as SO_3 , of 2 to 5 percent. Some of this sulfate may be very slowly soluble, thus reacting to produce ettringite only after the concrete attains rigidity.

We have also investigated incidences of DEF in cast-in-place concrete where neither accelerated heat curing nor high clinker sulfate were factors. Instead, the concrete may have attained high internal temperatures due to mass concrete placement or to subsequent exposure to sun or fire that was high enough to decompose the ettringite. Later, frequent exposure to water caused ettringite formation that cracked the concrete.

In other cases, information on the cement composition or the concrete curing conditions has not been developed, primarily due to the fact that distress of the concrete structure has



Fig. 3. Cast-in-place concrete piers for electrical transmission lines evidencing DEF cracking about 8 years after installation.

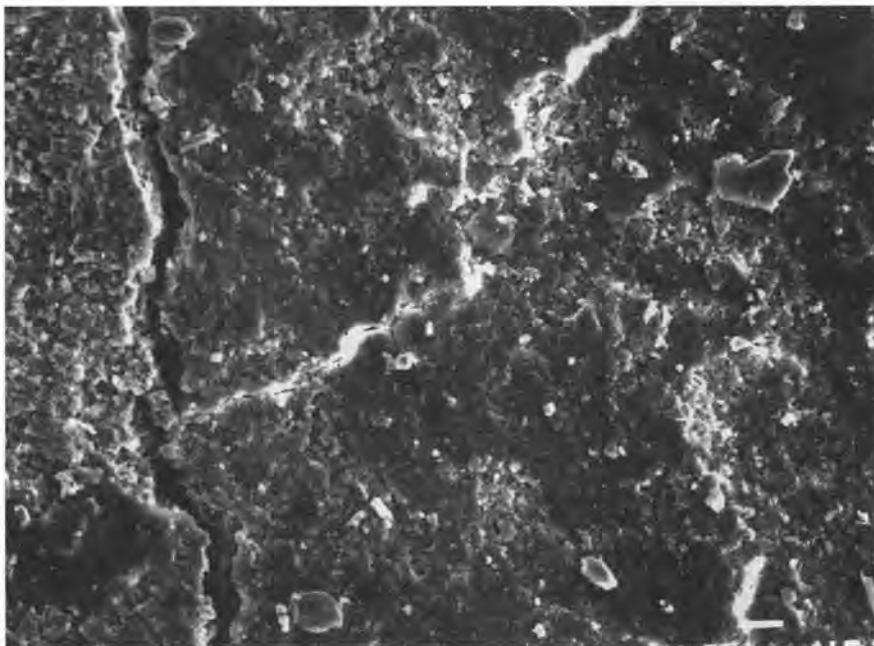


Fig. 4. Saw cut sample from concrete tie evidencing DEF cracking. Note the gel-like location under 500X magnification (see also Fig. 5).

only become evident after several years, and casting records are no longer available. As shown in Figs. 2 and 3, concrete cracking can be severe, and besides aesthetic considerations, structural concerns can be very real.

WHY ONLY NOW?

A major question has arisen about DEF: why did it not occur before 1980? We believe there are two answers: (1) it did occur, but it was not recognized; and (2) compositions of portland cements have changed radically during the last few decades and,

in some cases, perhaps unexpectedly for the worse.

The first answer relates to the fact that the ettringite of DEF has been found in many incidences to be dramatically disguised. Ettringite crystals normally have a needle-shaped morphology that allows most microscopists to easily recognize them. In DEF, however, the crystals may be so fine as to be only resolved using scanning electron microscopy (SEM) at magnifications of 5000 to as much as 25,000 (see Figs. 4 and 5). In several cases, DEF has been misdiagnosed as alkali-silica reaction (ASR).

Even with SEM, DEF may be un-

recognizable due to the preparation and detection techniques employed. Polished samples, epoxy impregnation, and use of only back-scattered electron techniques have been found to greatly reduce identification chances; instead, saw-cut samples and secondary electron techniques have consistently provided excellent results. Microprobe X-ray elemental analysis is very helpful, and even necessary in some cases, for distinguishing between ASR and DEF gel formations (see Fig. 6).⁷

The other answer to the question is explained by the fact that the composition of portland cement has changed dramatically since the Portland Cement Association (PCA) made their monumental studies of all of the types of portland cement produced in the 1940s.⁸ For example, SO₃ levels for portland cement have increased from a maximum of a little over 2 percent in the 1940s to often well over 4 percent now, and finenesses have likewise increased. Of greatest concern is the increase in clinker* sulfate levels at some cement plants due to changes in fuels or the disposal of wastes in cement kilns. The maximum clinker SO₃ level reported by PCA was 0.7 percent. At least a few companies now have production periods when the level is several times higher.

HOW TO PREVENT DEF

The very recent discovery of DEF and the restrictions on disclosure of concrete failure causes due to in-progress litigation or closed-record settlements have not permitted a good delineation of the parameters necessary to prevent DEF. Based only on our experiences to date, DEF may almost certainly be prevented by the first guide below, or by some or most of the other recommendations.

1. Exposure — We know of no products or structures that have failed that were not exposed to substantial, frequent wetting for periods of many months or even several years.

* Portland cement is made by intergrinding clinker from the cement kiln with gypsum (calcium sulfate dihydrate). The clinker itself contains at least a few tenths of a percent of other sulfate-containing compounds, such as alkali sulfates.

2. Air-entrainment — We know of only one incidence where concrete that was air-entrained has been reported to have suffered from DEF. As is also true for other failure mechanisms, air voids can act as relief valves or reservoirs for substances growing in hardened concrete. However, if they become filled with such substances, they may not provide freeze-thaw protection.

3. Pozzolan component — We know of only one incidence where DEF was reported for concrete that contained significant amounts of fly ash or other pozzolanic materials. The experience to date, however, may be insufficient to properly evaluate this factor. This is an area in which research is needed.

4. Curing temperature — Limiting the temperature of the concrete (not of the steam) to 158°F (70°C), or preferably 140°F (60°C), during curing may prevent the DEF that occurs due to heat-cure temperature, but not that due to some forms of clinker sulfate. Because many precasters have used temperatures as high as 190°F (88°C) successfully, this is probably an unnecessary burden under many circumstances, but precasters without sound, long-term experience at the higher temperatures should consider the cement composition and the proposed exposure, or tests in accordance with Recommendation 8, below, before exceeding the 140°F (60°C) limit.

5. Cement composition — According to Heinz and Ludwig, excessive heat curing may be a factor only with cements having a composition that falls within certain ranges relating to sulfate and aluminate concentrations. The primary concern is with SO₃ to Al₂O₃ ratios above about 0.5, with the maximum DEF potential at about 0.8. Unfortunately, many portland cements that meet all ASTM C 150 requirements will fail this restriction, and indeed, proper chemistry for other properties may require a ratio above 0.5. A 3 percent limit on SO₃ content has also been suggested as an alternative, but such a limit may be below optimum for many cements. Taylor⁹ also suggests that the magnesium and alkali (especially sodium) contents may be factors.

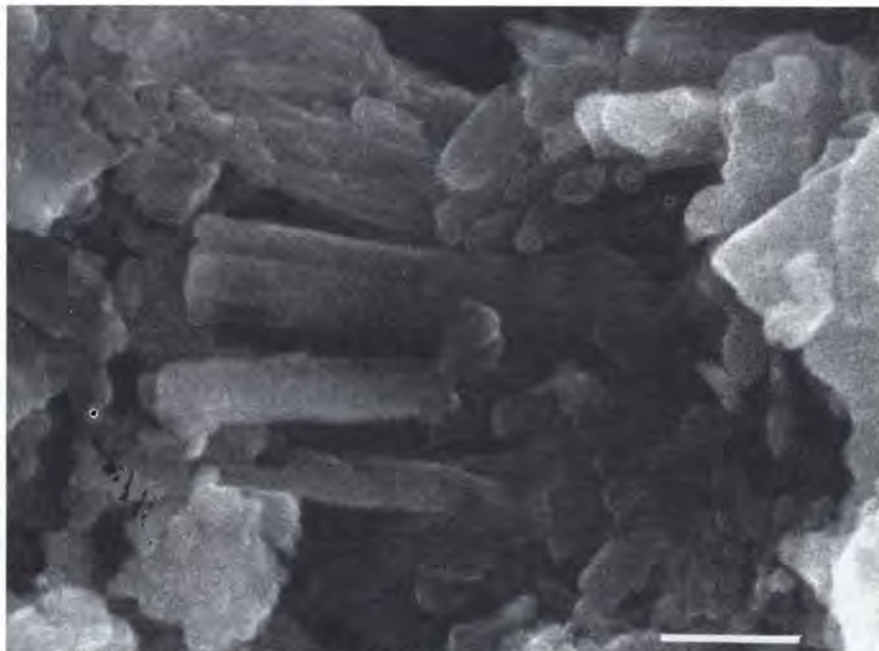


Fig. 5. A typical gel-like area under 15,000X magnification. The needles of ettringite are revealed.

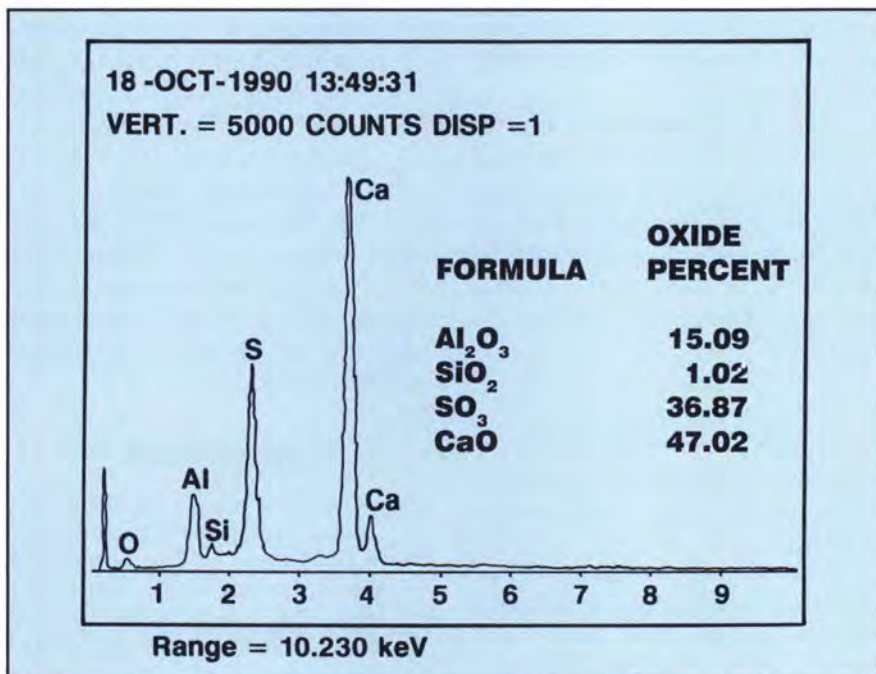


Fig. 6. X-ray elemental analysis of typical gel-like DEF locations, showing the elements of ettringite (calcium, aluminum, sulfur and oxygen), and computer calculation to oxides.

6. Clinker sulfate content — We believe that clinker sulfate levels should be limited to perhaps a maximum of 1.5 percent. This value may be increased if the alkali content is also proportionally high, but such high alkalis may lead to other problems. Unfortunately, cement companies do not include clinker sulfate contents on mill certificates as distinguished from

SO₃ contents of the cement as a whole. Further, there is no established procedure for determining the clinker sulfate content of portland cement. However, cement plants regularly determine clinker SO₃ levels and may provide the data on request.

7. Sulfate reactivity — ASTM C 265, which determines the unreacted sulfate content of portland cement after

1 day of exposure in water, may allow detection of excessive clinker sulfate. Unfortunately, the method has been removed from ASTM C 150 requirements for portland cement and replaced by an expansion test that we believe will not be reliably diagnostic. Precasting plants should request from the cement manufacturer the C 265 test results. Any value above 0.5 g of SO₃ per liter is cause for serious concern.

8. Concrete performance — A test to determine if a precast concrete product will undergo DEF if exposed to water has not attained recognition. The Dugan test,¹⁰ or a modification of it, may prove effective, but may also be so conservative as to rule out concrete that will perform acceptably except under the most extreme conditions. The test involves successive heating and water-exposure cycling. It was originally developed as a test for potential alkali-silica reaction, but found to be potentially more predictive of DEF caused by high curing temperatures.

9. Historical performance records — Historical records on the durability of concrete produced under certain conditions could be used as prognostic if no significant changes in the cement can be assured, and if more than ten years of exposure to water has occurred.

CONCLUSIONS

Based on investigations carried out so far, the following conclusions can be drawn:

1. DEF is caused by the destructive, expansive development of ettringite within hardened concrete, and is evidenced as cracks, and loss of strength.

2. The ettringite may be so fine as to look like alkali-silica gel. The cracking

patterns for DEF and ASR are similar.

3. DEF almost certainly will not occur if the concrete is not frequently exposed to substantial amounts of water.

4. Destructive DEF will probably not occur, or its effect will be lessened, if the concrete is well air-entrained.

5. Based on very limited experience, DEF may not occur if the concrete contains a substantial amount of pozzolan that will not itself introduce significant amounts of sulfate.

6. If the precast concrete is not air-entrained, and exposure to water will be frequent, then DEF may occur if either:

(a) The concrete temperature during curing or in service reaches a temperature high enough to decompose ettringite. Depending on cement composition, this temperature may be as low as 140°F (60°C).

(b) The clinker contains a substantial amount of slowly soluble sulfate. Clinker sulfate levels may be as low as 1.5 percent to cause DEF. For high-alkali cements, the lower SO₃ limit may be 2 percent or more.

7. Tests of cement by ASTM C 265, or of concrete by the Dugan procedure, may reveal a potential DEF problem for non-air-entrained concrete that will be exposed to substantial amounts of water.

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