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Concrete Sulfate Attack in a Sulfate-Free Environment

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Synopsis: The present paper provides an example of the application of the holistic model to the study of one of the most complex phenomenon in the science of concrete durability, namely the deterioration caused by delayed ettringite formation (DEF) in a sulfate-free environment. By adopting the holistic approach, a new model to explain this damage is proposed. The model is based on three essential elements: late-sulfate release, microcracking, and exposure to water. Late-sulfate release from a cement with high-sulfate content (especially that with high content of clinker sulfate in less available form) can cause the delayed deposition of ettringite in pre-existing microcracks after sulfate ions diffuse through the pore solution in concrete, either intermittently, or continuously exposed to environmental water. Microcracking may be promoted by alkali-silica reaction, steam curing at high temperatures, localized high stress in prestressed concrete structures or other causes.

Theoretically, the DEF-induced damage occurrence can be reduced or prevented by controlling at least one of the above three parameters. In practice, the best way of reducing the DEF-induced damage risk is either to avoid cements with high clinker sulfate that are responsible for the late-sulfate release, or to adopt lower and more homogeneous stress distribution derived from the prestressing process in precast elements, such as concrete ties.

Keywords: delayed ettringite formation; durability; microcracking; prestressed concrete elements; sulfate attack

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INTRODUCTION

Sulfate attack is related to the expansive character of the ettringite formation by reaction of internal (concrete) or external (from the environment) sulfate with the hydrated calcium aluminate of the hardened-cement matrix.

Not necessarily the ettringite formation produces a damaging effect. When it occurs *homogeneously* and *immediately* (within hours or days) in a mixture or in a deformable concrete - *early ettringite formation (EEF)* - the related expansion does not cause any significant localized disruptive action (Table 1). This happens when ground gypsum reacts with anhydrous calcium aluminates within some hours (set regulation) or when a calcium aluminate sulfate (C_4A_3S) hydrates within few days producing a relatively small, homogeneous, harmless and rather useful stress (expansive cements for shrinkage compensating concretes).

On the other hand, when ettringite forms *heterogeneously* and *later* (after months or years) - *delayed ettringite formation (DEF)* - the localized related expansion in a rigid hardened concrete produces cracking, spalling, and strength loss. Therefore only *DEF* - and not *EEF* - is associated with a damaging sulfate attack (Table 1).

There are two different types of *DEF*-related damage depending on the sulfate source (Table 2): external or internal sulfate attack. External sulfate attack (*ESA*) occurs when *environmental sulfate* (from water or soil) penetrates concrete structures. Internal sulfate attack (*ISA*) occurs in a sulfate-free environment for the *late sulfate release* from either gypsum-contaminated aggregates or sulfur-rich clinker phase (1). According to the terminology currently used, the term "*DEF*" is related to the internal sulfate attack only. However, more correctly **delayed** ettringite formation would mean that ettringite forms **later** regardless of the sulfate source.

HOLISTIC AND REDUCTIONIST APPROACHES

The holistic approach considers **concrete construction in its entirety with environmental and structural loading in service**, rather than concrete as material of laboratory curiosity. Mehta (2) adopted the holistic approach to explain the behavior of concrete structures in the field in contrast to what happens to laboratory specimens and in particular he studied the role played by microcracks in determining the concrete deterioration process.

Brittleness, combined with poor tensile strength, is responsible for microcracking in concrete structures subjected to thermal and drying shrinkage, as well as to static and cycling dynamic loading in service. According to Mehta (2) microcracks, promoted by weathering effects and loading in service, represent preferential paths for the penetration of aggressive environmental agents such as air, humidity, sulfate and chloride ions. Therefore, pre-existing discontinuous microcracks act as precursors in the corrosion of the reinforcement and in the deterioration of the cement matrix itself as well as that of the reactive aggregates, if any. Once any of these processes is initiated (all having an expansive-disruptive nature), microcracks grow to become macrocracks. After an initial period of a few years or more, the degradation process - in the form of cracking, spalling and loss of mass - increases very rapidly.

The holistic approach has been used by Mehta (2) to re-examine the four principal causes of concrete deterioration: external sulfate attack, alkali-silica reaction, corrosion of reinforcing steel, and freezing-thawing cycles. In the present paper, based on a previous work of the author (1), the holistic model is used to address the internal sulfate attack. According to the terminology currently used, in the present paper the term "*DEF*" is used to indicate the ettringite-related deterioration of concrete in a **sulfate-free environment.**

Different researchers have adopted a reductionist approach, instead of a holistic one, to explain concrete distress induced by *DEF*. Each has reached a different conclusion by relating the concrete distress with a specific predominating mechanism. Among these, the following hypothesis can be mentioned as the most important:

(*i*) ***DEF* promoted by high temperature steam curing:** In normal portland cement pastes ettringite, that forms during the plastic stage of fresh concrete, is destroyed by steam curing at 65-100°C; then ettringite forms again at later ages in concrete structures stored in water either intermittently or permanently and causes disruptive expansion of the hardened concrete in service. According to Heinz *et al.* (3,4), *DEF* expansion in concrete is due to the transformation of metastable monosulfate into ettringite when steam-cured concrete is exposed to normal temperature moist-curing at later ages. According to Lawrence (5), the correlation between expansion and sulfate content of the cement points out the importance of ettringite in the expansion mechanism of steam-cured mortar prisms; however, the expansive hydration of MgO may increase the sensitivity of cements to heat cure. On the other hand, Fu *et al.* (6-8) argued that, although steam curing of concrete at high temperatures is a key element, the *DEF* mechanism process is different from that based on thermal decomposition of ettringite: at temperatures above 65°C, calcium silicate hydrate (*C-S-H*) would adsorb very quickly sulfate from gypsum, so that this would not be available to react with the aluminate phase and produce normal ettringite; later sulfate ions, slowly released from the *C-S-H* phase, would diffuse through pore solution and feed the nucleation of ettringite crystals in the tip-zone of the pre-existing microcracks. In the case of *DEF* associated with steam curing the specific mechanism is highly controversial. On the one hand, Scrivener and Taylor (9) and others (10, 11) think that the *DEF* effect in steam-cured concretes is related to a uniform and homogeneous paste expansion that occurs in the post steam-curing exposure. Accordingly to Johansen *et al.* (10) the uniform paste expansion results in rim cracks around aggregates; subsequently ettringite deposition would fill the rim cracks, but this is considered to be benign since ettringite deposition is considered to play no role in the expansion and cracking of concrete. On the other hand, Diamond (12) and others (6-8) think that the expansion and cracking induced by *DEF* are related to the crystal pressure exerted by the growing ettringite crystals on their surroundings. In particular, on the basis of free-energy considerations, it was shown (7) that ettringite crystal nuclei should first form in the tip-zone of the pre-existing microcracks; after nucleation, the growth of these ettringite crystals would be responsible for the opening of the microcracks.

(*ii*) ***DEF* promoted by alkali-silica reaction (ASR) or other microcrack-causing mechanisms:** *ASR* is the primary cause of deterioration in the form of cracks and microcracks, whereas ettringite, that is found in the cracks in moist-curing conditions at later ages, is considered to have formed as a consequence of the pre-existing cracks rather than being the cause of it (13,14). Thaulow *et al.* (15) found mixtures of alkali-silica gel and ettringite in steam-cured prestressed concrete railroad ties. However, Diamond and Ong (16) found that, in the presence of siliceous reactive aggregates, initial expansion and cracking were caused by the *ASR*, but after about one month no more *ASR* gel formed and the subsequent further expansion was caused by deposition of ettringite. Steam curing at high temperatures is suspected to aggravate reactivity of silica and silicates with alkali (17,18). Therefore, according to Taylor (17), limestone aggregates would be preferable to siliceous aggregate in manufacturing *DEF*-free steam-cured concrete. Additional conditions that are considered essential to the *DEF*-damage process include: microcracking promoted by thermal stresses in steam-cured precast concrete (18,19), or freezing-and-thawing in service (3,4), or dynamic loading and fatigue stress (13). The use of ASTM Type III portland cement (20) or relatively high contents of SO_3 (> 3.6%), MgO (> 1.6%) and equivalent Na_2O (> 0.8%) in portland cements (21) are factors that would aggravate expansion of steam-cured concrete.

(*iii*) ***DEF* promoted by large amounts of sulfate in clinker and/or high cement sulfate content:** Portland cement contains a mixture of sulfur compounds from the cement clinker and from added calcium sulfate (e.g. gypsum, $CaSO_4 \cdot 2H_2O$) which acts as set regulator. The sulfates from different sulfur sources have different water-solubility kinetics: sulfate from the gypsum dissolves sufficiently fast to participate in the regulation of the setting of the cement, whereas sulfate from the clinker phase is usually unavailable for the setting regulation. Therefore, cements with the same *total* sulfate content, but with different proportions of sulfate from the clinker phase and that from the gypsum source, may perform in different ways.

In many present-day clinker kilns there are poly-functional burning systems which are capable of using either gaseous or liquid hydrocarbons, as well as solid small-particle coals, depending on the cheapest source of available fuels. The sulfur content of these different fuels can change and cause unwitting variations from one day to another of sulfate incorporated in the clinker phase. Moreover, the clinker sulfate content may increase with the use of high-sulfur organic residues, such as tires that are burned in cement kilns to destroy environmentally harmful products in a safe and cost-effective way.

According to Hime (22), present-day cements produced in kilns that burn sulfur-rich fuels or waste materials, can incorporate large amounts of sulfates, up to 3% by clinker mass. When high sulfate levels are not balanced by a high alkali content, the excessive SO_3 may occur as $CaSO_4$ or react with calcium aluminates or even occur as interstitial impurity in the alite and belite phases. According to Hime, all these forms of sulfate in the clinker phase are slowly soluble in the mixing water and, therefore, can lead to **late-sulfate release** which is essential for the delayed ettringite formation (*DEF*)-related damage. According to this recent perspective, based on field occurrence, *DEF* is not restricted to overheated steam-cured concretes, since precast Friday ties*, cured at the factory temperature, present the same distress incidence as the steam-cured products (23). Moreover, there is evidence from the field that cast-in-place concrete structures (12,22,23) may show evidence of the same *DEF*-induced damage occurrence as that of steam-cured precast concrete products. According to this hypothesis, *DEF* by itself causes microcracks radiating from localized areas of ettringite development, expansion of the cement matrix relative to coarse aggregates, and macrocracks due to the internal expansion relative to the exterior surface region (23). On the other hand, Miller and Tang (24) found that North American and European present-day clinkers may contain sulfate levels from a few hundredths of a percent to about 2.5%. However, they did not find $CaSO_4$ in the clinker phase and concluded that, under ambient curing conditions, the sulfur-containing phases of the present-day commercial clinkers are unlikely to cause expansive stress and cracking induced by internal sulfate attack.

Each of the above hypothesis - from (*i*) to (*iii*) - can be partly correct; however, they cannot solely explain all the available data from the field on the *DEF*-induced damage of concrete structures. For instance, it may be true that many *DEF*-induced concretes were subjected to steam curing at high temperatures, but there are also apparently proven cases of *DEF*-related deterioration in the absence of steam curing. On the other hand, it may be true

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* *Friday ties are manufactured on Friday and cured at room temperature because by Monday they would attain adequate strength to allow for cutting the prestressing strands.*

that *ASR* acts as the precursor of some *DEF*-related damages, but there are also *DEF*-distress cases in the absence of *ASR*. Finally, it may be true that present-day cements incorporate large amounts of slowly soluble sulfate in the clinker, but not all present-day concrete structures are subjected to *DEF*-induced damage. It is opinion of the author that, due to the reductionist approach, each researcher or research-team over-emphasized their own results and under estimated or rejected others. Moreover, each of the above hypotheses cannot give a satisfactory answer to the following questions:

1. Why are some specific concrete products (e.g., prestressed concrete **railway ties) more vulnerable to *DEF*-induced distress** than other precast or cast-in-place concrete structures?
2. Why is ***DEF*-induced damage so erratic** in the sense that, everything apparently being the same, it occurs only under some specific circumstances and not others?

FIELD EXPERIENCE OF DEF-RELATED DAMAGE

An attempt will be made in the present paper to integrate all the above mentioned information, as well as results from the field experience of this author, with the available knowledge on concrete science and technology.

The results from field experience directly available to the author include two different types of concrete structures: **a**) prestressed precast concrete ties and **b**) cast-in-place concrete structures.

For each of the above concrete structures, *DEF*-related damage cases were found with ettringite appearing, as a gel-like mass under the optical microscope, in the cracks of the damaged structures. By use of a scanning electron microscope and an X-ray elemental analyzer the gel was identified as fibrous consisting of calcium, sulfur, and aluminum. It was definitely confirmed by X-ray diffraction analysis indicating that the product was primarily ettringite.

a) Concrete ties. For the *DEF*-damaged concrete ties almost all the results published by Mielenz *et al.* (23) were confirmed, and in particular field observations revealed that:

- The *DEF*-induced damage incidence was identical whether concrete ties were steam cured or not.
- Unused stock-piled ties underwent the same distress-incidence as the ties in service subjected to vibrational distress caused by the passage of high-speed trains.
- Ties not exposed to rain (such as those in railroad tunnels or un-used ties below and in the middle of outdoor storage stacks) did not deteriorate.

In addition to these results, field experience showed the important role played by the **microcracks produced during the prestressing process** in determining the *DEF*-induced damage. Microcracks (i.e. cracks invisible to the naked eye) were detected by using an optical microscope, specially adapted for field experience. The appearance of microcracks (10-100 μm in thickness) on the surface of concrete ties was monitored either immediately after cutting the prestressing strands or later on in stock-piled products and those in service. In all the concrete ties of a plant, where there were complains for the *DEF*-induced damage, **microcracks were detected immediately after cutting the prestressing strands**. They initially appeared as microcracks parallel to the prestressing wires and later as irregular cracking.

Field observations of microcracks of un-used concrete ties revealed that their presence was related with the specific type of manufacturing process, and in particular with the local stress level induced in the concrete by the sudden cutting of the prestressing strands. Two typical processes are adopted for manufacturing prestressed concrete ties. In one of these - named *long-line method* (Fig. 1) and widely used all over the world - the same set of prestressing strands is used for 15 to 20 lined up concrete ties. Each concrete batch is in general placed in a row of 6 or 8 parallel ties. When the concrete attains adequate compressive strength, the prestressing strands are cut. At this time **excessive local stress can occur in the concrete area close to one end of the tie**, especially in the eight ties located at the two extreme parallel rows.

In the other process - named *anchored steel-plate method* (Fig. 2) - each concrete tie is individually prestressed using reinforcing wires anchored to steel plates by special cold-worked heads. The anchored steel plates, embedded in the concrete mixture at the ends of each tie, transfer the prestressed force from the wires to the concrete when this reaches adequate compressive strength. This process consumes more time and also workmanship, and therefore prestressed concrete ties processed according to this method are more expensive. However, as a matter of fact, in concrete ties manufactured with this process microcracks do not appear or occur to less extent at the time of prestressing, and the frequency occurrence of the *DEF*-induced damage seems to be lower than in concrete ties manufactured with the *long-line method*.

Not all the microcracked concrete ties subsequently evidenced macrocracks and deposition of ettringite into the cracks. The frequency of occurrence of the *DEF*-related distress was found to be high only in the presence of other two events accompanying the initial microcracking. These events are:

- relatively high cement sulfate level that sometimes surpassed the limit of 4%, in terms of SO_3 content, according to the European Norm EN 197/1;
- intermittent exposure to rain water, aggravated by alternate drying caused by sunny conditions.

The role played by the micro-climate (Fig. 3) was studied by examining unused, two-year old, stock-piled concrete ties, all microcracked as evidenced by the field optical microscope. Those exposed to the alternate actions of rain and sun (on the sides and specially at the tops of outdoor storage stacks) were severely macrocracked and *DEF*-damaged; those exposed to rain but in a permanent shadow condition evidenced a less severe distress; concrete ties permanently protected from both rain and sun exposure (below and in the middle of stacks) remained only microcracked without any further crack growth and apparent *DEF*-related damage.

b) Cast-in-place concrete structures. Many pedestals for electric power-line installations deteriorated very severely over a period of 2-3 years after being cast in place in 1993 (Fig. 4). Since they were located in an area (near Ancona, Italy) where siliceous reactive aggregate are frequently found, an *ASR*-damage was initially diagnosized. However, due to the unusual and severe macrocracking not always accompanied by the typical gel appearance of the *ASR* product, some cored samples were analyzed and massive local deposits of ettringite in the cracks were detected by XRD. No significant sulfate content ($<0.01\%$) was detected in the environmental ground surrounding the pedestals as well as in the coarse aggregate extracted from the concrete. The latter, on the other hand, was found to be a slowly reactive siliceous aggregate when tested according to the ASTM C 289 procedure. On the basis of the SO_3 content in the concrete, the known nominal portland cement content, and the concrete specific gravity, the SO_3 level for the cement used was assumed to be as high as 4.4%. The unusually high SO_3 level of the cement was related with the clinker sulfate as high as 2% according to the available information for the cement used at that time in the area. Most of the clinker sulfate is not available for early cement hydration reactions because of its lower (25) and /or slower (22) water solubility, especially when the alkali content in the clinker phase is relatively low (26,27). Therefore, the amount of total SO_3 in the cement (from the clinker source and the gypsum used for setting regulation) increases by increasing the clinker sulfate and sometimes surpasses the EN limit (4%). The required amount of gypsum *available* for the setting regulation, besides the *unavailable* sulfate from the clinker phase, can become relatively high in high-strength portland cement with high fineness and high C_3A content.

NEW PROPOSED MECHANISM FOR DEF-RELATED DAMAGE

The following factors are considered to be essential for the *DEF*-related damage: microcracks promoted by the manufacturing process itself (e.g. prestressing in railway ties) or *ASR* or other causes including those related to steam curing;

- exposure to wetting-drying cycles;

- late sulfate release from the cement clinker or other sources;
- migration of reactant ions ($SO_4^{=}$, Al^{+3}, Ca^{+2}) through the pore aqueous solution of concrete exposed to water or saturated air;
- deposition of ettringite inside the existing microcracks, and subsequent crack opening by ettringite swelling or crystal growth.

The holistic approach for the *DEF*-induced damage is based on the occurrence of three essential events. The three events are:

- **Microcracking**
- **Exposure to water or saturated air**
- **Late-sulfate release**

Each event, in turn, can be determined by one or more possible causes which will be considered in detail further on. First, a synthetic representation of the holistic approach for the *DEF*-related damage will be examined through the help of Fig. 5 where each event corresponds to a circle. The area in the middle of the triangle corresponds to situations of serious risk for *DEF*-related deterioration since all the three needed elements of the system are present: **late sulfate release** caused by cement with high sulfate content (especially that with high content of clinker sulfate in less available form) can feed the delayed deposition of ettringite in the **pre-existing microcracks** after diffusing through the pore solution in concrete **exposed to environmental water**. In the absence either intermittently or continuously of one of these elements, *DEF* cannot occur and this explains the erratic character of this phenomenon.

Each of the three needed elements of the system can be related to numerous causes. For instance, concrete microcracking can be promoted by one or more of the following causes:

- Curing at high temperatures (> 65°C), excessive heating/cooling rate or too short preliminary curing at room temperature
- *ASR* with microcracks around aggregate particles
- Weathering effects cycles including wetting/drying and heating/cooling changes
- Dynamic loads in service
- Plastic shrinkage in poorly cured slab structures
- Freezing/thawing cycles
- Excessively high porosity in aggregate particles
- Weak transition zone at the interface aggregate- or steel-cement matrix
- Localized high stress in prestressed structures.

Everything else being the same, steam-curing at high temperatures causes additional microcracking with respect to room temperature curing, and therefore there is a higher frequency of occurrence of *DEF*-induced damage in precast steam-cured concretes when cements with high sulfate content in the clinker phase are used. This also explains why in many laboratory studies (3-5, 7) only overheated steam cured specimens were subjected to *DEF*-related damage in contrast to what occured in the corresponding concrete specimens cured at room temperature.

The last cause of microcracking in the above list - that is localized high stress induced by the prestressing process itself - can occur in all the precast concrete ties, particularly in those manufactured by the *long-line method*. This provides a clear justification of why with this type of structure there is a higher frequency of occurrence of *DEF*-related damage than in any other concrete element. However, since this deterioration did not occur in concrete ties manufactured in the late 1970s by using the same method as that presently employed (24), an additional event must be identified to explain why the distress to some of these ties began to occur in the late 1980s. This additional event seems to be the late sulfate release, which, in turn, is attributable to a number of possible causes:

- High cement sulfate content is related to the clinker sulfate increase with the use of high-sulfur fuel or organic residues - such as tires - burned in cement kilns to destroy environmentally harmful products in a safe and cost-effective way (22).
- Other sources of slowly soluble sulfate from artificial lightweight aggregates or gypsum-contaminated natural aggregates, and shrinkage-compensating cements based on sulfo-aluminate products.
- Slowly released sulfate ions from that adsorbed on the *C-S-H* phase in high temperature (> 65°C) steam-cured concretes (6).
  Thermal decomposition of ettringite at high temperature in steam-cured concrete (3,4).

Only the first cause of late sulfate release in the above list can justify why there was an increase in the *DEF*-related distress-incidence, from the 1970s to the 1980s, particularly in concrete structures - such as ties - more prone to microcracking for the manufacturing process itself. On the other hand, in present-day manufactured concrete ties the *DEF*-induced damage seems to be an exceptional and discontinuous phenomenon rather than a general and continuous occurrence, although many ties per each process-day are microcracked. This erratic occurrence of the *DEF*-induced damage can be related either to intermittent use of sulfur-rich organic residues in the clinker kiln or to change in the sulfur content of ordinary fuels. In many present-day clinker kilns there are poly-functional burning systems that are capable of using either gaseous or liquid hydrocarbons, as well as solid small-particle coals, depending on the cheapest source of available fuels. The sulfur content of these different fuels can change and cause unwitting variations from one day to another of sulfate incorporated in the clinker phase.