A Holistic Approach to Concrete Damage Induced by Delayed Ettringite Formation

By M. Collepardi

Synopsis In the development of modern hydraulic binders cement chemistry played an outstanding role.

However, with the advent of material science and engineering, the focus of attention shifted from the chemistry of cement to concrete science and technology.

The holistic approach - which is the most recent milestone in this direction - considers concrete construction in its entirety with environmental and structural loading in service, rather than concrete as material of laboratory curiosity.

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). By adopting the holistic approach, a new model to explain the DEF-induced damage is proposed. This model is based on three essential elements: late sulfate release, microcracking, and exposure to water. 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, either intermittently, or continuously exposed to environmental water.

Each element, in turn, can be related to numerous causes. For instance microcracking may be promoted by alkali-silica reaction, steam curing at high temperatures, localized high stress in prestressed structures or other causes.

Theoretically the DEF-induced damage-occurrence can be reduced or prevented by controlling at least one of the above three elements. In practice, the best way of reducing the DEF-induced damage-risk is either to avoid cements with high clinker sulfate which 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: Durability, delayed ettringite formation, microcracking, prestressed concrete elements.

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INTRODUCTION

Since the invention of portland cement, chemistry has played an important role in the development of modern hydraulic binders. Toward the middle of the present century, with the advent of the discipline of material science and engineering, the role played by chemistry was progressively reduced in favor of a more productive global approach primarily based on concrete science and technology microstructure. The most recent approach, the holistic approach in the middle of '90, is the last important milestone in this process.

The present paper first discusses the change from the cement chemistry approach to that based on concrete microstructure. Then, it illustrates the use of the modern holistic model to study delayed ettringite formation, which is currently one of the problematic issues in the science of concrete durability.

FROM CEMENT CHEMISTRY TO CONCRETE SCIENCE AND TECHNOLOGY

The two important breakthroughs in the manufacture of portland cement, with respect to that of other available binders, were:

1) the chemical reaction at high temperatures of silica and alumina from the argillaceous material with lime from the calcareous rock;
2) the over-burning in the kiln to assure almost complete combination of lime with silica and alumina to produce silicate and aluminate phases.

The first breakthrough was substantially based on the theoretical and practical investigations of Vicat (1) on the artificial hydraulic lime, a sort of forerunner of modern portland cement. Vicat proved that the burning of an intimate mixture of calcareous and argillaceous materials, and then the conversion of the silica of the clay into a combined form, were the essential prerequisites in the hardening process of the new hydraulic binder.

The initial research in the chemistry of cement addressed primarily the phase composition of the anhydrous portland clinker, focusing particularly on solid-liquid changes at the temperatures of industrial kilns (1). As a consequence of these research efforts, the production of the industrial portland clinker was optimized in terms of the most effective thermal processes in the kiln including efficiency of fuel combustion, chemistry of high-temperature reactions, clinker cooling rate, and desired composition of mineralogical phases in clinker..

The contribution of chemistry was crucial not only for refinement of the production process of clinker, but also for research on the hydration of cement. For a long period of time, controversy existed whether setting and hardening of cement paste is explained by the crystallization hypothesis of Le Chatelier (2) or the gel hypothesis of Michaëlis (3). Even today there is no general agreement on the details of the hydration process responsible for stiffening, setting and hardening. From the time of the Le Chatelier-Michaëlis controversy, two mechanisms of hydration of portland cement are recognized: *through-solution* and *topochemical* or *solid-state* hydration. According to the through-solution mechanism, anhydrous compounds present in portland clinker dissolve into their ionic aqueous constituents, and then, because of their low solubility, solid hydrates precipitate from the supersaturated aqueous solution. According to the solid-state mechanism, water reacts directly at the surface of the anhydrous phases in cement particles which hydrate without going into aqueous phase.

Strength, durability and other engineering properties depend much more on microstructural characteristics (morphology of solid products, capillary pores, air voids, transition zone) and technological parameters (water-cement ratio, aggregate grading, compaction, curing) rather than on chemical aspects (4,5). The transition zone - the thin interfacial area between the coarse aggregate particles and the cement matrix - is more porous than the aggregate and the bulk cement paste, and represents the weakest link of the chain. It is susceptible to microcracking when subjected to tensile stresses promoted by differential movements between the aggregate and the bulk cement paste (4).

Brittleness, combined with poor tensile strength, is responsible for microcracking in concrete structures subjected to thermal shrinkage, drying shrinkage, static and cycling dynamic loading in service. The role played by microcracks in determining the concrete deterioration process has been examined by Mehta (6) who proposed a new model - the holistic model (7) - to explain the behavior of concrete structures in the field in contrast to what happens to laboratory specimens.

According to Mehta (6) 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 (Fig. 1). 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 form of cracking, spalling and loss of mass - increases very rapidly.

HOLISTIC APPROACH FOR DEF-PROMOTED CONCRETE DAMAGE

The holistic model has been used by Mehta (6) to re-examine the four principal causes of concrete deterioration: sulfate attack, alkali-silica reaction, corrosion of reinforcing steel and freezing-thawing cycles. In the present paper the holistic model will be used to address an other problematic cause of concrete deterioration, namely delayed ettringite formation (DEF) a phenomenon which has attracted considerable attention all over the world during the last decade. In the present paper the term DEF will be used to indicate the **ettringite-related deterioration of concrete in a sulfate-free environment regardless of whether or not the concrete member had been subjected to steam curing.**

Different researchers have adopted a reductionist approach 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:** normal ettringite, which forms as a consequence of the setting regulation 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.* (8,9), 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 (10), 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.* (11-13) 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, *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 (14) and others (15, 16) think that the DEF effect in steam cured concretes is related to an uniform and homogeneous paste expansion which occurs in the post steam curing exposure. Accordingly to Johansen *et al.* (15) 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 (17) and others (11-13) think that the expansion and cracking induced by DEF are related to the crystal pressure exerted by the growing ettringite crystal on their surroundings. In particular, on the basis of free energy considerations, it was shown (12) 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 microcracking-based mechanisms:** ASR is the primary cause of deterioration in form of cracks, whereas ettringite, which is found in the cracks in moist-curing conditions at later ages, is considered to have formed as a consequence of the existing cracks rather than being the cause of it (18,19). Thaulow *et al.* (20) found mixtures of alkali silica gel and ettringite in steam cured prestressed concrete railroad ties. However, Diamond and Ong (21) 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 (22,23). Therefore, according to Taylor (22), limestone aggregates would be preferable to siliceous aggregate in manufacturing DEF-free steam-cured concrete. Additional conditions which are considered essential to the DEF-damage process include: microcracking promoted by thermal stresses in steam cured precast concrete (23,24), or freezing-thawing in service (8,9), or dynamic loading and fatigue stress (18). The use of ASTM Type III portland cement (25) or relatively high contents of SO_3 (> 3.6%), MgO (> 1.6%) and equivalent Na_2O (> 0.8%) in portland cement (26) are factors that aggravate expansion of steam cured concrete.

(*iii*) **DEF promoted by large amounts of sulfate in clinker and/or high cement sulfate content:** according to Hime (27) "*present-day cements, produced in kiln that burn sulfur-rich fuels or waste materials, can incorporate large amounts of sulfur in the clinker. Some of this sulfur can be present as relatively slowly soluble sulfate that can react with aluminate compounds months or years after placement outdoors leading to delayed, destructive development of ettringite. The ettringite may occur as a gel-like mass that has the appearance of, and can be mistaken for, alkali-silica gel*". 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 calcium silicates or even occur as interstitial impurity in the alite and belite phases. Miller and Tang (28) 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 unlike to cause expansive stress and cracking induced by internal sulfate attack. According to Hime (27) all the forms of sulfate in the clinker phase are slowly soluble in the mixing water and, therefore, they can act as late sulfate release which is essential for the 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 (29). Moreover, there is experiential knowledge that cast-in-place concrete structures (17,27,29) may evidence 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 (29).

Each of the above hypothesis - from (*i*) to (*iii*) - can be partly correct; however, it cannot solely explain all the available experiential data 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 proved cases of DEF-related deterioration in the absence of steam curing. On the other hand, it may be true 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 of the present paper that, due to the reductionist approach, each researcher or research-team over-emphasized their own results and under-estimated or rejected all the others. Moreover, each of the above hypothesis 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 that are not yet fully understood?**

Field Experience of DEF-Related Damage

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

**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.*

The results from field experience directly available to the author of the present paper include three different types of concrete structures: prestressed precast concrete ties, cast-in-place concrete structures and asbestos-free fiber-reinforced cementitious products.

For each of the above concrete structures, DEF-related damage cases were found (Fig. 2-4) with ettringite appearing, as a gel-like mass under the optical microscope, in the cracks of the damaged structures. By use of a scanning eletron microscope and an X-ray elemental analyzer the gel was identified as fibrous consisting of calcium, sulfur and aluminum. This was confirmed by X-ray diffraction analysis indicating that the product was primarily ettringite.

Concrete ties. For the DEF-damaged concrete ties almost all the results published by Mielenz *et al.* (29) 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 (Fig. 5). The appearence 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. 6) 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 to 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. 7) - each concrete tie is individually prestressed using reinforcing wires anchored to steel plates by special cool-made heads. The anchor 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**.

However, in some cases DEF-induced damage was observed even in concrete ties manufactured by the anchor steel plate process. For instance, in one case field observations of precast concrete ties - cured at room temperature or steam cured at a temperature as low as 40°C - revealed DEF-induced damage when limestone aggregates were used, whereas no distress at all was discovered when siliceous aggregates were employed under the same conditions in terms of curing and mixture composition.

This result seems to be in conflict with the statement that to reduce the DEF-induced damage risk, limestone aggregates would be preferable to siliceous aggregates, since the latter contain constituents that react with alkali especially at high temperatures (22). The available limestone aggregate, remained for studies on the case history described above, appeared to be primarily pure $CaCO_3$, with less than 0.1% of siliceous material, and no sulfate at all. The specific gravity of some grains of this aggregate (about 15% by mass) was as low as 1.8-2.0 g/cm^3. The petrographical analysis revealed that this portion of the limestone aggregate consisted of pure calcite in form of small spheric particles with a large volume (about 25%) of interconnected pores (Fig. 8).

The unusually high porosity of this portion of limestone aggregate was responsible for the initial microcracking produced by the prestressing process even when the less risky anchored steel plate method was used. As a matter of fact, when this portion of high porosity aggregate was replaced by normal-weight aggregate (with a specific gravity of 2.7 g/cm^3) initial microcracking and subsequent DEF-related damage disappeared whether limestone or siliceous aggregate was used.

However, not all the microcracked concrete ties, manufactured either by the long line method or the anchored steel plate process, 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 which sometimes surpassed the limit of 4%, in terms of SO_3 content, according to the European Norm EN 197/1;
- intermittent exposure to raining water, aggravated by alternate drying caused by sunny conditions.

The role played by the micro-climate (Fig. 9) was studied by examining unused, 2-year old, stock-piled concrete ties, all microcracked as evidenced by the field optical microscope. Those exposed to the rain and sun alternate actions (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 grow and apparent DEF-related damage evidence.

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. 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 (Fig. 3) 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 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 informations for the cement used at that time in the area. Most of the clinker sulfate is not available for cement setting regulation because of its lower (30) and /or slower (27) water solubility, especially when the alkali content in the clinker phase is relatively low (31,32). 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. **Therefore, the following factors are considered to be essential for the DEF-related damage of these pedestals: microcracks promoted by ASR; exposure to wetting-drying cycles; late sulfate release from the cement clinker; 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.

Asbestos-free fiber-reinforced cementitious products. This type of cement product is manufactured in form of corrugated sheets by filtering an aqueous slurry containing high strength portland cement, cellulose fibers and supplementary cementitious materials such as fly ash and silica fume (33). The process includes steam curing at high temperatures of the filtered cementitious product.

Microcracks, detected by field optical microscope (Fig. 4), were found in all the examined un-used stock-piled products of the outdoor storage or sheets in service in form of industrial roofs. They were related with the mechanical and thermal stresses produced by the process itself and in general they did not change in size over a long period of time. However, in some exceptional cases, over a period of months, microcracks transformed into macrocracks with massive deposition of ettringite into the cracks, provided that the sheets were exposed intermittently or continuously to water. Since the two pre-requisites for the DEF-related damage (microcracking and exposure to water) were always present, the erratic behavior in ettringite formation was related with some exceptional use of cements with high clinker sulfate.

This special type of DEF-related damage, is mentioned here just because it occurs in the absence of fine and coarse aggregate. Based on the experiential data by Lawrence (26) relating with DEF, Taylor (22) argues that "*if there is no aggregate, that is, in a neat paste, expansion is either extremely slow or non existent*". The present field experience of industrial paste-based cementitious products indicate that ettringite can deposit not only in the microcracks formed around the aggregate particles, as it occurs in mortar and concrete mixes, but even in the cement paste. This agrees with the observed crack pattern examined by Diamond (17) in real concretes: "*rim cracks do not go all the way around some aggregate particles, and are entirely absent from others in the same field*"; moreover, Diamond observed a crack pattern "*generally connecting through segments running through the cement paste*".

New Proposed Mechanism for DEF-Related Damage

The holistic approach for the DEF-induced damage is based on a chain of three essential events. In the absence of one of these events the DEF-related deterioration cannot occur. The three events are:

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

Each event, in turn, can be determined by one or more possible causes which will be considered in details further on. First, a synthetic representation of the holistic approach for the DEF-related damage will be examined, through the help of Fig. 10 (in such a way that no part of the complex system is overlooked). Each corner of the triangle corresponds to a system in which only one of the three elements of the system is present, and this situation does not present any risk at all for the DEF-related occurrence.

Each side of the equilateral triangle in Fig. 10 represents the system in which only two elements are present in the absence of the third. In such a case, again, no risk exists for the DEF-related deterioration. For example, in microcracked concrete, not exposed to water, DEF cannot occur even if there is a potential late sulfate release due, for instance, to an excessive amount of unavailable clinker sulfate. In fact, in the absence of water, sulfate and other reactant ions (Al^{+3} and Ca^{+2}) cannot diffuse through the pore aqueous phase and migrate towards the existing microcracks to form ettringite.

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, either intermittently, or continuously **exposed to environmental water**. Diamond and Ong (21) found that the total amount of the ettringite deposited in ASR-induced cracks of mortar specimens was significantly increased as compared with uncracked companion specimens. The author of the present feels that this statement is true regardless of the specific cause responsible for microcracking.

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
- 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.

Moreover, the last cause of 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 (29), 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 related with 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 (27).
- Other sources of slowly soluble sulfate from synthetized 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 (11).
- Thermal decomposition of ettringite at high temperature in steam-cured concrete (8,9).

Only the first cause 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 exposure conditions (presence of water) or to the 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 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.

Chemical interactions - causing a decrease in the pH of the pore solution phase - can favor normal formation of ettringite from environmental sulfate attack (34). Therefore, one cannot exclude that carbonation as well as ASR can interact with the DEF process, creating more favorable conditions for ettringite deposition in the existing microcracks. In particular, since ASR consumes alkalies and OH^- from pore solution (21), this process can reduce the pH and presumably the ettringite deposit in the aqueous phase of pores and microcracks.

The other potential causes of late sulfate release - related with the sulfate contamination of aggregates, or the adsorption of sulfate on the *C-S-H* phase at high temperatures or thermal decomposition of ettringite in steam cured concrete - can occur, but cannot explain why there was a significant change in the DEF-induced damage-incidence during the last decade or so. Neither they can explain why microcracked concrete ties can evidence DEF-related distress regardless of the use of steam curing.

The third element - that is intermittent or continuous exposure to air or humid air - seems to be the one on which all the researchers agree. There is experiential knowledge that microcracked ties, with the same cement source causing DEF-related damage in concrete structures, do not show such a type of deterioration when they are protected from the contact with water. This field experience includes:

- Concrete ties in railroad tunnels (29)
- Stock-piled concrete ties below the outdoor storage stacks (29)
- Concrete ties in service when protected by hydrophobic treatment (18).

Recommendations to Prevent DEF-Induced Damage

On the basis of the proposed holistic model, DEF-related deterioration of concrete can be avoided provided that one or two of the above mentioned essential elements is precluded. The most easy preclusion apparently would relate to water exposure. However, in practice, permanent protection of concrete structures from exposure to water is very expensive by using the present-day available impermeable coatings or hydrophobizing products. This technique, may be considered for use with concrete structures in service showing initial DEF-related damage in order to reduce or block the deterioration process.

Therefore, the other two essential elements for the DEF-induced concrete damage should be taken into account first. One of these - microcracking - can be significantly reduced to harmless levels by adopting adequate measurements during the design and the execution phases. For instance, precast concrete ties with lower and more homogeneous stress distribution, deriving from the prestressing method itself, should be taken into careful consideration by the design engineers. Steam-curing process with lower thermal gradients, from controlled heating and cooling rates, can also reduce microcracking, and consequently mitigate the DEF-induced deterioration risk. Use of sound aggregates to prevent ASR-related cracking is a mandatory requirement regardless of the DEF-related deterioration. However, pozzolanic materials can advantageously be used to avoid or to reduce the risk of microcracking promoted by alkali-reactive aggregates when unwittingly used.

The most important challenge in preventing the DEF-induced deterioration of concrete structures is related to cement manufacture. First, cement producers should take into careful consideration the fact that clinker with lower sulfate content can significantly reduce the risk of DEF-induced damage in concrete structures. Moreover, there is experiential evidence that the risk of DEF-related damage significantly increases by using high-strength (high C_3S and C_3A) portland cements, whereas concrete mixtures with portland-pozzolan and portland-slag cements are much less prone to the DEF risk in steam-cured concretes (9,26,35). The behavior seems to be related with the lower amount of gypsum required for setting-time regulation and/or the lower amount of clinker sulfate content in blended cements. Pozzolanic materials, including silica fume at a dosage level as low as 10% by cement mass (35), can be additionally advantageous also in reducing the risk of DEF-induced damage through the pore-size refinement effect with consequent reduced diffusion rate of ions, in particular of sulfate ions, through the pore solution.

CONCLUSIONS

The change from a predominating chemical approach toward a more global approach in concrete science and technology appears to be very fruitful for addressing issues related to the durability of concrete structures.

Concrete damage induced by delayed attringite formation is one of the most complex in concrete durability. A holistic model was adopted to study this problem. According to this model three elements are essential for the occurrence of the DEF-related damage: microcracking, late sulfate release, and exposure to water.

Each of these elements, in turn, is influenced by a number of causes. In this perspective ASR and steam-curing are two of the possible causes of microcracking. Therefore, DEF-related distress could occur even in the absence of ASR and steam-curing.

Theoretically DEF-induced damage can be prevented by eliminating one of the three elements from the system. From a practical point of view, two approaches are possible. First, cements with high clinker sulfate content - those responsible for the late sulfate release - should be avoided. Second, microcracking should be reduced, particularly with precast concrete ties, by adopting lower and more homogeneous stress distribution from the prestressing process itself.

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Comments by Luigi Coppola and Roberto Troli were very valuable in the preparation of this paper. Kumar Mehta reviewed an earlier draft of the manuscript and his helpful comments were very valuable in the preparation of the final draft.

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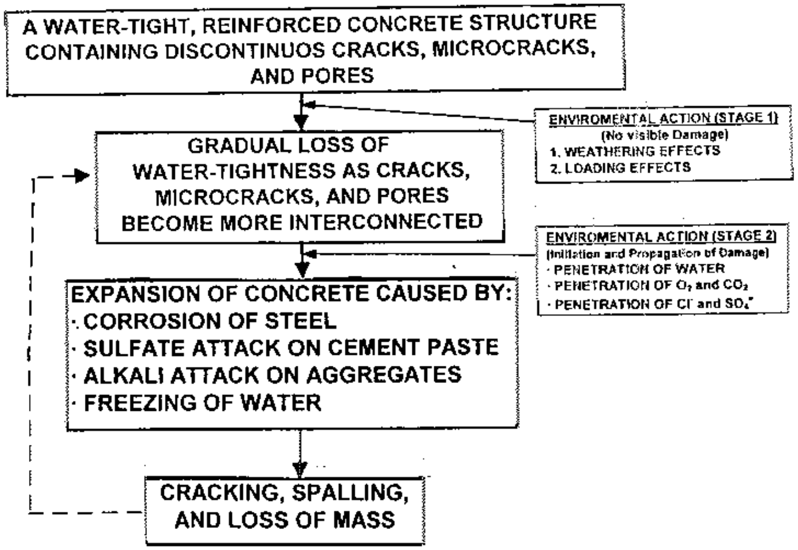

Fig. 1 - A holistic model of deterioration of concrete from environmental effects (6)

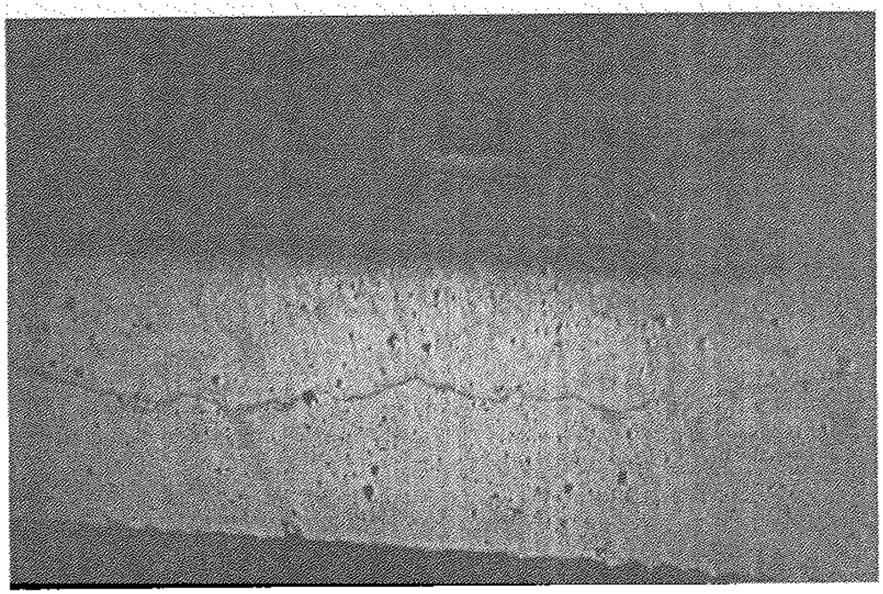

Fig. 2 - Cracking in un-used concrete ties.

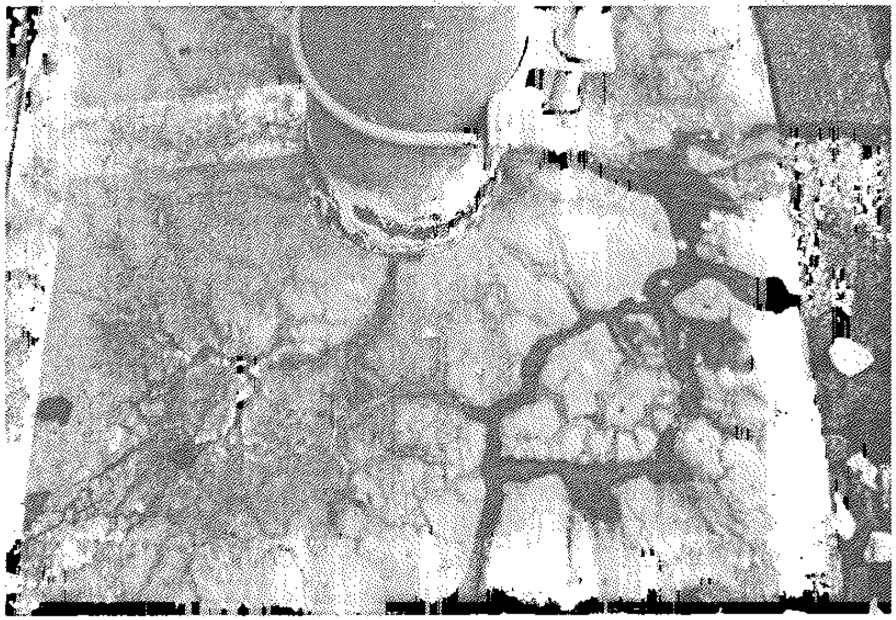

Fig. 3 - Cracking in cast-in-situ concrete pedestal for electric power line.

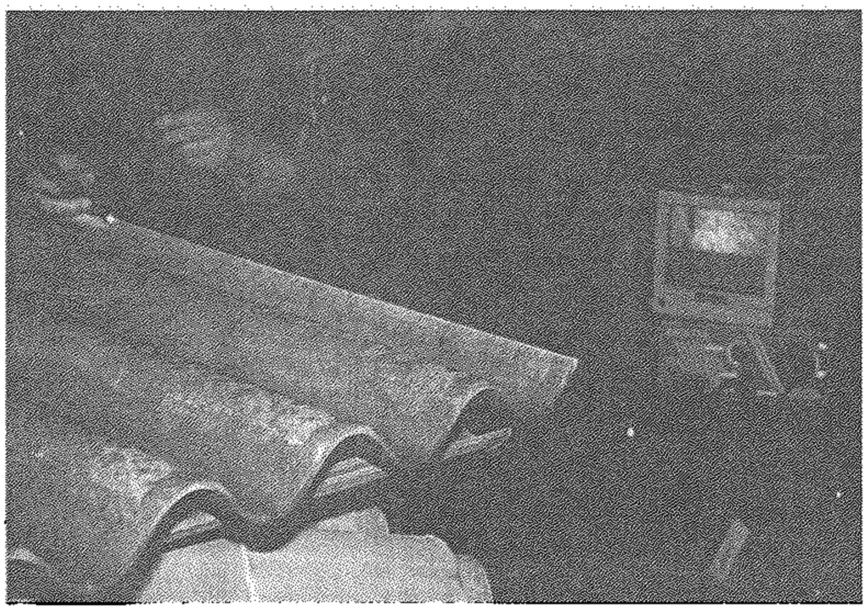

Fig. 4 - Microcracking in corrugated cementitious sheets: detection by field experience optical microscope of microcracks monitored on the screen.

Fig. 5 - Use of optical microscope for field experience to detect microcracking in concrete ties in service.

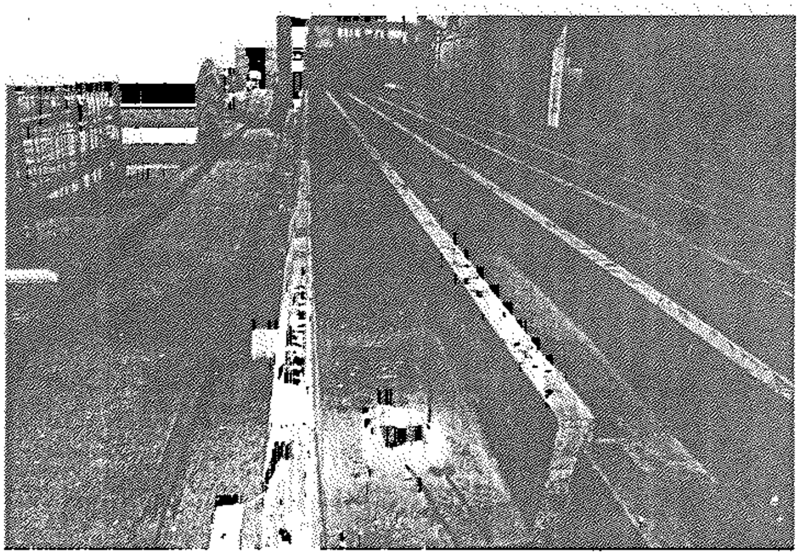

Fig. 6 - Parallel formworks of concrete ties in the long time method.

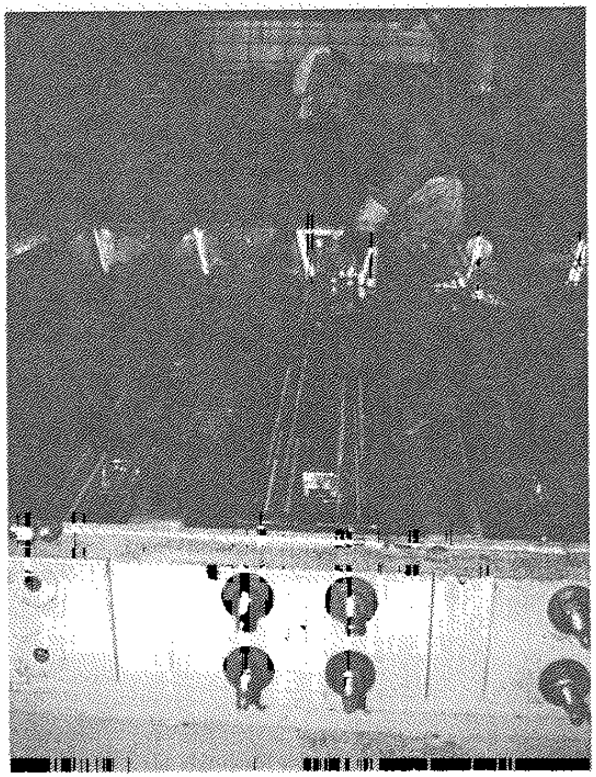

Fig. 7 - Formwork of concrete ties in the anchored steel plate method.

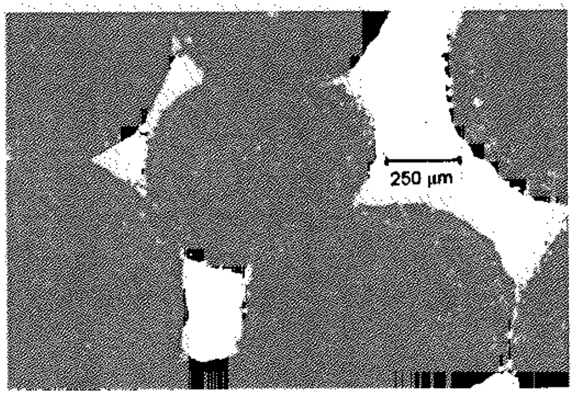

Fig. 8 - Petrographic examination of porous limestone aggregate.

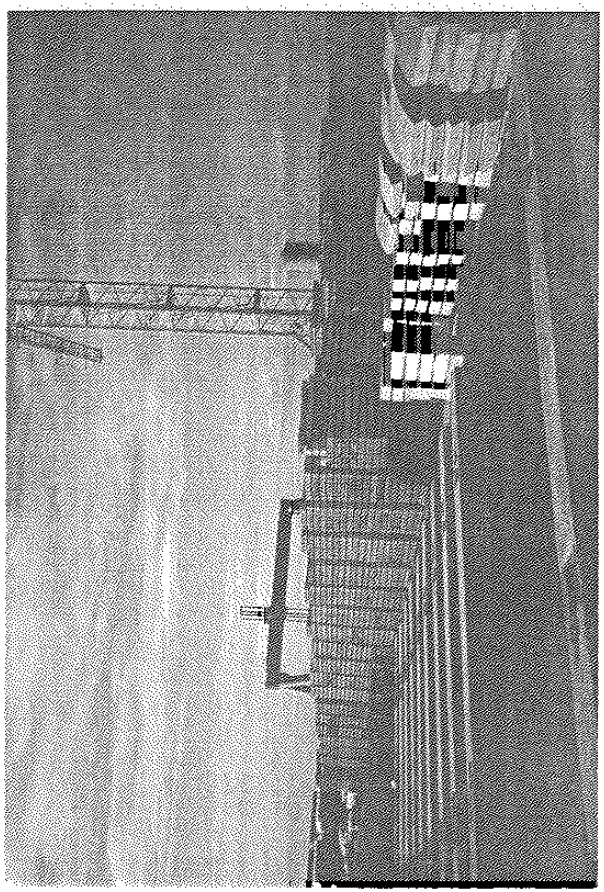

Fig. 9 - Un-used stock piled concrete ties exposed to different microenvironment (sun and shadow, dry and rain).

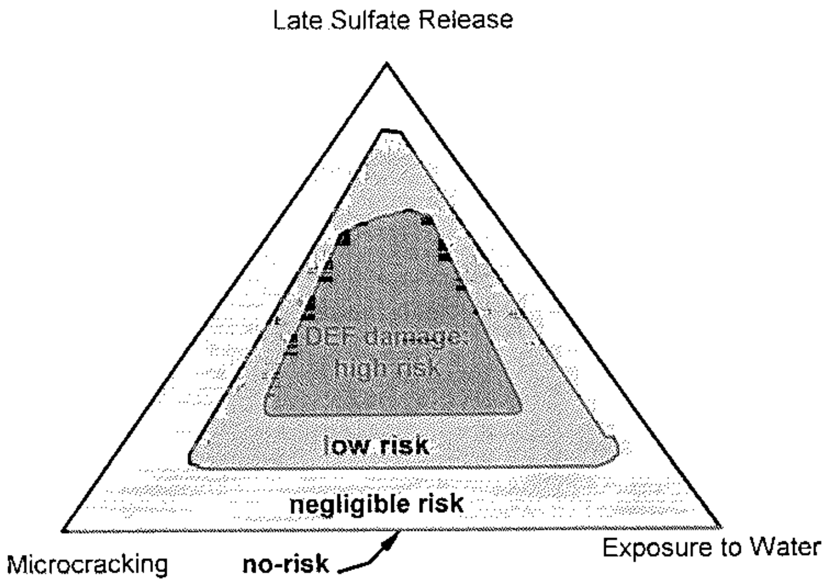

Fig. 10 - A holistic model showing DEF-damage as a function of late sulfate release, microcracking, and exposure to water.