Ettringite Formation and Sulfate Attack on Concrete

by M. Collepardi

Synopsis: The paper presents a critical review of the relationship between ettringite formation and sulfate attack. Ettringite formation is associated with expansion. However, not necessarily any ettringite-related expansion is related to sulfate attack.

Early ettringite formation (EEF) which occurs immediately (within hours) in a plastic fresh mixture does not produce any damaging expansion and is associated with the regulation of setting time of portland cement paste. Expansion after the hardening of cement paste can be advantageously used for development of chemical prestress in expansive cements.

Delayed ettringite formation (DEF) occurs at late ages and the related heterogeneous expansion in a very rigid hardened concrete can produce cracking and spalling. Two different types of DEF are examined depending on the sulfate source: DEF caused by external sulfate attack (ESA) or internal sulfate attack (ISA).

ESA, related to the interaction of environmental sulfate with the cement matrix, can be precluded by the use of impermeable concrete.

On the other hand, ISA occurs in a sulfate-free environment due to the interaction of internal sulfate (from cement or gypsum contaminated aggregate) with calcium-aluminate hydrates of the cement paste.

Two different mechanisms of DEF caused by ISA are examined. The first one is based on the thermal decomposition of ettringite in high-temperature cured concrete elements and the subsequent re-formation of ettringite at ambient temperature in a saturated atmosphere. According to the second mechanism ISA is based on a chain of three essential events (microcracking, late sulfate release, and exposure to water) and DEF could occur even at room temperature.

Keywords: Concrete, sulphate attack, ettringite, delayed ettringite formation.
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**INTRODUCTION**

Ettringite formation is considered to be the cause of most of the expansion and disruption of concrete structures involved in the sulfate attack (1). However, not necessarily any sulfate attack is caused by ettringite formation (2). Moreover ettringite formation can be advantageously used without any sulfate attack on concrete.

The purpose of this review is to present critical analysis of the relationship between ettringite formation and sulfate attack including some special cases of this attack such as those related to thaumasite formation or "delayed ettringite formation" as intended according to the terminology currently used (3,4).

The term "sulfate attack", as used here, means deterioration of concrete involving any type of sulfate interactions with cement paste independently of the curing temperature and sulfate source. In other words, both concrete structures cured at ordinary temperatures and those steam-cured will be examined irrespective of whether the source of sulfate is external or internal. This paper does not cover damage which is not specifically attributed to the chemical sulfate attack such as crystallization of water-soluble sulfate salts (5).

**ETTRINGITE FORMATION**

Ettringite formation is associated with expansion and many hypotheses of ettringite related expansion have been advanced (2-4). However, not necessarily any ettringite-related expansion produces damaging disruption of concrete structures.

When ettringite occurs **homogeneously** and **immediately** (within hours), it does not cause any significant localized disruptive action (early ettringite formation, EEF). This type of harmless ettringite formation happens, for instance, when gypsum reacts with anhydrous calcium aluminate in a through-solution reaction and acts as a set retarder in portland cement mixtures(Table 1):

\[
\begin{align*}
C_3A + 3(CaSO_4 \cdot 2H_2O) + 26 H_2O & \rightarrow C_3A \cdot 3CS \cdot H_2O
\end{align*}
\]
The retardation has been attributed to the early formation of an ettringite layer or membrane over the surfaces of the cement grains soon after mixing (3). This type of ettringite may also be called "normal" ettringite as opposite to "secondary" ettringite which will be defined later. The formation of "normal" ettringite occurs in a plastic concrete and does not produce any significant stress. Another example of harmless and useful EEF is Type K expansive cement containing a calcium aluminate sulfate (\(\text{C}_4\text{A}_3\text{S}\)) which, under proper restraint, hydrates within a few days producing uniformly distributed ettringite and homogeneous expansion throughout the hardened concrete:

\[
\text{C}_4\text{A}_3\text{S} + 6\text{Ca} (\text{OH})_2 + 8(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) + 74 \text{H}_2\text{O} \rightarrow 3(\text{C}_3\text{A} \cdot 3\text{C}_3\text{S} \cdot \text{H}_32)
\]

In such a case, the restrained expansion is advantageously transformed into a rather useful stress (0.2 - 0.7 MPa in shrinkage-compensated concrete and 3 to 8 MPa in self-stressed reinforced concretes) provided that the concrete has reached a certain strength level and a corresponding modulus of elasticity.

On the other hand, when ettringite forms later (after several months or years) - delayed ettringite formation (DEF) - the related heterogeneous expansion in a very rigid hardened concrete can produce cracking and spalling. The disruptive effect is due to the non-uniform expansion localized only in the area of the concrete structure where ettringite forms. Therefore DEF, and not EEF, is associated with a damaging sulfate attack (Table 2). There are two different types of DEF-related damage depending on the sulfate source (Table 3): 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 when the sulfate source is inside the concrete and comes from either cement with a high sulfate content or from aggregates contaminated with gypsum.

According to the terminology currently used (3,4), "DEF" or "secondary ettringite" (6) is related only to the internal sulfate attack particularly in heat-cured concrete structures where "normal" ettringite, responsible for setting regulation, is thermally decomposed and then forms again in an atmosphere that is saturated intermittently or continuously. However, correctly speaking the term delayed ettringite formation only means that ettringite forms later and therefore it should include both ESA and ISA as shown in Table 3. The following terms are used in the present paper: "ESA" or "ISA" to indicate DEF related to external or internal sulfate attack, respectively.
EXTERNAL SULFATE ATTACK

The ESA-induced damage, which is the traditional sulfate attack, is determined by the chemical interaction of a sulfate-rich soil or water with the cement paste. Soils containing sodium, potassium, magnesium, and calcium sulfate are the main sources of sulfate ions in groundwater. For ESA to occur the following three conditions must be fulfilled:

- **High permeability of concrete**
- **Sulfate-rich environment**
- **Presence of water**

A diagramatic representation of the holistic approach (7) to the ESA-related damage can be illustrated through the help of Fig. 1 (8) where each contributory element corresponds to a circle. Each circle corresponds to only one of the three elements, and this situation does not present any risk at all for damage to a concrete structure. The area in the middle, where the three circles overlap, corresponds to situations of serious risk for the ESA-related damage since all the above-mentioned three elements are present. In the absence of one of these elements the ESA-related damage cannot occur. For instance, in porous and/or microcracked concrete not exposed to water, the ESA-related damage does not happen, even if sulfate ions are present in the environment because, in the absence of water, these ions — for instance in dry soil — cannot migrate through the interconnected pores of the concrete.

The ESA-related damage manifests itself in several forms including cracking, spalling, loss of strength and adhesion. The specific manifestation of the ESA-related damage depends on which one of the following three chemical processes is predominant:

i) Sulfate attack on CH and C-S-H to form gypsum:

\[
\begin{align*}
\text{CH} + \text{SO}_4^{2-} + 3\text{H}_2\text{O} & \rightarrow \text{C-S-H}_2 \\
(\text{gypsum})
\end{align*}
\]

This process may cause expansion and spalling. However, its most important feature is the loss of strength and adhesion of the cement paste due to decalcification of C-S-H which is responsible for the binding capacity of the cement paste (2). This process may occur with all the sulfate salts (containing Na⁺, K⁺, Mg²⁺) except calcium sulfate.
ii) Sulfate attack on calcium aluminate hydrates (C-A-H) and monosulfate hydrate (C₃A·CS·H₂₁₈) to form ettringite:

\[
\begin{align*}
\text{SO}_4^{\text{2-}} \cdot 2\text{H}_2\text{O} & \quad \text{H}_2\text{O} \\
\text{C-A-H} & \quad \text{C}_3\text{A} \cdot \text{CS} \cdot \text{H}_32 \\
\text{ettringite} & \quad (\text{C-A-H})
\end{align*}
\]

This process is mainly responsible for cracking and spalling as a result of expansion produced by delayed ettringite formation. This process may occur with all the sulfate salts including calcium sulfate which acts directly on C-A-H and/or monosulfate hydrate.

iii) Sulfate attack on C-S-H and CH in the presence of carbonate ions to form thaumasite:

\[
\begin{align*}
\text{SO}_4^{\text{2-}} , \text{CO}_3^{\text{2-}} & \quad \text{H}_2\text{O} \\
\text{CH} & \quad \text{CS} \cdot \text{C} \cdot \text{H}_15 \\
\text{thaumasite} & \quad (\text{C-S-H})
\end{align*}
\]

The thaumasite formation is accompanied by the most severe loss of strength and adhesion, which is able to transform hardened concrete into a pulpy mass, since a significant part of C-S-H can be destroyed according to the reaction shown above. This process (9) may occur with every type of sulfate salts and is favored by humid atmospheres and low temperature (<10°C).

**INTERNAL SULFATE ATTACK**

The ISA-related damage is relatively "new" with respect to the "traditional" sulfate attack (ESA) since it was detected in the middle of 1980's in prestressed concrete railway ties (10). Two different mechanisms of DEF caused by ISA well be examined in this paper:

- Thermal decomposition and re-formation of ettringite in a saturated atmosphere at room temperature;
- Holistic approach based on microcracking, late sulfate release, and exposure to water.
Thermal Decomposition Mechanism

According to one school of thought (3,4,6) "normal" ettringite, formed at early age is destroyed by high-temperatures (> 70°C) steam curing. Therefore, ettringite develops again at later ages in concrete structures exposed to water (either intermittently or permanently) and causes expansion or cracking. According to this school of thought (3,4) alkali silica reaction (ASR) has a particularly important effect in promoting expansion from DEF related to internal sulfate attack. In the presence of reactive aggregates, ASR-related expansion would begin during the heat treatment and cracking would immediately occur. Then ettringite forms in these cracks or other pre-existing weakness and is considered responsible for the subsequent additional expansion and cracking, if any. The following questions cannot find convincing answers from the above hypothesis (3,4):

- Why are prestressed concrete railway ties much more vulnerable to ISA-induced distress than other precast steam-treated concrete structures?
- Why before the 1980's ISA-related deterioration did not occur in concrete structures, particularly in prestressed concrete ties (10,11), even if steam curing at temperatures as high as 70°C was adopted at that time?
- Why is ISA-related distress so erratic (11) in the sense that, with the steam curing treatment, sometimes the damage occurs and sometimes it does not?
- Why ISA-induced distress does occur even in cast-in-place concrete structures cured at ordinary temperatures (10-14), although it is fair to admit that a higher frequency of this type of damage occurs in precast steam-cured concretes?

Before presenting an alternative hypothesis (11) which can give reasonable answers to the above questions, it is proper to give further comment in regard to the last question. According to Taylor (3) and Lawrence (4) DEF related to ISA may also occur in large sections and massive elements of non-steam-treated concrete, where the heat of hydration of the cement or an external heat source during service, may have caused 70°C or more temperature rise in concrete at early age. Accordingly ISA-related DEF could happen even in non-steam-cured concrete provided that thermal decomposition of ettringite at or above 70°C had occurred.

According to the personal experience of the author as well as of other researchers (10-14), ISA-related DEF does occur even in non-steam-cured concrete at temperatures much lower than 70°C that are insufficient to cause thermal decomposition of the "normal" ettringite. This happens, for instance, in non-steam-cured "Friday concrete" ties which are not mass concrete structures. These concrete 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. Mielenz et al. (10) and Collepardi (11) found that ISA-related DEF may occur whether concrete ties are steam-cured or not, and this does not conform to the hypothesis (3,4) that ISA-related DEF is necessarily caused by thermal decomposition of ettringite at high temperatures (>70°C).

Temperature measurements in concrete elements cured at room temperature, with different cement content, thickness and shape would determine whether or not thermal decomposition of ettringite can occur.

**Holistic Approach Mechanism**

A hypothesis exposed by the author (11), which satisfactorily addresses the above four questions, is based on the role played by the late sulfate release (from cement or aggregate) on delayed deposition of ettringite in the pre-existing microcracks. Intermittent or continuous exposure to environmental water or saturated air causes swelling or crystal growth of ettringite leading to crack opening, and subsequent damage in form of macrocracking.

The holistic approach according to this mechanism for the ISA-related DEF (11) is based on the presence of three essential elements:

- **Microcracking**
- **Late sulfate release**
- **Exposure to water**

This model can be represented in Fig. 2 where each element corresponds to a circle. The area in the middle, where the three circles overlap, corresponds to situations of serious risk of ISA-related damage since all the three needed elements of the system are present. In the absence of one of these elements ISA-related damage cannot occur.

**The Role of Microcracking in ISA**

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, 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 aggregate-cement or steel-cement interface
• Localized high stress in prestressed structures.

On the basis of this model, factors related to steam-curing (precuring time, heating and cooling rates, maximum temperature) play a subordinate role since they can only promote the occurrence of microcracking. This means that ISA-induced DEF may occur even in the absence of heat-curing provided that other causes, such as ASR, excessive stress, weathering effects, etc., can promote microcracks. On the other hand, everything being the same, steam curing at high temperatures causes additional risk of microcracking with respect to room temperature curing and therefore there is a higher frequency of occurrence of ISA-induced DEF in steam-treated concrete structures. This can also explain why in some laboratory studies (6, 15, 16) specimens cured at room temperature (in the absence of any mechanism responsible for microcracking) were not subjected to ISA-induced DEF in contrast to what occurred in the corresponding overheated steam-cured specimens.

According to the holistic approach, ASR is just one of the possible causes of microcracking promoting the ettringite deposition into pre-existing microcracks. DEF related to ISA was detected even in a paste cement system where microcracks could not be caused by ASR due to the absence of any reactive form of aggregate (11).

On the basis of this model, one can explain why prestressed concrete railway ties are more vulnerable to DEF-related damage induced by ISA than any other precast or cast-in-situ concrete structures. The higher frequency of ISA-related DEF occurrence in concrete ties is related to the excessive microcracking caused by localized stress induced by the cutting of the prestressing strands in concrete ties manufactured according to the "long line method" (11). On the other hand, when lower and more uniform stress distribution is adopted - such as in the "anchored steel plate method" - the frequency occurrence of the ISA-related DEF is much lower in the prestressed concrete ties produced in this manner (11). The evidence of this behavior as a function of the manufacturing process is a special feature of this model based on the holistic approach related to experiential knowledge rather than laboratory studies alone.
The Role of Late Sulfate Release in ISA

Modern cements, manufactured in kilns that burn sulfur-rich fuels or organic residues - such as old rubber tires - can incorporate large amounts of sulfate (up to about 2.5%) in the clinker phase (17). Some of this sulfur, according to Hime (14), is present as relatively slowly soluble sulfate. It is not available, for the early ettringite formation according to the reaction [1], but would be available later to produce delayed ettringite formation.

According to the holistic model (11), delayed ettringite formation, related to late sulfate release, can occur only if pre-existing voids, primarily in form of microcracks, are available. This important relationship between late sulfate release and pre-existing microcracks in determining the ISA-related DEF, again is based on the experiential knowledge related to the manufacturing process of prestressed railway ties. For instance, in many concrete ties, where there were complaints for the ISA-related DEF, microcracks were detected, by using an optical microscope, either immediately after cutting the prestressing streams or later on in stock-piled products. Then microcracks transformed into macrocracks (visible to the naked eye) and delayed deposition of ettringite into these cracks was detected by XRD and SEM. In addition to the slowly soluble sulfate in the clinker phase, related to the high-sulfur fuels or organic residues, late sulfate release can be attribute to other possible causes:

- Sulfate release from gypsum-contaminated aggregates, for the relatively coarse size of the calcium sulfate particles, is not immediately available for EEF and then can feed DEF.
- Thermal decomposition (3,4,6,15,18) of "normal" ettringite in overheated concrete is potentially another internal source of late sulfate release.
- Sulfate ions are slowly released from that adsorbed on the C-S-H phase in high temperature steam-cured concretes (19).

The last two potential sources of late sulfate release were theoretically available even before the 1970's, but then they cannot explain why there was a significant increase in the incidence of ISA-related DEF during the last two decades, particularly in the manufacture of prestressed concrete ties. However, they are included in the holistic model of the present paper (Fig. 2) as other potential sulfate resources in addition to those considered in a previous paper (11).

The late sulfate release, related to the clinker sulfate increase with the use of high-sulfur fuels or organic residues in the last two decades, can more easily justify why there was an increase in ISA-induced distress incidence, from the 1970s to the 1980s, particularly in prestressed concrete ties more prone to microcracking from the manufacturing process itself. On the other hand, ISA-
induced damage seems to be an exceptional and discontinuous phenomenon rather than a general and continuous occurrence. This erratic occurrence of the ISA-related damage can be related to the intermittent use of sulfur-rich organic residues in the clinker kiln or to the 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 of sulfate incorporated in the clinker phase.

In agreement with the school of thought (3, 4) based on thermal decomposition of "normal" ettringite (>70°C) as responsible for ISA-related DEF, some researchers (17, 20-26) think that the sulfate content of the clinker phase can be ruled out as a source for the delayed ettringite formation at ambient temperature. According to these researchers, even for clinkers with high sulfur levels (SO$_3$ = 2.5-3%) all the clinker sulfate would be rapidly available to form "normal" ettringite within several minutes (25) or few days at most (26).

There is another reason why the important role played by late sulfate release from the clinker phase is denied by the researchers in favor of the thermal decomposition of "normal" ettringite (> 70°C) as responsible for ISA-related DEF (3, 4, 17, 20-24): according to this school of thought laboratory studies indicate that even with sulfur-rich clinkers there is no risk of ISA-related DEF at ambient temperature. However, according to the holistic approach presented by Fig. 2, late sulfate release by itself cannot cause any ISA in the absence of water exposure and/or pre-existing microcracking. In laboratory studies only concrete specimens subjected to steam-curing (particularly those cured at high temperatures, with excessive heating/cooling rate or too short preliminary curing at room temperature) can microcrack. Other causes of microcracking at room temperature (restrained hygro-thermal changes, excessive and/or non-uniform stress in prestressed structures, loading in service, etc.) might be present in the field concrete structures. Therefore, it should not be surprising that ISA-related DEF can occur even in concrete structures cured at ambient temperature in the field (10-14), whereas it can occur only in overheated concrete specimens when studied in laboratory (17, 20-24).

The Role of Exposure to Water in ISA

The third needed element for the ISA-induced damage is the intermittent or continuous exposure to water or humid air (Fig.2). The presence of water filling the pore system of concrete is essential for the migration of reactant ions — SO$_4^{2-}$, Al(OH)$_4^-$ and Ca$^{2+}$ — up to microcracks where ettringite deposition can occur. Field experience indicates that concrete ties exposed to the rain and sun alternate actions (on the sides and especially at the tops of outdoor storage
stacks) are more severely damaged by ISA than those exposed to rain but in a permanent shadow condition (11, 27). This different behavior could be attributed to the important role played by the degree of supersaturation in favoring the deposition of ettringite. On the other hand there is experiential knowledge (10, 28) that microcracked concrete ties, with the same cement source and concrete composition causing ISA-induced damage in other wet concrete structures, do not show such type of deterioration when they are protected from contact with water (concrete products protected by hydrophobic treatments or stock-piled ties below the outdoor storage stacks). This confirms the important role played by water in the migration of reactant ions from the cement paste up to the site of microcracks, and then resulting in the deposition of ettringite crystals into the microcracks and the subsequent crack opening.

CONCLUDING REMARKS AND RECOMMENDATIONS

Ettringite formation by reaction of internal or external sulfate with anhydrous or hydrated calcium aluminates has an expansive character. However, not necessarily the ettringite formation produces damaging expansion. When it occurs immediately (within several hours) in a fresh mixture (early ettringite formation EEF), there is no expansion. EEF is advantageously used for setting time retardation of portland cement.

On the other hand, when ettringite forms heterogeneously at late ages (after months or years), — delayed ettringite formation (DEF) — in a rigid hardened concrete, it can produce cracking and spalling.

There are two different types of DEF-related damages depending on the sulfate source: external or internal sulfate attack. External sulfate attack (ESA) usually occurs when environmental sulfate (from water or soil) penetrates into a concrete structure. It can be prevented or reduced by using impermeable concrete.

Internal sulfate attack (ISA) occurs in a sulfate free-environment by the late sulfate ions release from either cement or gypsum-contaminated aggregates. Of these two internal sulfate sources, the latter is relatively rare because it can be prevented by controlling the sulfate content of the aggregates. The ISA-induced damaged caused by the late sulfate release from the cement can be related either to thermal decomposition of ettringite and sulfate release from C-S-H or to the increase in the sulfate content of the clinker phase, particularly during the last two decades, due to the use of sulfur-rich fuels or organic residues that are being burned in clinker kilns to destroy environmentally harmful products in a safe and cost-effective way. Unfortunately, it is not easy to detect the sulfate content of the clinker phase since only the total sulfate content — including that from gypsum acting as set regulator — can be easily and quickly determined in a routine control.
The hypothesis of thermal decomposition of ettringite in steam-cured concrete, as the main source of DEF caused by ISA, is less convincing for at least two reasons:

- **DEF** caused by ISA occurs even in non-steamed concrete structures at room temperature
- **DEF** caused by ISA was not detected before the 1980s, when millions of prestressed concrete ties were manufactured without any significant damage in service, although steam-curing was also adopted for these concrete products.

Hopefully, to confirm or reject the thermal decomposition mechanism, future research should address the two above aspects:

1. **Laboratory and field tests** to measure the maximum temperature attainable in concrete structure as a function of content and type of cement, thickness and shape of concrete elements, environmental temperature, etc.
2. **Statistical studies** in the field of precast concrete industries, particularly in the area of prestressed concrete ties, to investigate whether other factors dealing with the process (maximum temperature, heating/cooling rates, preliminary curing, etc.) were modified from 1970's to 1980's, so that they could change the incidence of the ISA-related distress in that period of time.

Independently of the mechanism, the risk of ISA induced damage can be prevented provided that one of the following essential elements is precluded:

- **Microcracking**
- **Late sulfate release**
- **Exposure to water**

Apparently the easiest preventive method 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 hydrophobic or impermeable coatings.

Microcracking can be significantly reduced to harmless level 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 process itself, should be taken into careful consideration by design engineers. On the other hand, producers of precast concrete elements should take into account that steam-curing with lower thermal gradients, from controlled heating and cooling rates, can also reduce microcracking and consequently the ISA-induced damage risk.

Finally, cement producers should investigate why certains cements are more prone to ISA-damage than others. In particular, they should study the role played by the total sulfate content of the cement as well as that of the clinker.
phase in sound and microcracked concrete elements, cured at room or high temperature, and then exposed to water or saturated atmosphere. In the meantime, blended cements — particularly pozzolanic and blast furnace slag cements — should be preferred (15, 29) instead of high early strength portland cements, in the manufacture of concrete products, such as prestressed concrete ties, which are more vulnerable to delayed ettringite formation.

REFERENCES


Table 1 - Early Ettringite Formation (EEF) "Normal" Ettringite.

- It occurs homogeneously and immediately (within hrs or days).
- The related expansion, if any, does not cause a localized and disruptive action since it occurs in a deformable concrete.
- It is due to ground gypsum which reacts with calcium aluminates of the portland clinker phase (set regulation) or to sulfate-based expansive agents in shrinkage compensating concretes.

Table 2 - Delayed Ettringite Formation (DEF) "Secondary" Ettringite.

- It occurs heterogeneously and later (after months or years).
- The related expansion produces cracking, spalling, and strength loss since it occurs in a rigid, stiff, hardened concrete.
- Its damaging effect is related to environmental or internal sulfate source (sulfate attack).

Table 3 - Delayed ettringite formation by external and internal sulfate attack.

<table>
<thead>
<tr>
<th>EXTERNAL SULFATE ATTACK</th>
<th>INTERNAL SULFATE ATTACK</th>
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<tbody>
<tr>
<td>It occurs when environmental sulfate (from water or soil) penetrates concrete structures in service.</td>
<td>It occurs in a sulfate-free environment for the late sulfate release from gypsum-contaminated aggregates, sulfur-rich clinker phase and/or high-sulfate cement.</td>
</tr>
<tr>
<td>It occurs in a permeable concrete.</td>
<td>It needs preliminary microcracks where deposition of ettringite crystals can occur.</td>
</tr>
<tr>
<td>It occurs in a moist environment favoring diffusion of SO$_4^{2-}$ through the aqueous phase of the capillary pores.</td>
<td>It occurs in a moist environment favoring diffusion of SO$_4^{2-}$ and other reacting ions (Ca$^{2+}$ and aluminate) through water-saturated capillary pores.</td>
</tr>
</tbody>
</table>
DEF RELATED TO EXTERNAL SULFATE ATTACK (ESA)

- Permeability
  - Capillary pores (high w/c and poor curing)
  - Macropores (low w/c and improper compaction of fresh concrete related to its inadequate workability)
  - Microcracks (loadings in service and cyclic heating/cooling or wetting/drying)
- Presence of water
  - Moist environment
- Sulfate-rich environment
  - Water
  - Soil

DEF RELATED TO INTERNAL SULFATE ATTACK (ISA)

- Microcracking
  - Restrainted thermal & drying shrinkage
  - High temperature steam curing
  - Alkali-silica reaction
  - Loading in service
  - Excessive and non-uniform stress distribution in prestressed RCS
- Presence of water
  - Moist environment
- Late sulfate release
  - Sulfur-rich clinker phase
  - Gypsum-contaminated aggregates
  - Thermal decomposition of ettringite?
  - Sulfate release from C-S-H?

Fig. 1 – Ternary representation of the DEF related to ESA.

Fig. 2 – Ternary representation of the DEF related to ISA.