

SULPHATE ATTACK AND ALKALI-SILICA EXPANSION

M. Collepari, ENCO, Engineering Concrete, Ponzano Veneto (TV) Italy

ABSTRACT : A holistic approach was adopted to examine concrete durability problems by taking into account physical aspects (such as capillary porosity, micro-cracking, macro-voids) and chemical reactions. A ternary representation of the complex damage process in reinforced concrete structures was used by examining the coexistence of the main three elements effecting the concrete durability: *a*) interconnected porosity, *b*) exposure to aggressive agents, and *c*) presence of water.

This model was adopted to examine two specific examples of the concrete damage dealing with the cement matrix, the embedded aggregates:

-sulfate attack of the cement matrix;

-alkali-aggregate reaction.

Keywords: alkali-silica reaction, durability, sulfate attack

Mario Collepari is President of ENCO, Engineering Concrete, Ponzano Veneto (Italy). He is author or co-author of numerous papers on concrete technology and cement chemistry. He is also the recipient of several awards for his contributions to the knowledge of superplasticizers and their use in concrete.

INTRODUCTION

According to the holistic model proposed by Mehta (1, 2), a well-constituted, properly consolidated, and cured concrete continues to be substantially watertight and durable as long as capillary pores and microcracks in the interior do not become interconnected pathways leading to the surface of concrete. Loading effects as well as heating/cooling or wetting/drying cycles in service are responsible for the propagation of microcracks that normally exist in reinforced concrete structures (*RCS*) at the transition zone between the cement matrix and aggregates or at the interface between the cement mortar and reinforcing bars. This mechanism (Fig. 1) that happens in *RCS* in service, but not necessarily in laboratory concrete specimens, causes a gradual loss of watertightness (Stage 1). Then initiation and propagation of damage of *RCS* can occur due to the penetration of environmental aggressive agents (water, air, and ions such as Cl^- , SO_4^{2-} , Na^+) through the interconnected porosity. Due to the expansive character of all the interactions between the concrete components (cement matrix, aggregate, reinforcing steel) on the one hand, and the aggressive agents on the other, damaging effects such as cracking, spalling, loss of mass, and strength reduction can occur and then increase more and more the permeability (Stage 2).

According to this model, no apparent damage will be observed during Stage 1 corresponding to the gradual loss of watertightness, whereas in Stage 2 the damage occurs slowly at first, then at an increasingly rate (Fig. 2).

AN OTHER VIEW OF THE HOLISTIC MODEL- TERNARY REPRESENTATION

According to the above description of the holistic model, pre-existing micro-cracks and their interaction with the environmental action play a dominant role in determining the long-term durability behavior of **well constituted, properly consolidated and cured concrete**.

However, this material refers to *RCS* characterized by a low capillary porosity of the cement matrix (related with a low water-cement ratio and moist curing), and the absence of macro-voids caused by an un-proper consolidation of the fresh mixture related with its inadequate workability.

An other view of the holistic model will be presented in this paper in order to put more emphasis in the important role played by the water-cement ratio (w/c) and concrete workability - both affected by the use of superplasticizers - in determining the durability behavior of *RCS*. This presentation is based on the selection of the most important elements affecting the damage process. For instance Fig. 3 offers an other view of the holistic model through a **ternary representation** of the damage process determined by the co-existence of the following three principal elements.

- i)* **Interconnected porosity.** It is related not only to *micro-cracks* caused by the environmental action (weathering and loading effects) but even to the *capillary porosity* of the cement matrix (caused by high w/c and inadequate curing) and *un-proper consolidation* producing macro-voids particularly when stiff concrete mixtures are placed.
- ii)* **Exposure to aggressive agents.** It is related to the main three chemical mechanisms of degradation of *RCS*:
 - a) sulfate attack
 - b) corrosion of reinforcing bars
 - c) alkali-silica reaction (*ASR*)
- iii)* **Presence of water.** It is related to the intermittent or continuous penetration of the environmental water determining the durability behavior of *RCS*. Water acts as aggressive agent by itself (freezing-thawing) or concurrently with other aggressive agents (CO_2 , O_2 , Cl^- , SO_4^{2-} , alkali) in the three mentioned degradation mechanisms. Moreover, it also acts as liquid carrier for reactant ions diffusing through the interconnected pores of the cement matrix.

A synthetic representation of the holistic approach for the damage of *RCS* can be examined through the help of Fig. 3

where each element corresponds to a circle. Each area of the circle 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 damage of *RCS*. The area in the middle, where the three circles overlap, corresponds to situations of serious risk for the damage since all the three needed elements are present: **interconnected porosity**, **environmental water**, and **exposure to aggressive agents**.

In the absence of one of these elements the damage of *RCS* cannot occur. For instance, in porous and/or micro-cracked concrete not exposed to water the damage does not happen even if there is a potential presence of environmental aggressive agents such as $\text{SO}_4^{=}$ and Cl^- : in the absence of water, these ions cannot migrate through the interconnected pores and neither the sulfate attack of the cement matrix nor the corrosion of the metallic reinforcement can occur. The following examples will illustrate this point.

Sulfate attack

This attack is related to the expansive character of the ettringite formation by reaction of internal (into the 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 ($\text{C}_4\text{A}_3\text{S}$) 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 thermal decomposition of ettringite (3).

Figures 4 and 5 give a view of the holistic model through a ternary representation of the *ESA*- and *ISA*-related damage respectively. In particular the *ESA* induced damage is determined by the co-existence of the following three elements:

- **Permeability**
- **Sulfate-rich environment**
- **Presence of water**

On the other hand, the *ISA*-induced damage is related to the co-existence of the following three elements:

- **Micro-cracking**
- **Late sulfate release**
- **Presence of water**

The positive role played by superplasticizers, in reducing the *w/c* and then the permeability of the cement matrix, is very important in the *ESA* since this effect significantly retards the penetration of SO_4^- ions from the environment into the concrete and consequently reduce the corresponding *DEF*-related damage. On the other hand, the *ISA* may occur even in superplasticized concretes with very low *w/c* since sulfate is

* According to the terminology currently used "*DEF*" is related to the internal sulfate attack only in a sulfate-free environment (3). However, more correctly **delayed** ettringite formation means that ettringite forms **later** independently of the sulfate source.

already available into the concrete (Fig. 5) feed the delayed deposition of ettringite.

Alkali-silica reaction

Due to interaction between certain aggregates (containing amorphous silica or strained quartz) and the highly alkaline solution of the pore aqueous phase, concrete can deteriorate and this reaction is known as "alkali-silica reaction" (*ASR*). The alkali content of the pore aqueous phase depends primarily on the alkali content of the clinker phase and even on the exposure to environmental sodium salts (sea water and deicing agents).

The three elements needed for the *ASR* (Fig. 6) are:

- **Alkali content**
- **Alkali-reactive silica**
- **Presence of water**

Superplasticizers can mitigate the damaging effect of *ASR* by reducing the concrete permeability and then the penetration of water as well as of environmental sodium salts. On the other hand, superplasticizers appear to be less effective in preventing *ASR*-related damage when alkalis come from the clinker phase, then when they are initially into the concrete. In such a case, the best way of preventing *ASR*-related damage is the use of pozzolanic materials in combination with a water-reducing admixture, if any.

CONCLUSIONS

A synthetic view of the holistic approach for the deterioration of reinforced concrete structures was proposed through a ternary representation of the damage process determined by the co-existence of the following three principal elements:

- interconnected porosity
- exposure to aggressive agents

- presence of water

The following examples of concrete deterioration were examined by using this ternary representation:

- external sulfate attack;
- internal sulfate attack;
- corrosion of reinforcing bars;
- alkali-silica reaction.

External sulfate attack, corrosion of reinforcing bars, and alkali-silica reaction promoted by the alkali penetration from the environment (sea water, deicing salts) can be significantly mitigated by using superplasticizers due to the reduction in concrete permeability and then in the penetration of aggressive agents (SO_4^- , Cl^- , CO_2 , O_2 , Na^+) from the environment into the concrete.

On the other hand, superplasticizers play a less important role in damaging processes, such as internal sulfate attack or alkali-silica reaction promoted by high alkali cement content, where the aggressive agents (SO_4^- and alkali ions) are already available into the concrete.

REFERENCES

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Table 1 - Early and delayed ettringite formation

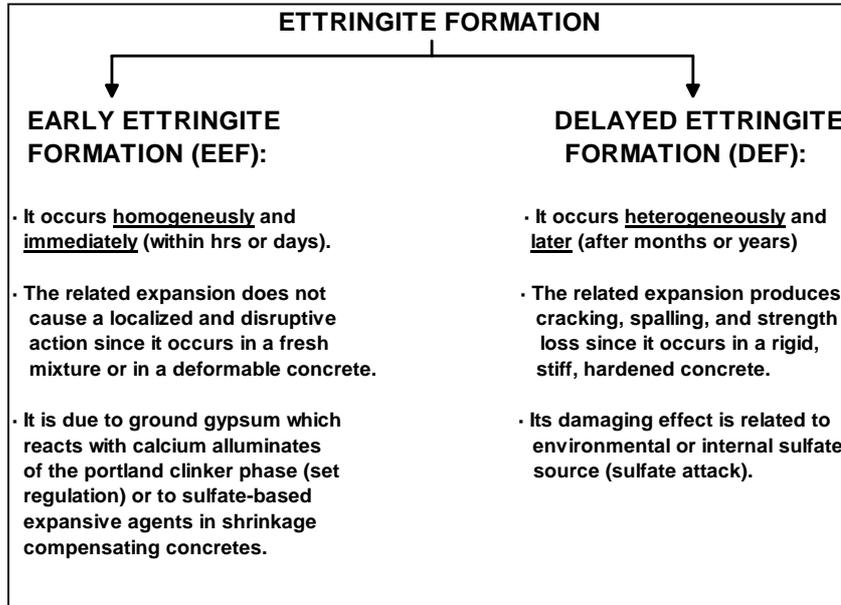
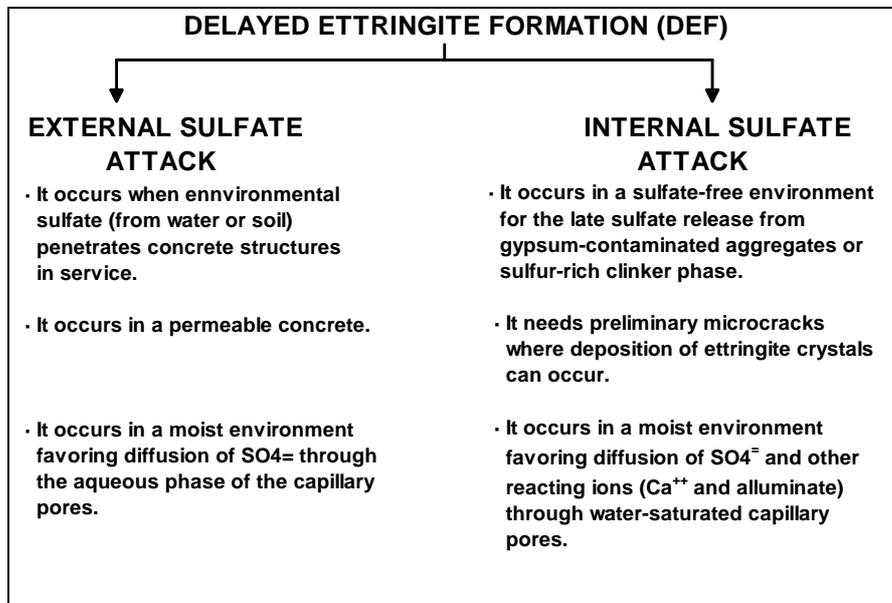


Table 2 - Delayed ettringite formation by external and internal sulfate attack



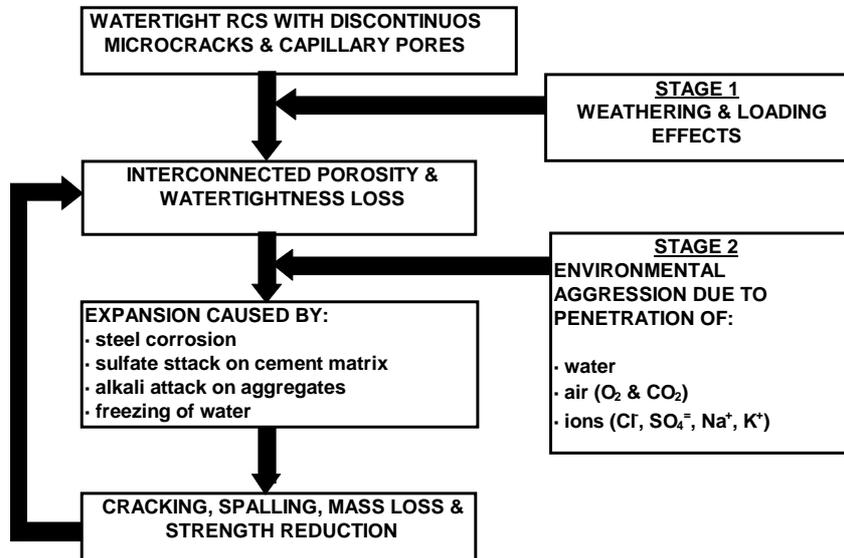


Figure 1. A holistic model of concrete deterioration from environmental effects. Adapted from Mehta (1, 2).

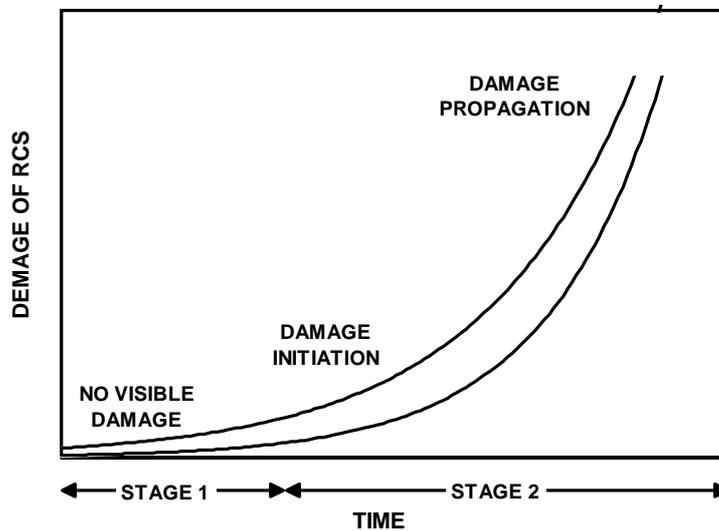


Figure 2. A two-stage damage model for reinforced concrete structures (RCS). Adapted from Mehta (1, 2).

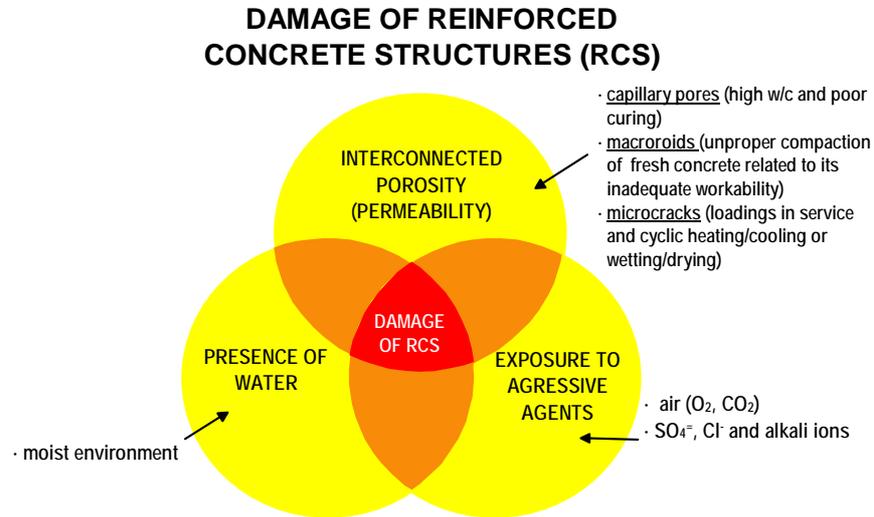


Figure 3. Ternary representation of the damage of RCS.

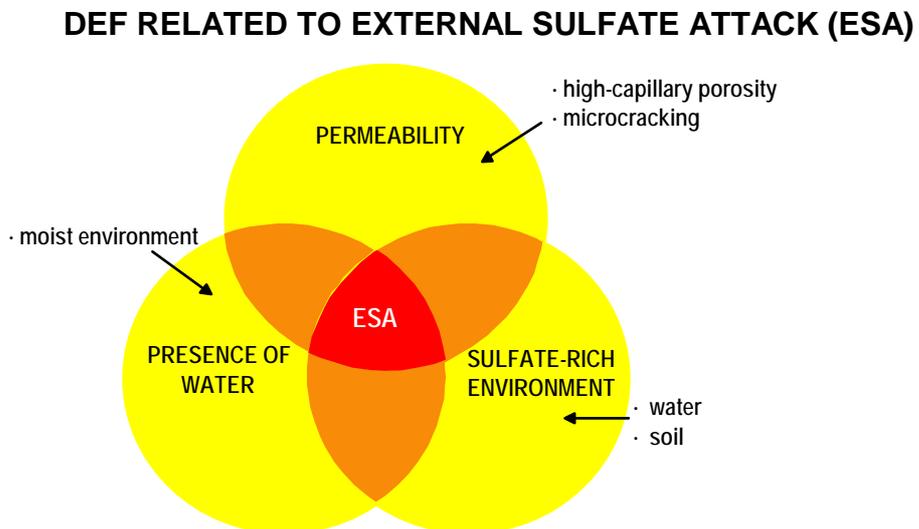


Figure 4. Ternary representation of the DEF related to ESA in RCS.

DEF RELATED TO INTERNAL SULFATE ATTACK (ISA)

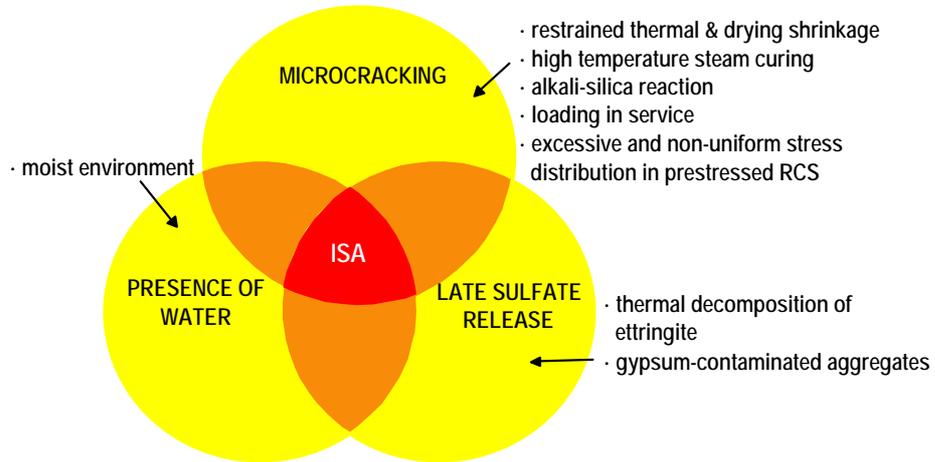


Figure 5. Ternary representation of the DEF related to ISA in RCS.

ALKALI-SILICA REACTION (ASR)

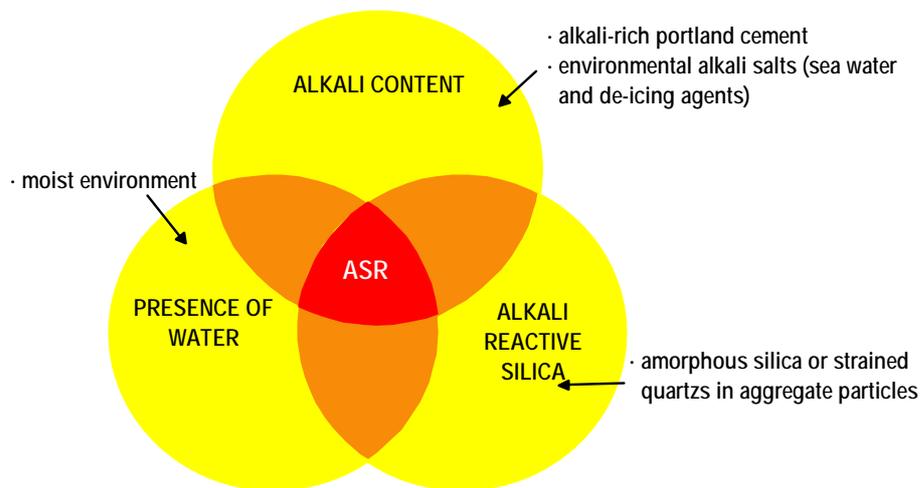


Figure 6. Ternary representation of the ASR concrete damage.

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