Concrete Durability in a Marine Environment

M. Collepardi

Synopsis: The holistic model of the damage process of reinforced concrete structures is preliminary shown in the present paper by examining the coexistence of the main factors affecting the concrete durability: *a*) interconnected porosity, *b*) exposure to aggressive agents, and *c*) presence of water.

In particular, this model is adopted to examine the durability of reinforced concrete structures exposed to a marine environment. At least three aggressive agents in sea water can cause deterioration of the reinforced concrete structures: chloride, sulfate and alkali ions. The specific aggressive action of each aggressive agent is examined: corrosion of the metallic bars caused by chloride ions, damage of the cement paste carried out by sulfate attack, and swelling disruption of concrete if alkali-reactive aggregates are present in the concrete.

In order to prevent the damage of concrete structures exposed to a marine environment the following measures should be adopted: to reduce the water-cement ratio by using superplasticizers; to employ cementitious binders based on the combination of portland cement with mineral addition such as fly ash and/or blast furnace slag.

Mario Collepardi is Honorary Member of the American Concrete institute. He is President of ENCO, Engineering Concrete, Italy. He is the author or coauthor of about 400 papers on concrete technology and cement chemistry. He is also the recipient of several awards for his contribution to the fundamental knowledge of superplasticizers and their use in concrete.

INTRODUCTION: THE HOLISTIC MODEL

According to the holistic model proposed by Mehta (1), 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..

This mechanism causes a gradual loss of watertightness. Then initiation and propagation of damage of Reinforced Concrete Structures (*RCS*) can occur due to the penetration of aggressive agents available in a marine environment (water, air, and ions such as Cl^-, $SO_4^=$, Na^+) through the interconnected porosity. Due to the expansive character of all the interactions between the RCS 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.

AN OTHER VIEW OF THE HOLISTIC MODEL

According to the above description of the holistic model, pre-existing microcracks 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.

An other view of the holistic model (2) 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. 1 offers a 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 *microcracks* 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 *unproper consolidation* producing macrovoids 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 continuos penetration of the environmental water determining the durability behavior of *RCS*. Water can act as aggressive agent by itself (freezing-thawing) or concurrently with other aggressive agents (CO_2, O_2, Cl^-, $SO_4^=$, alkali) in the three mentioned degradation mechanisms. Moreover, water 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. 1 where each element corresponds to a circle. Each area of the three circles 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 dot occur even if there is a potential presence of environmental aggressive agents such as $SO_4^=$, Cl^-, and alkali ions (Na^+ and K^+) : in the absence of water, these ions cannot migrate through the interconnected pores; consequently, the sulfate attack of the cement matrix, the corrosion of the metallic reinforcements and the alkali-aggregate reaction cannot occur. The following examples will illustrate this point.

CORROSION OF REINFORCING BARS

The three elements needed for the corrosion of reinforcing bars (Fig. 2) are:

- **Depassivation of steel**
- **Oxygen diffusion from air**
- **Intermittent presence of water**

In the following paragraphs each of the above elements is examined.

Depassivation of steel

Before the corrosion initiation, the surface of the steel bars is covered by a thin impermeable layer of iron oxide which protects the metallic substrate from the corrosion of steel and this protection is called *passivation*. This impermeable layer is stable as long as the environmental marine chloride ions (Cl^-) are not in contact with the surface of metallic bars. When chloride ions completely penetrate the concrete cover, then the thin impermeable layer, which protects the steel from

corrosion, is destroyed and the loss of this self-protection is called steel *depassivation*.

Depassivation means potential vulnerability of the metallic reinforcements. It can be also caused by penetration of CO_2 from humid air which lowers the PH because of the neutralization of $Ca(OH)_2$ according to the reaction [1]:

$$Ca(OH)_2 + CO_2 ==> CaCO_3 + H_2O \qquad [1]$$
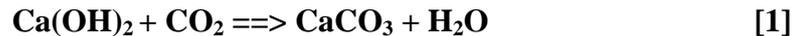
When the carbonation process [1] occurs, after a certain period of time the concrete cover is completely penetrated by CO_2, then PH of the cement paste embedding the metallic bars changes from 13 to 9 and consequently the steel passivation is lost.

Depassivation of the metallic bars caused by the presence of Cl^- of the environmental sea water is much quicker and damaging than that caused by carbonation. Therefore, steel vulnerability induced by corrosion in reinforced concrete structures exposed to marine environment is much more severe than that of the corresponding concrete structures exposed to humid air and then to the carbonation process [1]. Moreover, in the presence of chloride ions there is a local and severe reduction of the steel cross section, known as *pitting corrosion*, which occurs with higher risk of collapse of the *RCS* with respect to the uniform corrosion caused by carbonation.

The time when the depassivation starts depends on the interconnected porosity, the cover thickness, and the penetration rate of the cement paste by Cl^- or CO_2. This time is called dormant or induction period. In order to prolong the induction period, and then the durability of the reinforced concrete, for at least 50 years of service life, the following measures should be adopted according to the European Norms EN 206 and Eurocode 2:

-the water-cement ratio (w/c) must be not higher than 0.45 for structures exposed to marine environment, and 0.50 for those exposed to humid air;

- the cover thickness must be at least 45 mm for reinforced concrete in a marine environment and 30 mm for the structures exposed to humid air.

Oxygen diffusion from air

Figure 2 indicates that not necessarily steel depassivation means corrosion of rebars. Even the penetration of O_2 and water from humid air is needed to feed the corrosion process according to the following reaction:

$$2Fe + 2H_2O + O_2 \Rightarrow Fe(OH)_2 \qquad [2]$$

and then the corrosion rate significantly depends on the permeability of the concrete cover to air because the diffusion of oxygen from air is needed to feed the corrosion process.

Intermittent presence of water

Diffusion of oxygen from air cannot occur, or it occurs at a negligible rate, in a fully and continuously water-saturated cement matrix as that of a concrete permanently under sea water. Therefore, an intermittent presence of water due to discontinuous exposure to sea water and air (such as those in the tidal zone and in splashing zone of a marine environment) is the most favorable condition to supply both the Cl^- ions needed to depassivate the metallic reinforcements and the reactant products (H_2O and O_2) needed to feed the corrosion process.

Steel corrosion according to the model of Tuutti

Figure 3 shows a schematic trend of the corrosion rate according to the model of Tuutti (3) in two different situations (**A** or **B**). In the initial period of time there is no corrosion in *RCS* exposed to a marine environment. This period corresponds to the time taken by chloride to completely penetrate the concrete cover after which the steel has lost its initial passivation and the corrosion can start. This time is t_1 for the **A** situation and t_2 (much longer than t_1) for the situation **B**. This time is called dormant or induction period, after which the corrosion starts according to different rate (**I**, **II** or **III**) depending on the availability of oxygen and water to feed the corrosion of steel according to the process [2].

The corrosion rate **I** in Fig. 3 corresponds to a very slow diffusion of oxygen as for instance occurs in marine concrete completely and permanently submerged in sea water and then with a water saturated cement paste. In such a case the corrosion process is negligible.

The corrosion rates **II** and **III** correspond to marine concretes not permanently submerged in sea water and then exposed to both the diffusion chloride ions and penetration of humid air needed to feed the corrosion according to the process [2]. In particular the most severe corrosion rate **III** corresponds to a marine concrete in the splashing or tidal zone and then exposed to chloride penetration, discontinuous oxygen diffusion and intermittent presence of water.

In order to completely remove the corrosion risk at least for the period of time (t_d) expected for a durable concrete, the dormant period time must be increased from t_1 in the situation A to t_2 in the situation B of Fig. 3, so that $t_2 \geq t_d$ .This change can occur either by increasing the concrete cover, that is path way of chloride ions from the environment to the metallic reinforcement, or by reducing the water-cement ratio and then the interconnected porosity of the cement paste. An alternatively way to reduce the corrosion rate to a negligible extent is the use of the more expensive stainless steel.

Prevention of corrosion in concrete structures in marine environment

The diffusion of chloride ions trough the concrete capillary pores occurs according the second Fick's law (4):

$$\partial C / \partial t = D (\partial^2 C / \partial x^2) \qquad\qquad [3]$$

Where C is the chloride content at the time t in the concrete depth (x) penetrated by chloride and D is the diffusion coefficient of Cl^- ions through the concrete and

it depends on its the permeability. When the concentration of chloride on the concrete surface is constant, the penetrated concrete depth (x) is related with the square root of the time (t) and the diffusion coefficient (D) through the following linear equation (4):

$$x = 4 \cdot (D \cdot t)^{1/2} \qquad \qquad [4]$$

According to the equation [4] the extrapolated penetration (x) at longer times can be easily determined due to the linear trend of x as function of $\sqrt{t}$. Figure 4 shows the influence of the *w/c* on the diffusion of Cl⁻ ions into 28-day wet cured concretes manufactured with 350 kg/m^3 of portland cement and permanently immersed in sea water for about 3 years. The *w/c* of the control concrete mixture without superplasticizer is 0.60 and can be reduced to 0.45 by or to 0.30 by using respectively 0.8% or 1.4% of a policarboxylate-based superplasticizer by weight of cement. Therefore superplasticizers can significantly decrease the corrosion rate of reinforcing bars since a lower *w/c* reduces the penetration of Cl⁻ ions into the concrete surface in contact with a chloride source as that of sea water (2). Table 1 shows the extrapolated time (from Fig.4) which is needed for chloride ions of sea water to penetrate a concrete cover of 40 mm. The adoption of a *w/c* as low as 0.30 increases up to 65 years the time of penetration of a concrete cover of 40 mm.

The use of a cementitious material based on the partial replacement of portland cement by pozzolanic additions such as fly ash, granulated ground blast furnace slag or silica fume further reduces the chloride diffusion through the concrete cover (4). Figure 5 shows that, at a given water-cement ratio of 0.45, 10% of silica fume appears to be much more effective than 25 % of fly ash or ground blast furnace slag in reducing the Cl⁻ penetration with respect to the control concrete mixture containing 350 kg/m^3 of portland cement. However, the replacement of portland cement by both fly ash (25%) and ground blast furnace slag (25%) performs even better than 10% of with silica fume which is very expensive and not easily available. Table 2 shows the extrapolated time (from Fig. 5) which is needed for Cl⁻ to penetrate 40 mm of concrete with a *w/c* of 0.45. The combined use of fly ash and slag (both replacing 25% of portland cement) significantly increases (from 5 to 170 years) the time needed to penetrate a concrete cover of 40 mm.
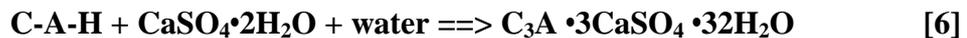
The influence of the pozzolanic additions on the chloride penetration exposed to sea water can be ascribed to the pore refinement of the cement paste which reduces the interconnected porosity and then the water permeability of the concrete structures. Moreover, the addition of the pozzolanic additions increase the electrical resistivity of the concrete (5) and this could cause a further retard in the diffusion of all the ionic species, including Cl⁻, through the capillary pores of the cement paste.

Therefore the two following measures should be adopted to prevent the corrosion in *RCS* in a marine environment: a) use of superplasticizers to reduce the porosity of the cement paste; b) use of pozzolanic additions to further reduce the interconnected porosity and to increase the electrical resistivity. Moreover, the

increase in the thickness depth of the concrete cover increases the path of chloride ions from the marine environment to the metallic reinforcements and therefore improves the long term durability of *RCS* exposed to sea water.

SULFATE ATTACK

The sulfate attack is based on the formation of gypsum ($CaSO_4 \cdot 2H_2O$) produced by reaction [5] of sulfate ion with $Ca(OH)_2$ of the hydrated portland cement and that of the subsequent expansive formation of ettringite ($C_3A \cdot 3CaSO_4 \cdot 32H_2O$) produced by reaction of gypsum with the calcium aluminate hydrates (C-A-H) of the hardened cement matrix in the presence of water [6]:

$$SO_4^= + Ca(OH)_2 + H_2O ==> CaSO_4 \cdot 2H_20 \qquad [5]$$

$$C\text{-}A\text{-}H + CaSO_4 \cdot 2H_2O + water ==> C_3A \cdot 3CaSO_4 \cdot 32H_2O \qquad [6]$$

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 3). This happens when ground gypsum reacts with anhydrous calcium aluminates within some hours (set regulation) or when a calcium aluminate sulfate ($4CaO \cdot 3Al_2O_3 \cdot SO3$) 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 3).

There are two different types of *DEF*-related damage depending on the sulfate source (Table 4): external or internal sulfate attack. According to the terminology currently used "*DEF*" is related only to the internal sulfate attack in a sulfate-free environment. However, more correctly **delayed** ettringite formation means that ettringite forms **later** independently of the sulfate source (6,7).

In a concrete marine work the external sulfate attack (*ESA*) certainly occurs when the *environmental sulfate* (from sea water) penetrates the porous concrete.

Internal sulfate attack (*ISA*) occurs in a sulfate-free environment for the *late sulfate release* from either gypsum-contaminated aggregates or to a lower extent to sulfur-rich clinker phase (4). *ISA* may occur in a marine concrete structure as well as in all the other concrete works where gypsum-contaminated aggregates or sulfur-rich clinker are used. Therefore, *ISA* is not really related to any specific aggressive agent of the sulfate in sea water.

Figures 6 and 7 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:

- **Microcracking**

- **Late sulfate release**

- **Presence of water**

The positive role played by superplasticizers in reducing the *w/c*, and then the interconnected porosity of the cement matrix (8), is more important for the *ESA* than for the *ISA* since a lower porosity of the cement paste significantly retards the penetration of $SO_4^=$ ions from the environment into a less permeable concrete and consequently reduces the corresponding *DEF*-related damage. On the other hand, *ISA* may occur -to a lower extent- even in superplasticized concretes with very low *w/c* since sulfate is already available into the concrete and needs only microcracks -formed for some reasons on the concrete surface (Fig.7)- to feed water needed the delayed deposition of ettringite.

In some special marine environments where the temperature is permanently lower than 10 °C, as in The North Sea of Norway, the ettringite formation in a concrete structure, according to reaction [5], may be replaced by the more aggressive formation of thaumasite ($CaSiO_3 \cdot CaSO \cdot CaCO_3 \cdot 15 H_2O$ according the reaction [7] :

$$\textbf{C-S-H+CaSO}_4 \textbf{·2H}_2 \textbf{0+CaCO}_3 \textbf{+water => CaSiO}_3 \textbf{·CaSO}_4 \textbf{·CaCO}_3 \textbf{·15 H}_2 \textbf{O} \quad \textbf{[7]}$$

where C-S-H is the calcium silicate hydrate mainly responsible for the strength of the cement paste. Due to the disappearance of C-S-H, the thaumasite formation is accompanied by a complete breakdown of the concrete. However, thaumasite does not form in all the marine environments where the temperature is higher than 10 °C.

Besides water-reducing admixtures such as superplasticizers, pozzolanic additions in form of silica fume, fly ash and/or blast furnace slag can significantly reduce the sulfate attack (8). This effect seems to be based on both a chemical and a physical effect: in the presence of pozzolan there is a change in the chemical composition of the cement matrix due to the reduction of $Ca(OH)_2$ and then in the potential formation of gypsum according the reaction [5]; moreover, due to the additional formation of C-S-H as a consequence of pozzolanic reaction, there is physical change of the cement matrix due to its pore refinement and then to a lower permeability to environmental aggressive agents including sulfate. Therefore the following two measures should be adopted to manufacture *RCS* exposed to the sulfate attack of sea water: a) use of superplasticizers to decrease the *w/c* by and then to reduce the interconnected porosity; b) use of pozzolanic additions to reduce both the interconnected porosity and the $Ca(OH)_2$ content of the cement paste in order to decrease the risk of gypsum formation precursor of

the sulfate attack. So, these two products are the same as those adopted to protect the *RSC* from corrosion of the metallic bars.

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 (9) 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 as in sea water.

The three elements needed for the *ASR* (Fig. 8) are:

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

Superplasticizers can mitigate the damaging effect of *ASR* of alkali-reactive aggregates, if any, by reducing the concrete permeability and then the penetration of sea water containing sodium salts. 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.

Therefore, the use of both superplasticizers and pozzolanic materials is again the best way to prevent *ASR* in a marine concrete in case it contains alkali-reactive aggregate.

CONCLUSIONS

A holistic approach for the deterioration of marine reinforced concrete structures has been proposed through a ternary representation of the damage process determined by the co-existence of the following three elements:

- interconnected porosity
- exposure to aggressive agents
- presence of water

The following events of deterioration in concrete structures exposed to a marine environment were examined by using this ternary representation:

- corrosion of the reinforcing bars caused by chloride ions;
- break-down of the cement paste caused by the sulfate attack;
- alkali-silica reaction causing disruptive expansion of the aggregate.

Corrosion of reinforcing bars, sulfate attack of the cement paste, and alkali-silica reaction of reactive alkali-aggregate reaction promoted by the penetration of ions from the sea water can be significantly reduced by lowering the *w/c* through the use of superplasticizers, which causes a decrease in the porosity of the cement paste and then a lower concrete penetration by all the aggressive agents from a marine environment.

The partial replace of portland cement by pozzolanic additions such as silica fume, fly ash and blast furnace slag can further mitigate the aggressive action of chloride, sulfate and alkali ions all coming from a marine environment.

Moreover, a further measure to specifically protect the *RCS* from the corrosion of the metallic reinforcements is the increase in the thickness of the concrete cover due to a longer path of concrete which must be completely penetrated by chloride ions of the marine environment.

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Table 1 – Influence of the w/c on the penetration time of 40 mm of concrete by Cl⁻

w/c	Time
0.60	7 months
0.45	5 years
0.30	65 years

Table 2–Influence of pozzolans on the penetration time of 40 mm of concrete by Cl⁻

Concrete Mixture	Time (years)
Control	5
25% fly ash	15
25% slag	25
10% silica fume	65
25% fly ash + 25% slag	170

Table 3 – Early and delayed ettringite formation
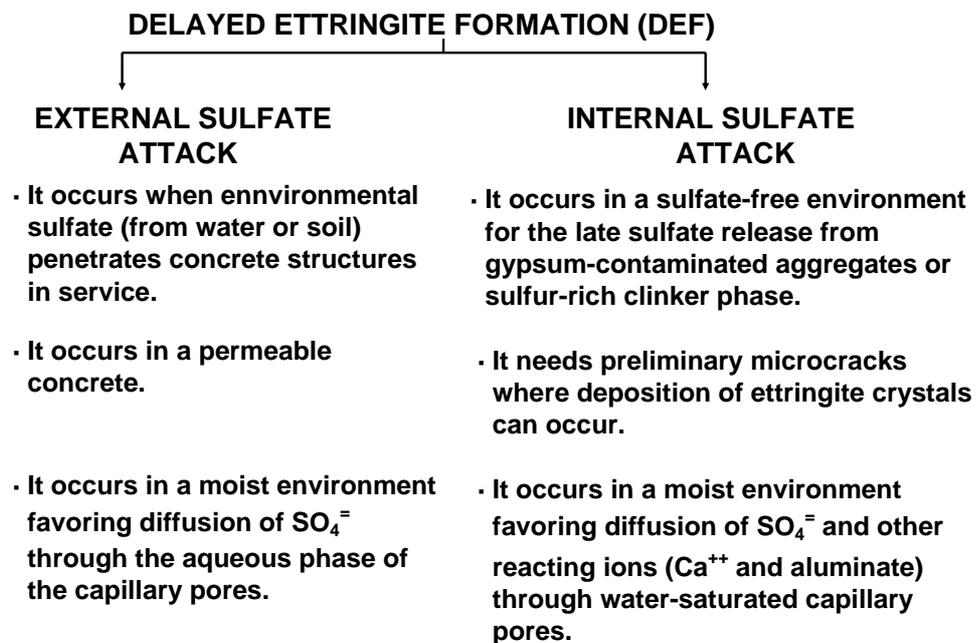
ETTRINGITE FORMATION

EARLY ETTRINGITE FORMATION (EEF):

· It occurs homogeneously and immediately (within hrs or days).

· The related expansion does not cause a localized and disruptive action since it occurs in a fresh mixture or 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.

DELAYED ETTRINGITE FORMATION (DEF):

· It occurs heterogeneously and later (after months or years)

· The related expansion causes 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 4 – Delayed ettringite formation by external and internal sulfate attack

DELAYED ETTRINGITE FORMATION (DEF)

EXTERNAL SULFATE ATTACK	INTERNAL SULFATE ATTACK
· It occurs when ennvironmental sulfate (from water or soil) penetrates concrete structures in service.	· It occurs in a sulfate-free environment for the late sulfate release from gypsum-contaminated aggregates or sulfur-rich clinker phase.
· It occurs in a permeable concrete.	· It needs preliminary microcracks where deposition of ettringite crystals can occur.
· It occurs in a moist environment favoring diffusion of $SO_4^=$ through the aqueous phase of the capillary pores.	· It occurs in a moist environment favoring diffusion of $SO_4^=$ and other reacting ions (Ca^{++} and aluminate) through water-saturated capillary pores.

DAMAGE OF REINFORCED CONCRETE STRUCTURES (RCS)

INTERCONNECTED POROSITY (PERMEABILITY)

· capillary pores (high w/c and poor curing)
· macrovoids (low w/c and unproper compaction of fresh concrete related to its inadequate workability)
· microcracks (loadings in service and cyclic heating/cooling or wetting/drying)

DAMAGE OF RCS

PRESENCE OF WATER

· moist environment

EXPOSURE TO AGRESSIVE AGENTS

· air (O_2, CO_2)
· $SO_4^=$, Cl^- and alkali ions

Fig. 1 – Ternary representation of the damage of RCS

CORROSION OF REINFORCING BARS:
$$2Fe+2H_2O+O_2 \rightarrow 2Fe(OH)_2$$

DEPASSIVATION OF STEEL

Concrete permeability and then penetration of:
· Cl^- ions (from sea water or de-icing salts): pitting corrosion
· CO_2 (from air): reduction in the pH (<11) of cement matrix

· discontinuous exposure to water and humid air

CORROSION

INTERMITTENT PRESENCE OF WATER
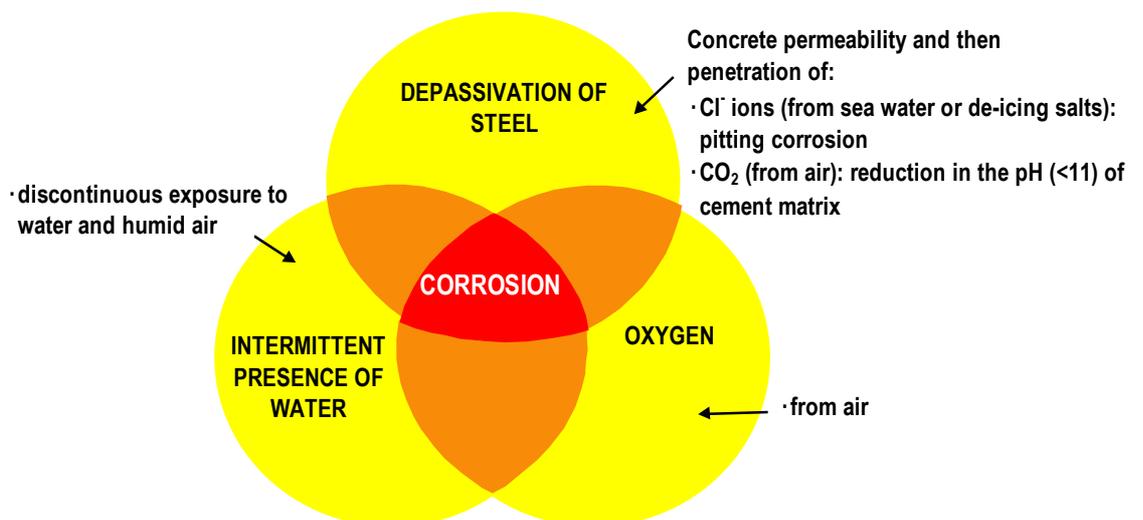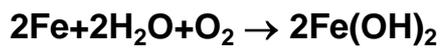
OXYGEN

· from air

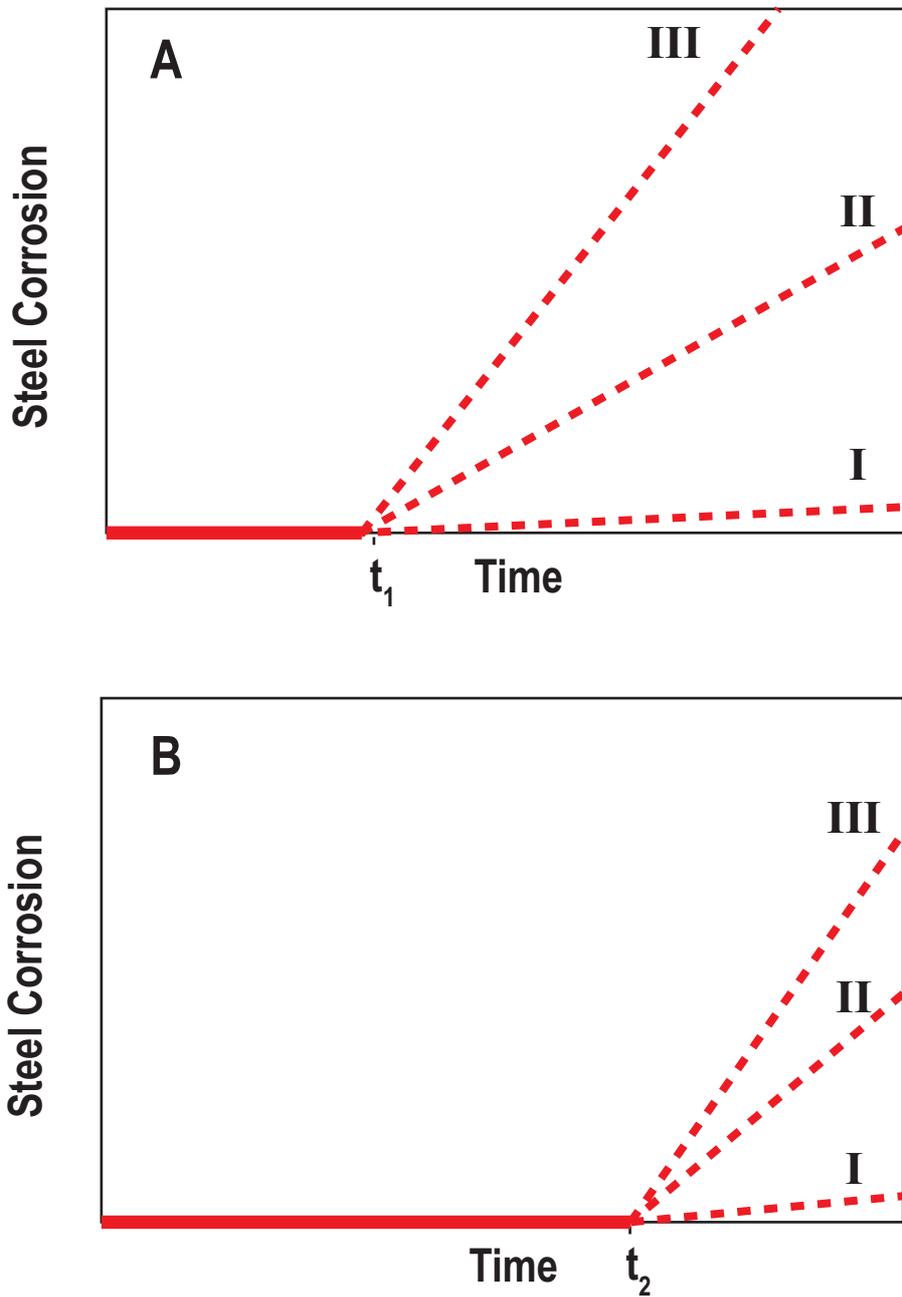**Fig. 2 – Ternary representation of the corrosion process in RCS**

Fig. 3 – Schematic trend of the steel corrosion in reinforced concrete structures according to the model of Tuutti (3)
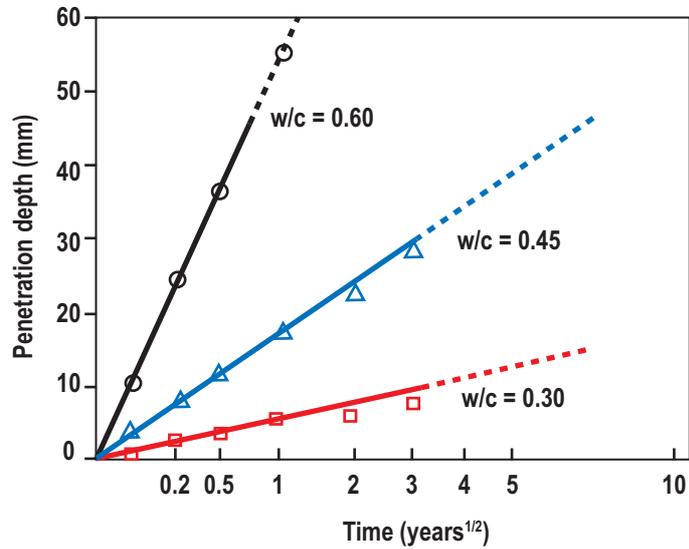
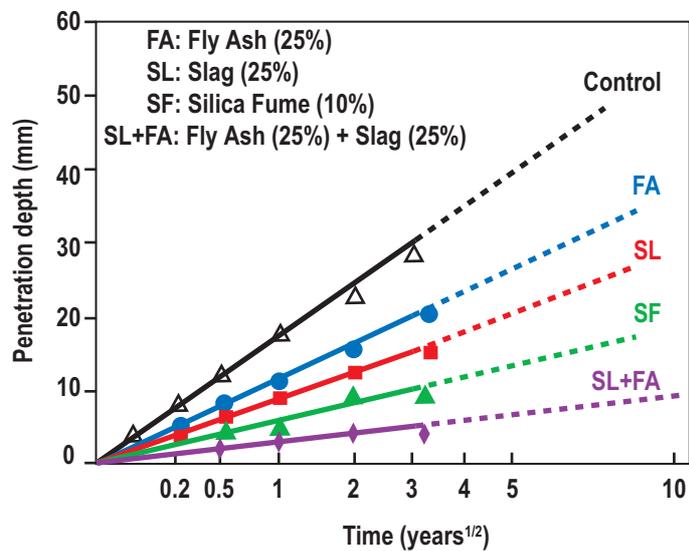**Fig. 4 – Influence of w/c on the chloride penetration into 28-day wet cured concretes**

Fig. 5 – Influence of mineral addition on the chloride penetration in 28-day wet cured concretes with w/c = 0.45. Control mix contains 350 kg/m^3 of portland cement.
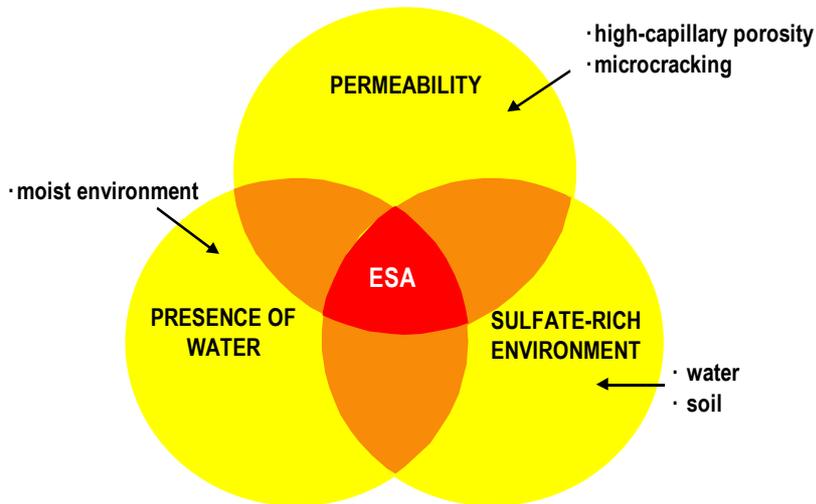
DEF RELATED TO EXTERNAL SULFATE ATTACK (ESA)

·high-capillary porosity
·microcracking

PERMEABILITY

·moist environment

ESA

PRESENCE OF WATER

SULFATE-RICH ENVIRONMENT

· water
· soil

Fig. 6 – Ternary representation of DEF related to external sulfate attack (ESA) of concrete

DEF RELATED TO INTERNAL SULFATE ATTACK (ISA)

·restrained thermal & drying shrinkage
·high temperature steam curing
·alkali-silica reaction
·loading in service
·excessive and non-uniform stress
 distribution in prestressed RCS

MICROCRACKING

·moist environment

ISA

PRESENCE OF WATER

LATE SULFATE RELEASE

·sulfur-rich clinker phase
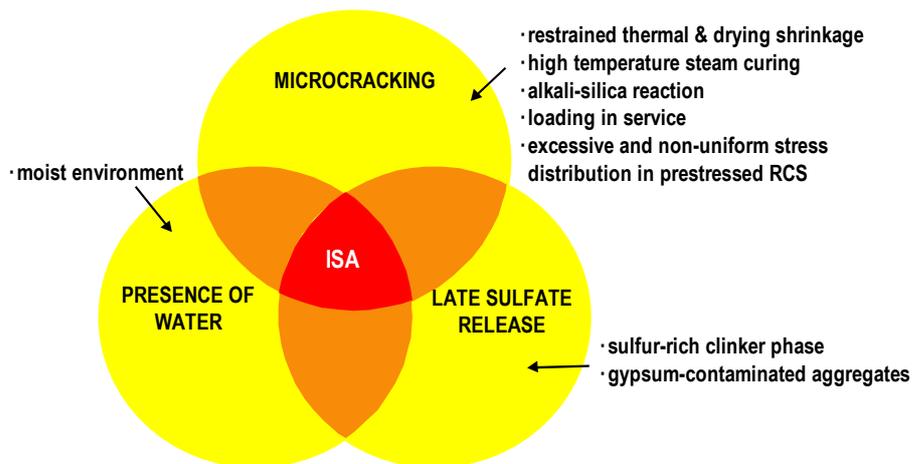·gypsum-contaminated aggregates

Fig. 7 – Ternary representation of DEF related to internal sulfate attack (ISA) of concrete
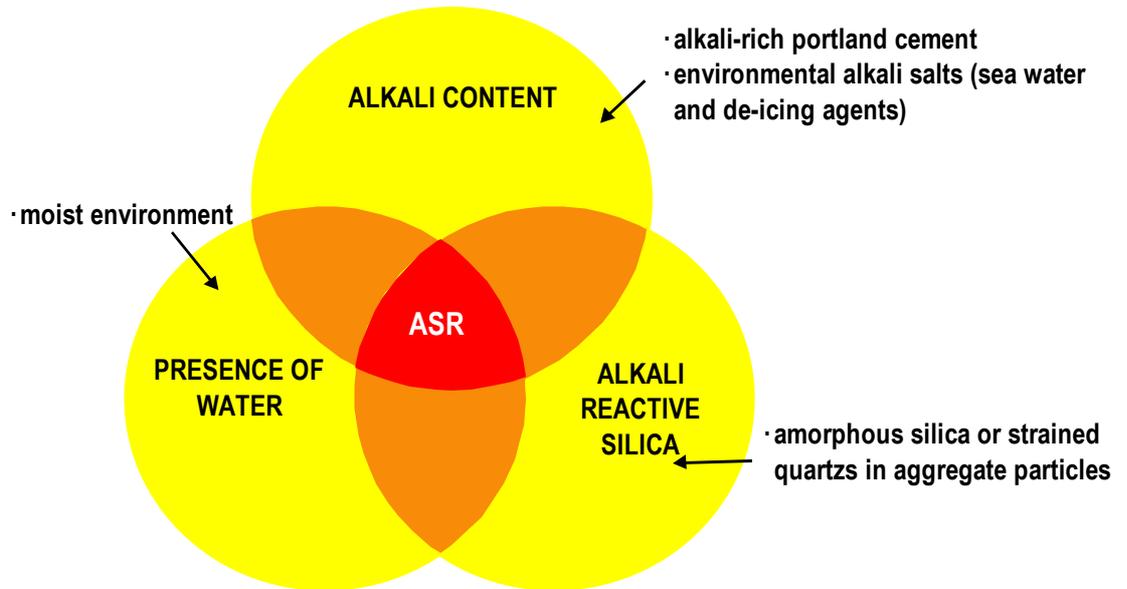
ALKALI-SILICA REACTION (ASR)

Fig. 8 – Ternary representation of concrete damage caused by alkali-silica reaction (ASR)