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EXTERNAL SULFATE ATTACK ON CONCRETE

Abstract: Durability of concrete may be defined in different ways one of them is that it is the ability of concrete to resist weathering action, chemical attack, and abrasion while maintaining its desired engineering properties. Many factors determine the durability of concrete and its life such as: concrete ingredients, their proportioning, interactions between them, placing and curing practices, and the service environment. Concrete is resistant to most natural environments and many chemicals. However, concrete is sometimes exposed to substances that can attack and cause deterioration. For example, sulfates can attack concrete by reacting with hydrated compounds in the hardened cement paste. Sulfate attack on concrete structures in site is a very complex process due to its complex behaviour and the overlapping of several phenomena simultaneously

Key words: concrete, durability, chemical process, sulfate attack, Na_2SO_4, $MgSO_4$

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1. DURABILITY OF CONCRETE

Concrete durability can be defined as the ability of concrete to resist to the attack of environmental, physical and chemical aggressive conditions, through the time. A concrete structure should be able to maintain the expected performance during its service life [1].

The durability and service life of a concrete structure is determined by the interaction between the structure and its environment. Depending of the type and importance of the structure, its service life may be between 10 and 100 years and more (

Table 1) [2].

Table 1- Design service life of structures [2]

Design service life t_{SL} [years]	Examples
10	Temporary structures (structures of parts of structures that can be dismantles with a view to being re-used should not be considered as temporary)
10-25	Replaceable structural parts, e.g. gantry girders, bearings
15-30	Agricultural and similar structures
50	Building structures and other common structures
100	Monumental building structures, bridges, and other civil engineering structures

Concrete structures designed and built in accordance with the current codes of practice with regard to materials characteristics, architectural and structural design, processes of execution, inspection and maintenance procedures, normally do not deteriorate prematurely. However, some older and some new concrete structures show (or will show) decreased durability due to insufficient cover to the reinforcement, porous concrete, reactive aggregates or faulty design [2]. If the aggressiveness of the structure's environment has not been adequately identified and dealt with during the design and construction process, premature deterioration may render the structure unfit to serve its purpose [2].

It has become evident that all deterioration mechanisms depend upon an aggressive substance penetrating from the surrounding environment into the outer layer of concrete – the cover, so it is the essential about concrete durability is related to the intrinsic properties of this material. Knowing and understanding the transport mechanisms of liquid and gaseous substances into and within concrete structures is, therefore, the most important element in ensuring sufficiently durable concrete structures. This is also the fundamental basis for quantifying durability in the form of service life performance [2].

Figure 1 shows what it is important for permeability and durability of concrete [1]. Generally, it is known that higher permeability allows water and aggressive elements to enter leading to different type of attack in concrete.

In addition to permeability, there are a number of other parameters that affect the durability of concrete (for instance composition and proportion of component materials in concrete, curing of concrete, exploitation conditions and many others).
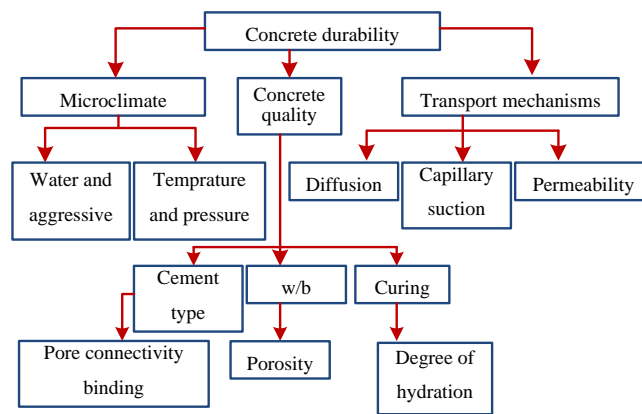

Figure 1 – Concrete durability [1]

The development of nearly all types of deterioration mechanism can be modelled by a two-phase curve as illustrated in Figure 2. This is the basis for defining the service life of a structure [2].
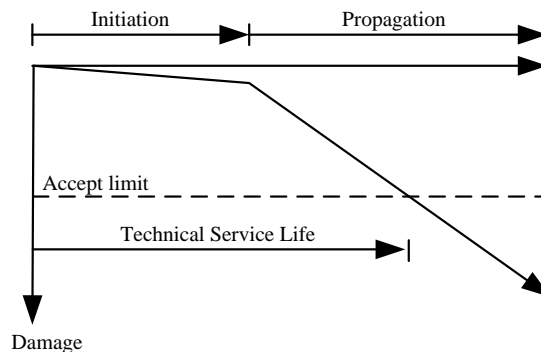

Figure 2 – The service life of concrete structures. A two-phase modelling of deterioration [2]

1. The initiation phase.

During this phase no noticeable weakening of the material or reduction in the function of the structure occurs, but some of the protective barrier is broken down or overcome by the aggressive media.

2. The propagation phase.

During this phase an active deterioration develops and loss of function is observed. A number of deterioration mechanisms develop with time at an increasing rate.

For the majority of ordinary structures placed in aggressive environments a conscious choice of cement type, concrete mix (especially w/c ratio), concrete cover, curing (moisture and temperature control) and geometry of the exposed parts of the structure, will normally result in a satisfactory service life [2].

The deterioration of concrete structures includes mechanical, chemical, physical process or combination of them (Figure 3) [2].
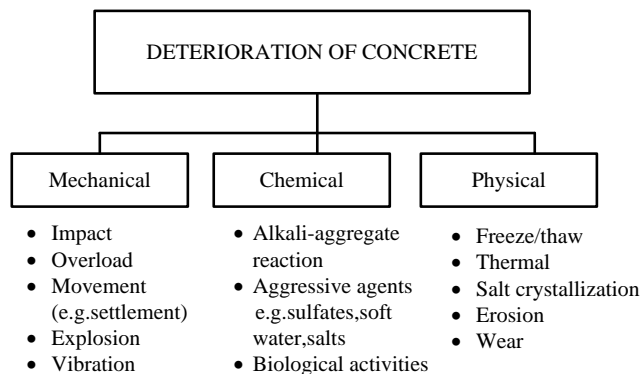
Figure 3 – Common causes of deterioration of concrete structures [2]

In this paper the emphasis is on the chemical attack on concrete structures.

2. CHEMICAL PROCESSES

Well-designed and constructed concrete will perform satisfactorily when exposed to most atmospheric conditions, most soils and many kinds of chemicals. However, in some chemical environments the useful life of even the best concrete will be shortened unless specific measures are taken. For significant attack to occur, the chemical must be in solution and sufficiently concentrated or reach a critical concentration after evaporation of the solution.

The most important the chemical reactions which lead to a decrease in quality and to increased deterioration of the concrete are [2]:

- Reduction of the pH value of the concrete due to carbonation;
- Reaction of alkalis with reactive aggregates in the concrete;
- Reaction of sulfates with the aluminates in the cement;
- Reaction of acids, ammonium salts, magnesium salts and soft water with hardened cement;
- Effects of biological activities.

According to EN 206-1 the environmental actions are classified as exposure classes and for chemical attack designed classes are XA1, XA2 and XA3 (Table 2). Another table in EN 206-1 (Table 3) shows limiting values for each of these classes (XA1, XA2 or XA3).

Table 2- Classes for chemical attack according to EN 206-1

Chemical attack		
XA1	Slightly aggressive chemical environment	Concrete exposed to natural soil and ground water according to Table 2
XA2	Moderately aggressive chemical environment	Concrete exposed to natural soil and ground water according to Table 2
XA3	Highly aggressive chemical environment	Concrete exposed to natural soil and ground water according to Table 2

Table 3- Limiting values for exposure classes for chemical attack from natural soil and ground water

Chemical characteristic	Reference test method	XA1	XA2	XA3
Ground water				
SO_4^{2-} mg/l	EN 196-2	≥ 200 and ≤ 600	> 600 and $\leq 3\ 000$	$> 3\ 000$ and $\leq 6\ 000$
pH	ISO 4316	$\leq 6,5$ and $\geq 5,5$	$5,5$ and $\geq 4,5$	$< 4,5$ and $\geq 4,0$
CO_2 mg/l aggressive	EN 13577	≥ 15 and ≤ 40	> 40 and ≤ 100	> 100 up to saturation
NH_4^+ mg/l	ISO 7150-1	≥ 15 and ≤ 30	> 30 and ≤ 60	> 60 and ≤ 100
Mg^{2+} mg/l	EN ISO 7980	≥ 300 and $\leq 1\ 000$	$> 1\ 000$ and $\leq 3\ 000$	> 3000 up to saturation
Soil				
SO_4^{2-} mg/kg[a] total	EN 196-2[b]	$\geq 2\ 000$ and $\leq 3\ 000$[c]	$> 3\ 000$c and $\leq 12\ 000$	> 12000 and ≤ 24000
Acidity according to Baumann Gully ml/kg	prEN 16502	> 200	Not encountered in practice	

a Clay soils with a permeability below 10−5 m/s may be moved into a lower class.
b The test method prescribes the extraction of SO4 2– by hydrochloric acid; alternatively, water extraction may be used, if experience is available in the place of use of the concrete.
c The 3 000 mg/kg limit shall be reduced to 2 000 mg/kg, where there is a risk of accumulation of sulfate ions in the concrete due to drying and wetting cycles or capillary suction.

The most common forms of chemical attack of concrete stone are:

- Sulfate attack
- Clorides attack
- Acids attack
- Other substances

At this point accent is on the sulfate attack.

3. SULFATE ATTACK

Sulfate attack is one of the durability problems associated with concrete. Sulfate attack has often been discussed in terms of the reaction between solid hydration products of cement and sulfate ions in solution. The source of sulfate ions are soil, groundwater, rivers, seawater, cooling towers, industrial wastes, in combination with cations such as sodium, potassium, magnesium and calcium ions [3].

It has been difficult to define the precise nature of the mechanisms of sulfate attack because of its complex behaviour and numerous overlaping reactions [3]. The major problem in assessing materials is that the form of attack in sulfate environments is variable [4]. The extent to which concrete is affected by sulfates depends on several factors such as permeability of concrete, water/cement ratio, type of cement (i.e. cement composition), exposure conditions, cation type in sulfate salts, sulfate ions concentration, the environment and exposure period. The microstructure of the concrete is changed under this attack. These changes may vary in the type of severity, but they commonly include chemical sulfate attack and physical attack caused by salt crystallization in pores [5][6]. Cracking, expansion and loss of bond between the cement paste and aggregate are common damages. The expansion resulting from sulfate attack is generally attributed to the formation of gypsum and ettringite, although there is some controversy surrounding the exact mechanisms causing the expansion [7][8][9].

The conversion of the hydration products of cement to the harmful products such as ettringite, gypsum and thaumasite additionally leads to decalcification of calcium silicate hydrate (C-S-H) that causes weakening of the paste [10][11]. This attack is very complex and it may be gradual, but it can cause serious damage to concrete structures [6][12].

In numerous literature sources, sulfate attack is categorized into **chemical** versus **physical** and into **internal** versus **external**.

Example of chemical sulfate attack is formation of ettringite and gypsum. The reaction is known to result in an increase in solid volume of the system, and may or may not lead to the expansion of concrete. The so-called physical sulfate attack, often called also sulfate salt crystallization or salt hydration distress, usually refers to formation of sodium sulfate decahydrate, $Na_2SO_4 \cdot 10H_2O$, followed by its repeated recrystallization into sodium sulfate anhydrite, Na_2SO_4, and vice versa. The term physical does not seem to be correct in characterizing this reaction, as hydration and dehydration of sodium sulfate, not unlike portlandite or ettringite or gypsum formation, are chemical processes – chemical processes with physical consequences. The physical and chemical aspects of action of sulfate on concrete cannot be clearly separated.

Internal sulfate attack refers to situations where the source of sulfate is internal to concrete. The source of sulfate can be the cement, supplementary materials such as fly ash or slag, the aggregate, the chemical admixtures, or the water.

External sulfate attack is caused by a source external to concrete. Such sources include sulfates from ground water, soil, solid industrial waste, and fertilizers, or from

atmospheric SO_3, or from liquid industrial wastes. In literature, the greatest attention has been paid to this type of attack.

Depending on the quality of the concrete and the environmental conditions, a complex mechanism of sulfate action can cause various chemical and physical changes in the concrete. Some of chemical changes include [13]:

- Removal of Ca^{2+} from certain hydration products (decomposition of portlandite/calcium-hydroxide (CH) and C-S-H) – leaching;
- Changes in the ionic composition of the pore liquid phase;
- Formation of hydrous silica (silica-gel);
- Decomposition of still unhydrated clinker components;
- Decomposition of previously formed hydration products;
- Formation of gypsum, ettringite, thaumasite;
- Formation of magnesium compounds, such as magnesium hydroxide ($Mg(OH)_2$)-brucite and magnesium silico-hydrate (M-S-H);
- Penetration into concrete of sulfate anions and subsequent formation and repeated recrystallization of sulfate salts (for example $NaCl$, K_2SO_4, $MgSO_4$).

These chemical changes are also associated with physical changes:

- Complete alteration of the pore structure and microstructure of the solid phase;
- Increase in porosity and permeability;
- Volume expansion and the appearance of micro-cracks;
- Surface swelling, spalling, exfoliation;
- Softening of paste;
- Formation of salt deposits on the surface and exfoliation in cracks;
- Loss of strength;
- Reduction of modulus of elasticity.

Generally, the basic mechanisms for the detrioration of concrete due to the action of sulfate may be classified as:

1. Volume changes

Expansion as a result of the formation of new products under the sulfate attack is only possible if the sulfates are in the dissolved state. The reactions form a significantly larger volume of solid phases which cannot be accommodated by the capacity of the pore system. Internal stresses increase and the concrete swells and then cracks. The expansion does not have to cause deterioration if the concrete has the capacity to withstand these changes. Also, the expansion depends on how many water molecules are absorbed by the new products.

2. Decomposition of compounds

The sulfate attack may cause the decomposition of cement hydration products such as C-S-H and CH as they become unstable due to the decrease in pH.

3. Salt exfoliation

Deposits of different salts can occur not only on the surface but also in the inside of the concrete element, which is exposed to sulfate. The solubility of salts such as Na_2SO_4 and $MgSO_4$ increases significantly with increasing temperature. The pores in concrete can be saturated with salt solution when the temperature drops, e.g. during the night, salt crystals can also grow rapidly and cause pressure on the interior of the concrete. Also, the salt solution may suddenly crystallize due to the vibration, e.g. passing traffic.

The most commonly occurring salts for sulfate resistance tests are sodium sulfate (Na_2SO_4) and magnesium sulfate ($MgSO_4$), as these salts most commonly occur in the water and soil that surround the concrete structure. These cation types (Na^+ or Mg^{2+}) related to sulfate ions define the mechanism of attack and significantly influence concrete deterioration [6].

3.1. SULFATE ATTACK WITH Na_2SO_4

Sodium sulfate (i.e. sulfate ion) reacts with hydration products of cements, resulting in the formation of ettringite ($3CaO·Al_2O_3·3CaSO_4·32H_2O$) and gypsum ($CaSO_4·2H_2O$). The provision of Ca^{2+} ions, necessary for ettringite and gypsum formation, is supplied by portlandite (CH) or by decalcification of C-S-H gel. Decalcification of C-S-H gel affects the loss of bonding and it is very dangerous. Gypsum is usually formed under mortar/concrete surface. In this region, aluminium ions are primarily consumed for the formation of ettringite and, therefore, sulfate ions can react only with the remained calcium ions [11] and form gypsum. The most common reactions that occur between cement components and Na_2SO_4 are shown in the Figure 4.
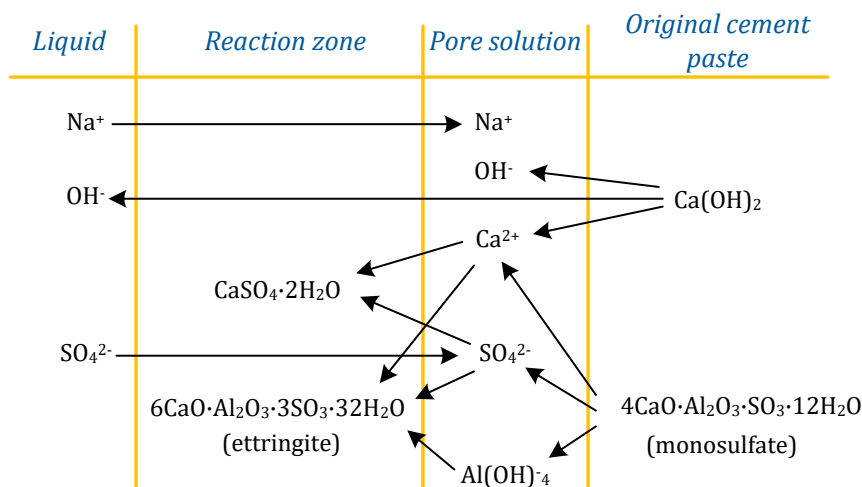

Figure 4-Reactions taking place between Portland cement components and sodium sulfate solution

3.2. SULFATE ATTACK WITH MgSO$_4$

The interaction of ion species from MgSO$_4$ solution and hydration products of cements gives M-S-H gel and brucite (Mg(OH)$_2$) in addition to gypsum and ettringite, which are common reaction products in both solutions (Na$_2$SO$_4$, MgSO$_4$). M-S-H gel does not have binding capacity. In the presence of brucite, decalcification of C-S-H gel is more prominent due to brucite low solubility [14]. The saturated solution of brucite has a pH of 10.5, which is too low to maintain the stability of C-S-H, and the stability of calcium aluminate sulfate [6].The reaction of MgSO$_4$ with calcium hydroxide is also followed by the formation of brucite layer on the specimen surface and gypsum under it. The most common reactions that occur between cement components and MgSO$_4$ are shown in the Figure 5.
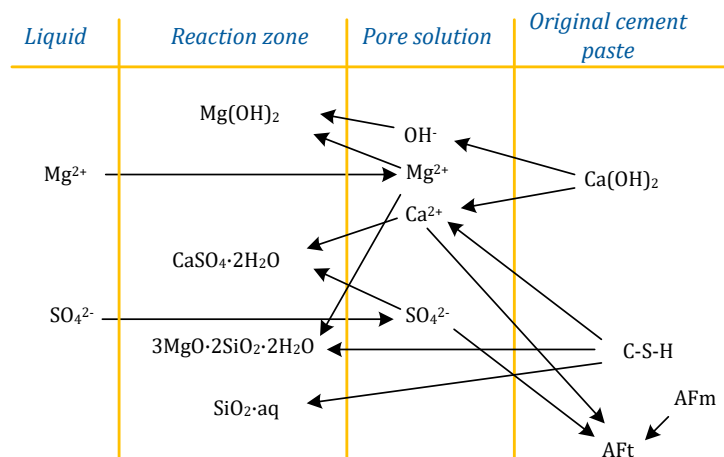

Figure 5-Reactions taking place between Portland cement components and magnesium sulfate solution.

3.3. RECOMMENDATIONS FOR IMPROVING SULFATE RESISTANCE

To mitigate this attack, concrete codes (EN 206-1) recommend a maximum value of w/c ratio, minimum value of compressive strength, minimum amount of cement and type of cement (Table 4).

Table 4- Recommendation limiting values for composition and properties of concrete exposed to chemical attack according to EN 206-1

Class of chemical attack	Max w/c	Min strength class	Min cement content (kg/m^3)	Other requirements
XA1	0.55	C30/37	300	
XA2	0.50	C30/37	320	Sulfate-resisting cement
XA3	0.45	C35/45	360	

With the exception of official codes, researchers in the field of sulfate attack have come to the conclusion, from the experience of examining this phenomenon, that

measures other than those included in the official standards can be taken to increase the resistance of concrete to the attack of sulfate:

- Adequate thickness of the structural elements;
- Proper installation and curing of concrete (for example short-term air exposure);
- Application of the sulfate-resistant or mixed cement (less CH, aluminum bonding for mineral addmixtures and does not later participate in the formation of ettringite, different content of C-S-H, reduction of porosity);
- A small increase in gypsum initially that can bind aluminum to itself at the onset of hydration.

It is very important to consider the cation that is involved in the reaction when choosing the appropriate material, if possible.

Slag is recognized as an efficient Supplementary cementitious material (SCM) in improving the sulfate resistance, particularly at a higher level of cement replacement, as in the case of CEM III. Slag hydrated products are similar to Portland cement one [15]. The most abundant is C-S-H with modified morphology [16] and lower C/S ratio than in PC. Due to this C/S ratio, the degree to which aluminium replaces silicon is high. Additionally, hydrotalcite-like phase is formed. If the replacement level of Portland cement with slag in slag-blended cements increases, the amount of monosulfate, ettringite and CH decreases [17]. A lowered availability of these compounds can reduce the damage caused by sulfate attack due to a direct reduction in the quantity of ettringite and gypsum [9][18]. Their formation extent is limited due to the lack of Ca^{2+} ion and due to the lack of aluminium ions forming monosulfate, the only one that can form ettringite. Namely, a part of aluminium ions are included into hydrotalcite or C-S-H gel structures, so the rest is enough to form only a small amount of monosulfate or ettringite. Also, slag can refine the pore size distribution and reduce the pore connectivity in mortar/concrete, which also contributes to the overall durability of concrete.

3.4. VISUAL APPEARANCE

The effects of sulfate attack on concrete structures in real conditions can be seen in the Figure 6 and Figure 7:
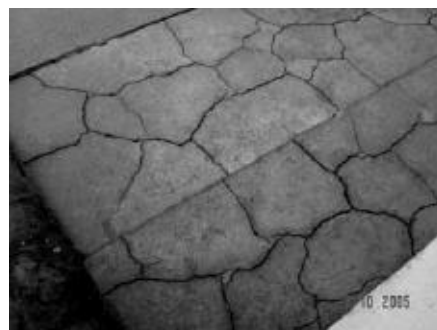

Figure 6-Railroad tiles [6]

Figure 7-Concrete block [2]

The structure of concrete at the micro (Figure 8 and Figure 9) and macro levels (Figure 10 and Figure 11), after testing in the laboratory, is shown in the following figures.
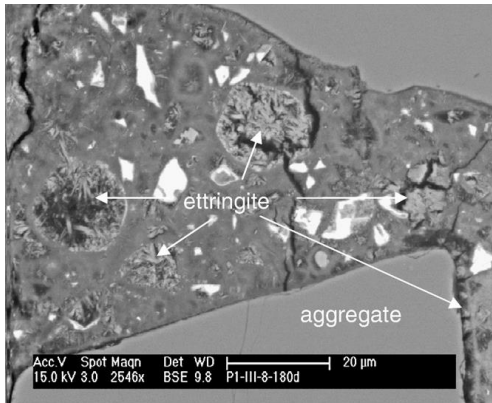

Figure 8-SEM image of samples exposed to Na$_2$SO$_4$ [19]
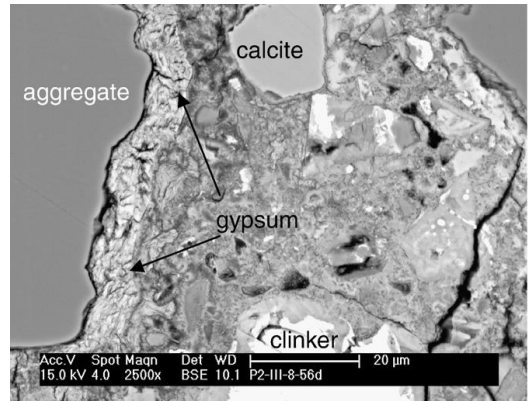

Figure 9-SEM image of samples exposed to Na$_2$SO$_4$[19]

Figure 10-Appearance of samples exposed to Na$_2$SO$_4$

Figure 11-Appearance of samples exposed to MgSO$_4$

4. CONCLUSION

Sulfate attack on concrete structures in site is a very complex process due to the overlapping of several phenomena simultaneously. The environment never has the same conditions, which makes it difficult to examine this phenomenon and to choose appropriate methods to be standardized. Namely, in the field of testing concrete for sulfate attack, there are still no standard methods used to evaluate sulfate resistance. The methods most commonly used for laboratory testing of the sulfate resistance of concrete are mass change, strength change, length change, determination of porosity and supplemented by various microscopic methods. These methods are not standardized but have been refined and supplemented by researchers.

However, the lack of standard methods makes it difficult to compare the results obtained, as well as to make decisions and conclusions about improving sulfate resistance.

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