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SPECIAL MOBILITY STRAND

EXTERNAL SULFATE ATTACK ON CONCRETE

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Durability of concrete



Durability of concrete may be defined in different ways:

- It is the ability of concrete to resist weathering action, chemical attack, and abrasion while maintaining its desired engineering properties.
- It is the ability of concrete to resist to the attack of environmental, physical and chemical aggressive conditions, through the time.
- It is the ability to last a long time without significant deterioration.





Durability of concrete

A **durable material** helps the environment by conserving resources and reducing wastes and the environmental impacts of repair and replacement.

The production of replacement building materials depletes natural resources and can produce air and water pollution.

The **durability** and **service life** of a concrete structure is determined by the interaction between the structure and its environment.



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Durability of concrete

Depending of the type and importance of the structure, its **service life** may be between 10 and 100 years and more .

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



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Durability of concrete

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.**

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.



Durability of concrete

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**.

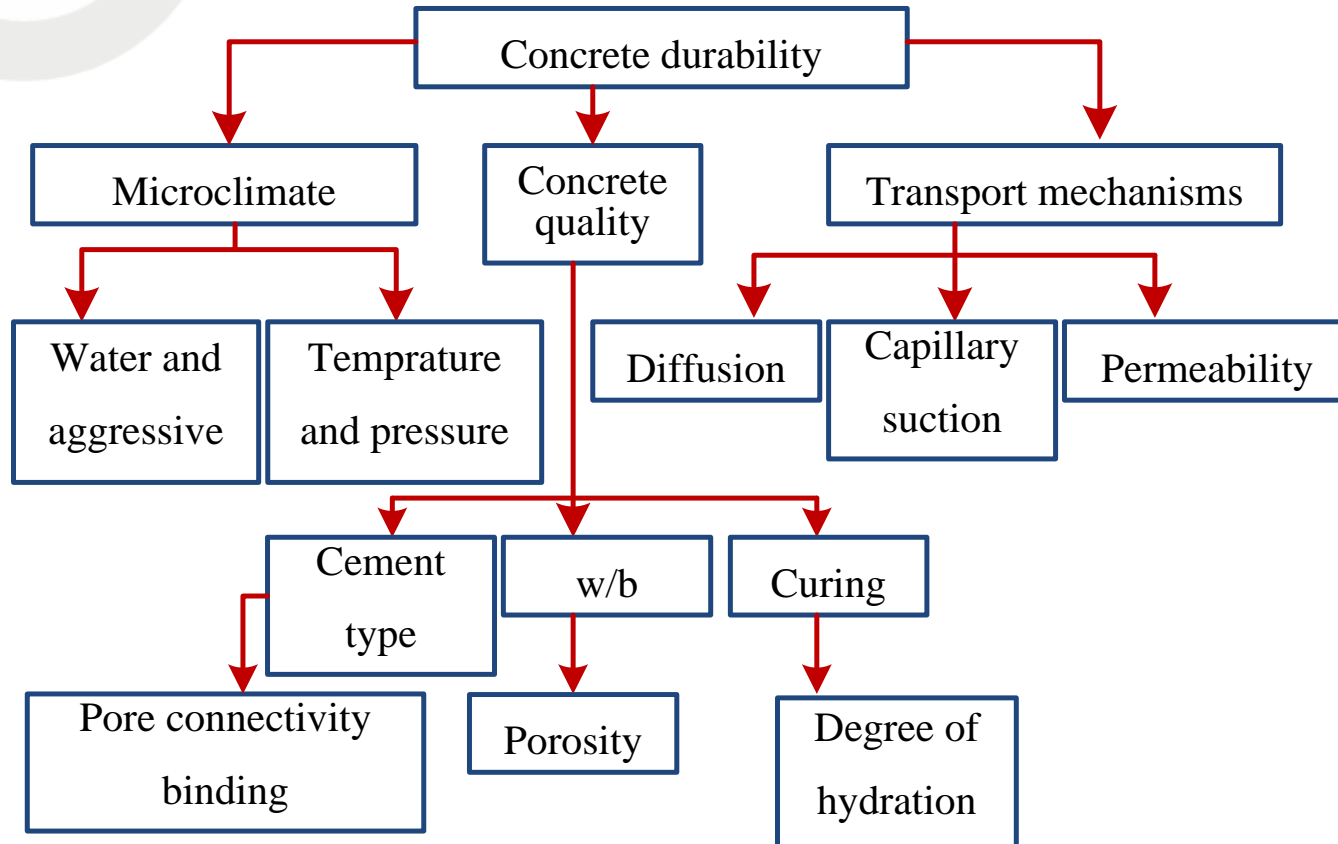
Knowing and understanding the **transport mechanisms** of liquid and gaseous substances into and within concrete structures is, therefore, the most important element in ensuring sufficiently durable concrete structures.



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Durability of concrete



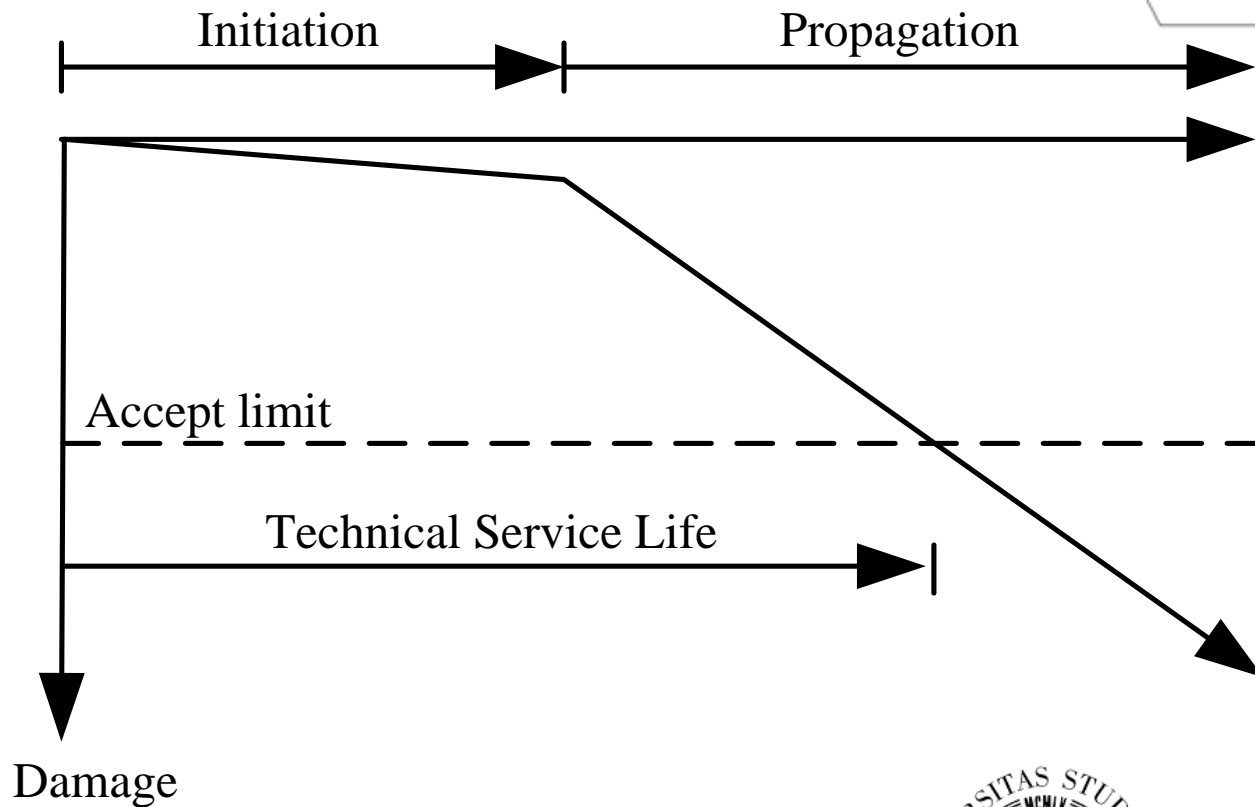
Torgal, Fernando Pacheco, Jalali, Said. (2011). *Eco-efficient construction and building materials*. London: Springer.

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Durability of concrete

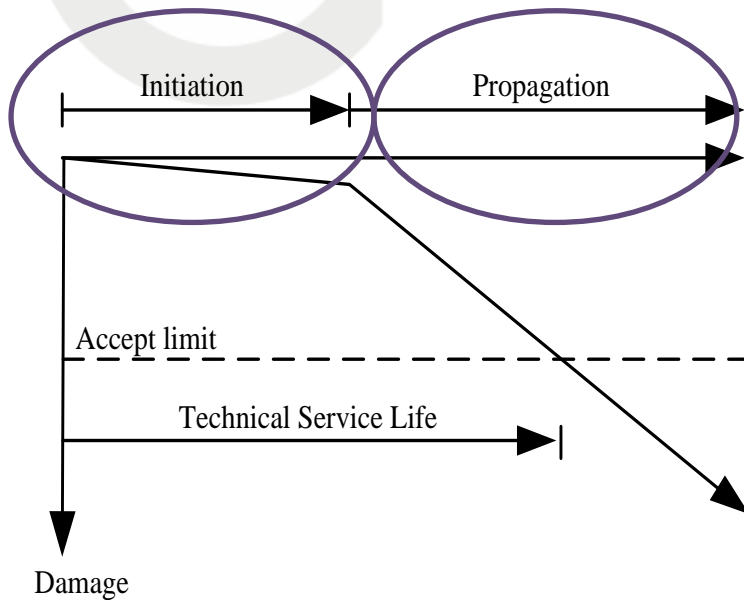
A two-phase modelling of deterioration



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Durability of concrete



1. Initiation phase

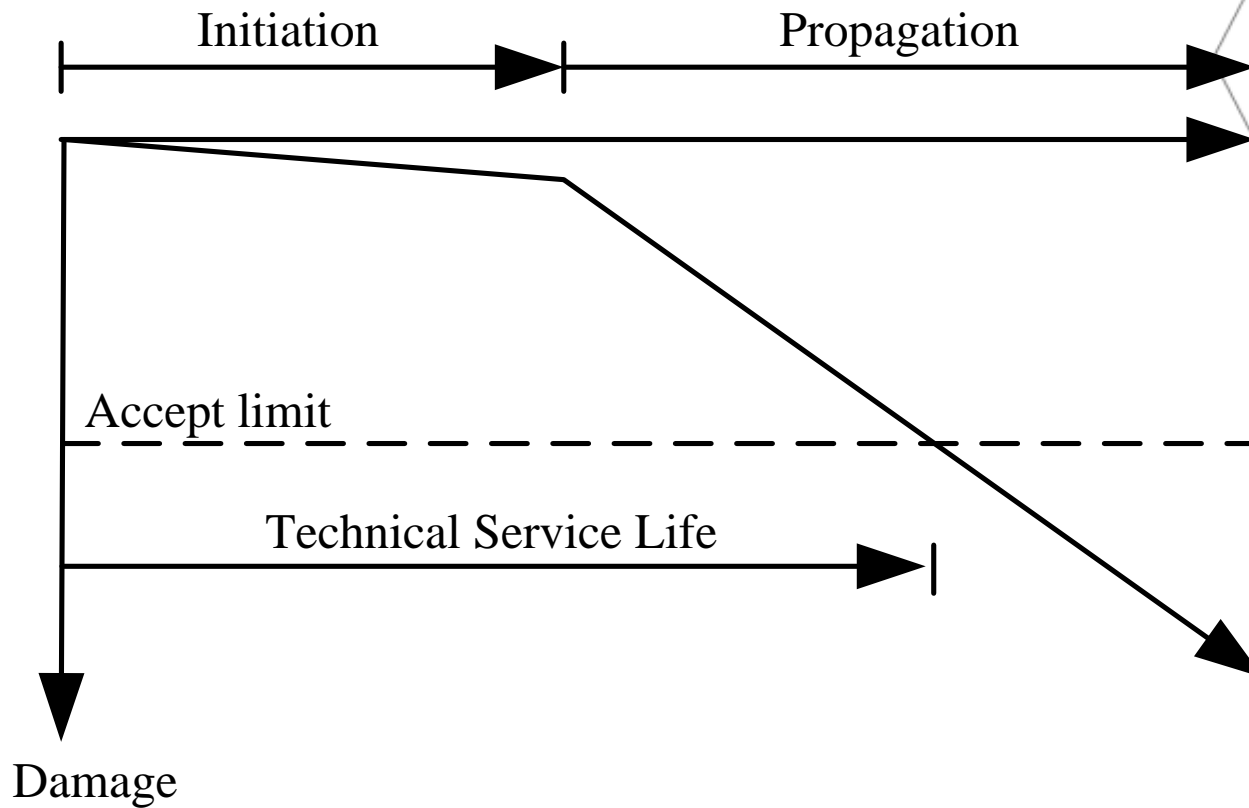
During this phase no noticeable weakening of the material or reduction in the function of the structure occurs, but some of the protective barrier is broken down or overcome by the aggressive media.

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.



Durability of concrete



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Durability of concrete

For the majority of ordinary structures in aggressive environments:

- **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,**

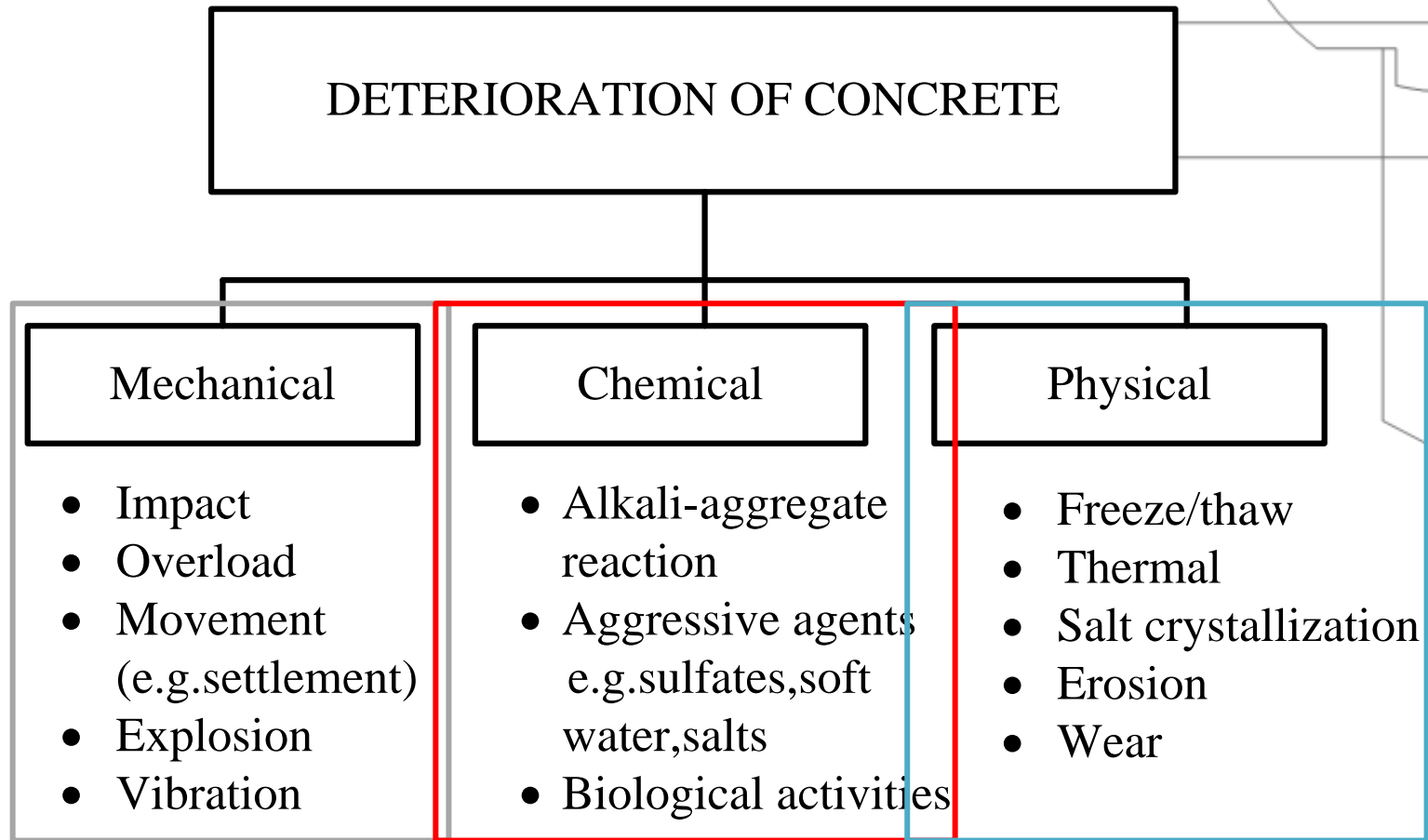
will normally result in a satisfactory service life.



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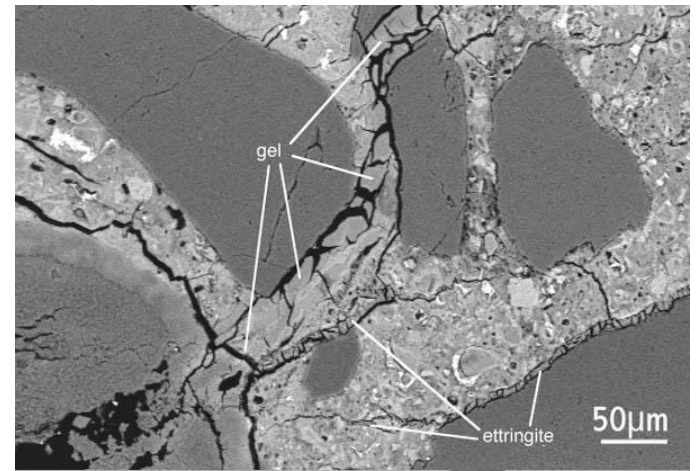


Durability of concrete



Chemical processes

- **Alkali-aggregate reaction**
 - ✓ alkali-silica reaction (ASR)
 - ✓ alkali-carbonate reaction (ACR)



Chemical processes

- **Acid corrosion**



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Chemical processes

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

- **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.**



Chemical processes

The exposure classes according to EN206-1:

- **XO** –no risk of corrosion or attack
- **XC** –risk of carbonation induced corrosion
- **XD** –risk of chloride-induced corrosion (other than sea water)
- **XS** –risk of chloride induced corrosion (sea water)
- **XF** –risk of freeze thaw attack
- **XA** –chemical attack



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Chemical processes

Chemical attack

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

Chemical processes

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 ≤ 3 000	> 3 000 and ≤ 6 000
pH	ISO 4316	≤ 6,5 and ≥ 5,5	5,5 and ≥ 4,5	< 4,5 and ≥ 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 ≤ 1 000	> 1 000 and ≤ 3 000	> 3000 up to saturation
Soil				
SO ₄ ²⁻ mg/kg ^a total	EN 196-2 ^b	≥ 2 000 and ≤ 3 000 ^c	> 3 000 ^c and ≤ 12 000	> 12000 and ≤ 24000
Acidity according to Baumann Gully ml/kg	prEN 16502	> 200	Not encountered in practice	





Sulfate attack

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.



Sulfate attack

It has been difficult to define the precise nature of the mechanisms of sulfate attack because of **its complex behaviour and numerous overlapping reactions**.

The major problem in assessing materials is that the form of attack in sulfate environments is variable.

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.



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Sulfate attack

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.

Common damages:

- **Cracking,**
- **Expansion**
- **Loss of bond between the cement paste and aggregate.**

The expansion resulting from sulfate attack is generally attributed to the formation of **gypsum and ettringite.**



Sulfate attack

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.

Sulfate attack is categorized into:

- **Chemical** → Gypsum, ettringite
- **Physical** → Sulfate salt
- **Internal** → Source of sulfate is internal
- **External** → Source of sulfate is external



Sulfate attack

Chemical changes:

- Removal of Ca^{2+} from certain hydration products (decomposition of 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: $\text{Mg}(\text{OH})_2$ and M-S-H.
- Penetration into concrete of sulfate anions and subsequent formation salts.





Sulfate attack

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.



Sulfate attack

Generally:

1. Volume changes

Sulfate reactions form a significantly **larger volume** of solid phases which cannot be accommodated by the capacity of the pore system.

The expansion does not have to cause deterioration if the concrete **has the capacity** to withstand these changes.



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Sulfate attack

Generally:

Jedinjenje		Zapremina (cm ³ /mol)
Ca(OH) ₂	kalcijum-hidroksid	33,1
Mg(OH) ₂	brucit	24,6
CaSO ₄ ·2H ₂ O	gips	74,2
Na ₂ SO ₄ ·10H ₂ O	mirabilit	219,8
MgSO ₄ ·7H ₂ O	epsomit	146,8
4CaO·Al ₂ O ₃ ·19H ₂ O	tetra-kalcijum-aluminat-hidrat	369,2
3CaO·Al ₂ O ₃ ·CaSO ₄ ·12H ₂ O	monosulfat	312,7
3CaO·Al ₂ O ₃ ·3CaSO ₄ ·32H ₂ O	etringit	714,9
Al(OH) ₃	gibsit	32,0
K ₂ Ca(SO ₄) ₂ ·6(OH) ₂	singenit	127,8



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Sulfate attack

2. Decomposition of compounds

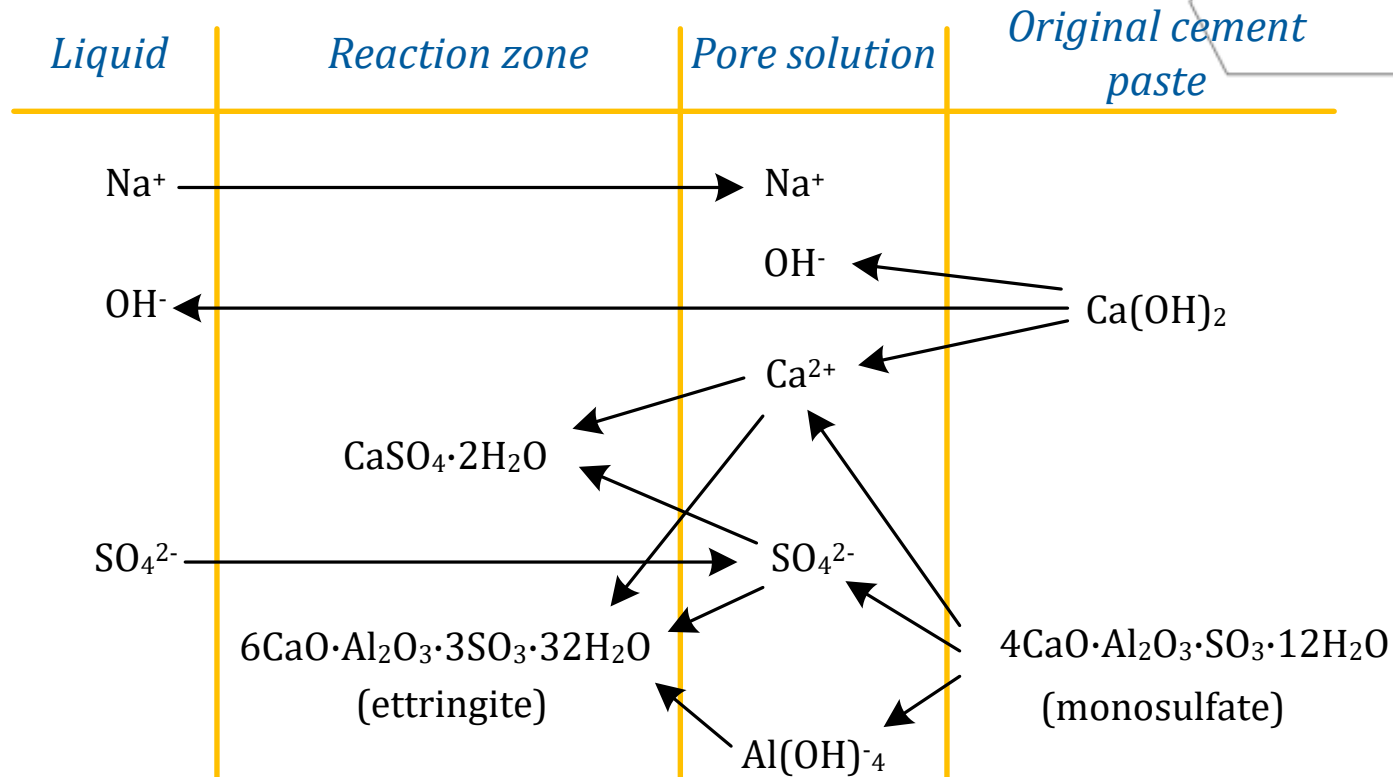
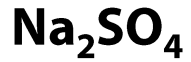
The sulfate attack may cause the **decomposition** of cement hydration products such as C-S-H and CH as they become unstable due to the decrease in pH.

3. Salt exfoliation

The solubility of salts 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.



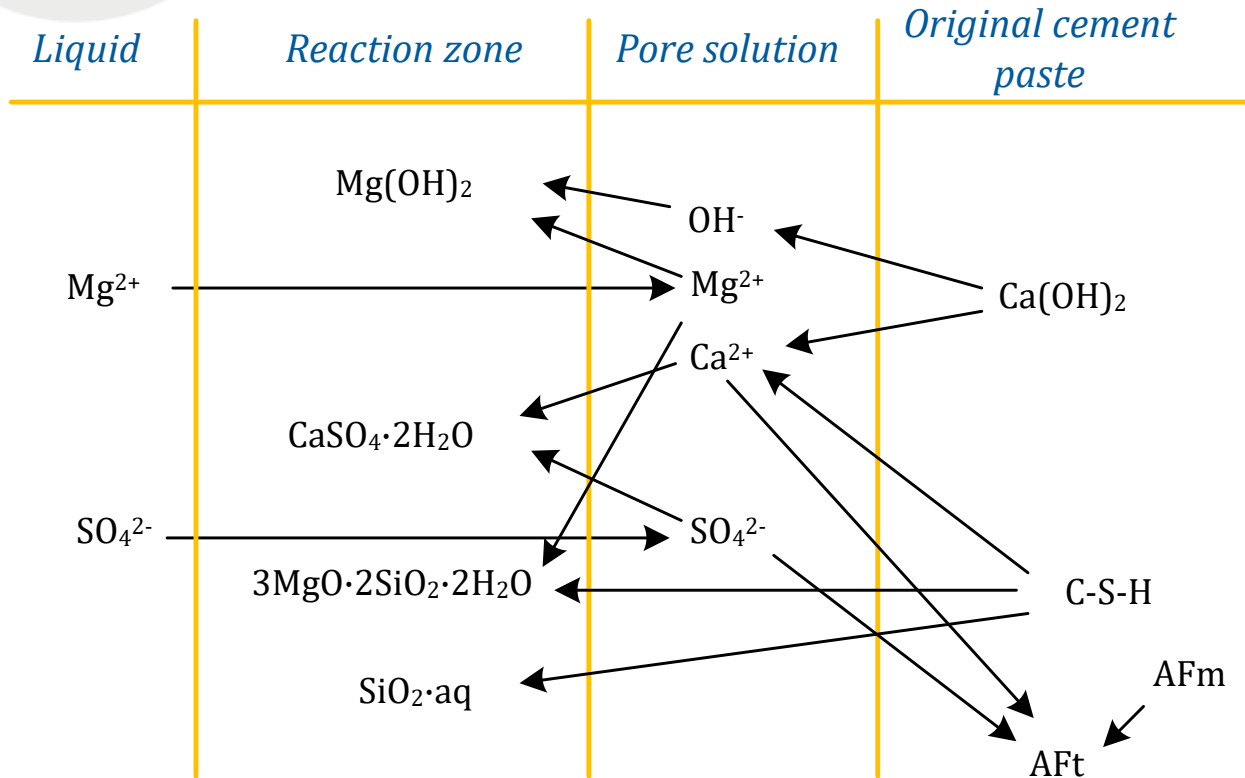
Sulfate attack



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Sulfate attack



Sulfate attack

Recommendation to mitigate sulfate attack according to **EN 206-1**

Maximum
water/cement ratio

Minimum cement
content

Minimum value of
strength

Type of cement



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Sulfate attack

Recommendation to mitigate sulfate 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	Sulfate-resisting cement
XA2	0.50	C30/37	320	
XA3	0.45	C35/45	360	



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Sulfate attack

Measures for improving sulfate resistance according to **researchers**:

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

A small increase in
gypsum initially that
can bind aluminum
to itself at the onset
of hydration.



Sulfate attack

For the evaluation of sulfate resistance of concretes, the following testing methods is commonly used:

- mass change,
- strength change,
- length change,
- determination of porosity
- capillary water absorption and
- microstructural analysis.



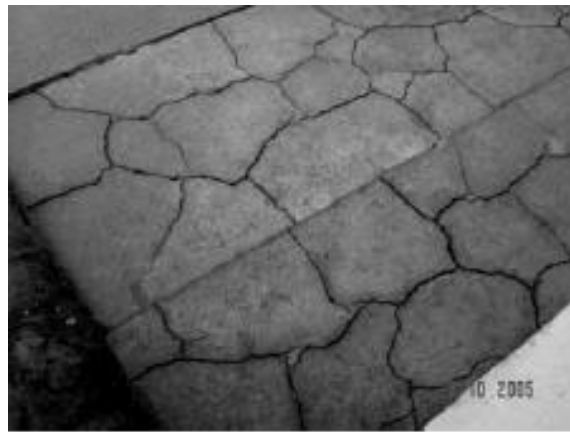
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Visual appearance-in site



Railroad tiles



Concrete block



Bridge column

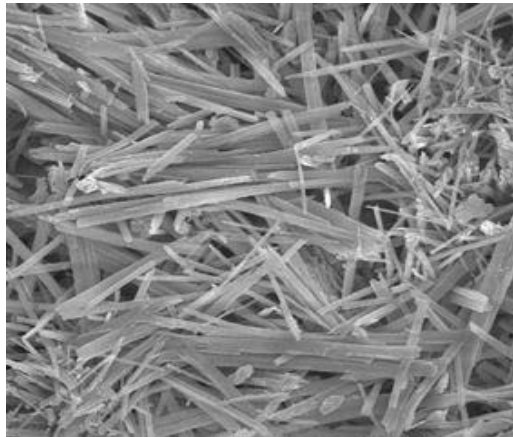
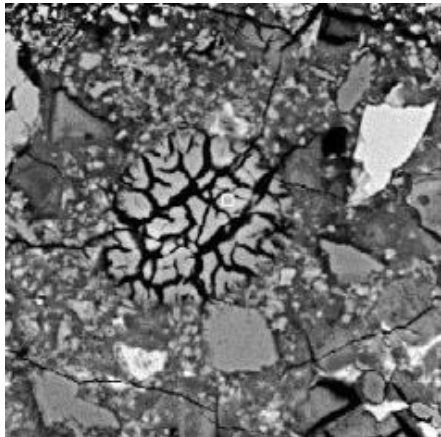
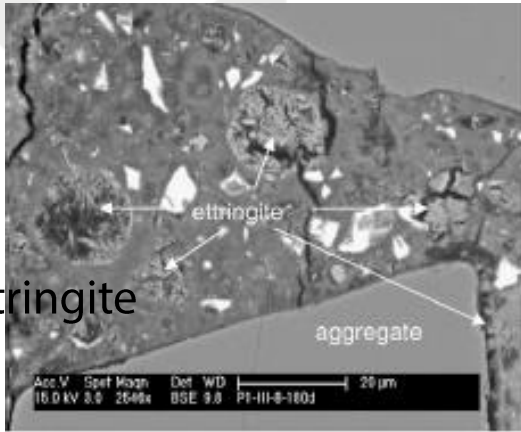


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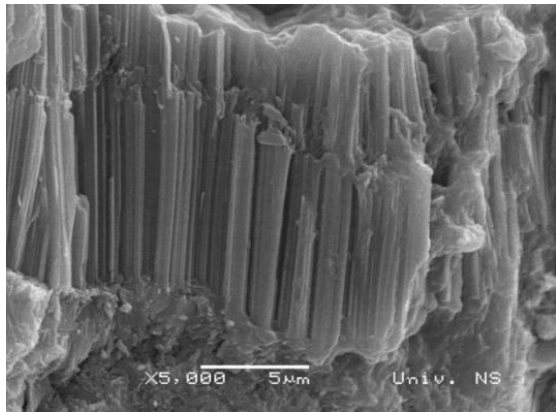
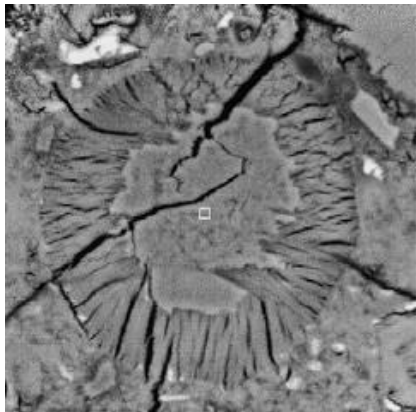
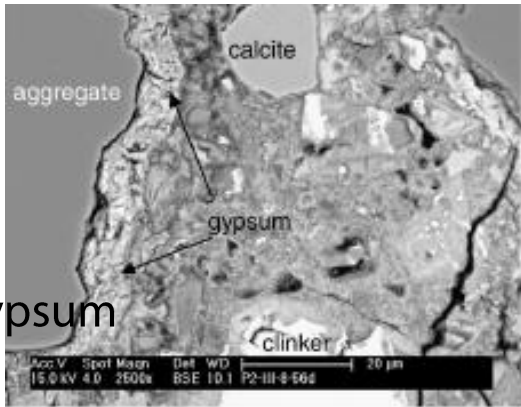


Sulfate attack-micro

Ettringite



Gypsum



Sulfate attack-laboratory

Na_2SO_4



RA,CEM I

MgSO_4



RA,CEM I



Sulfate attack-laboratory

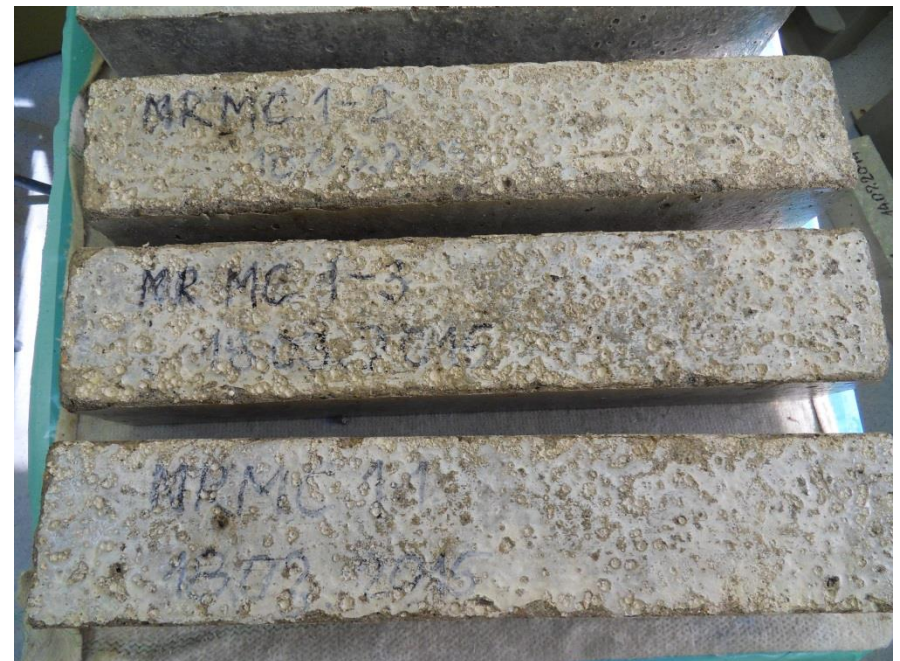
Na_2SO_4

RA,CEM I



MgSO_4

RA,CEM I



Conclusion

- Sulfate attack on concrete is a slow process but with significant consequences.
- 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.



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