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Cement

www.LC3.ch





Durability of cementitious materials

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Durability

- » The ability to withstand wear, pressure, or damage
- » The ability to last a long time without significant deterioration




First RC bridge in America (1889)




Expressway built in 1960s

Thomas, Folliard and Scrivener (2008)

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Objective

- » Understanding of various deterioration processes
- » Mechanism
- » Identification
- » Mitigation/prevention

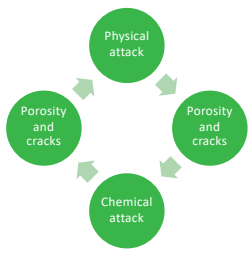
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Deterioration processes

- » Physical attack
 - » Abrasion
 - » Erosion
 - » Cavitation
 - » Physical salt attack
 - » Freeze-thaw
 - » Fire damage
- » Chemical attack
 - » Corrosion
 - » Alkali aggregate reaction
 - » Sulphate attack
 - » Acid attack
 - » Biogenic attack



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graph TD
    PA((Physical attack)) --> PC((Porosity and cracks))
    PC --> CA((Chemical attack))
    CA --> PA
  
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Physical attack

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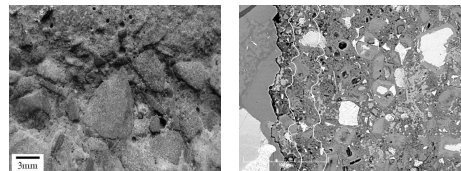
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Abrasion

- » Physical wear due to hard particles
- » Abrasion resistance
 - » Ability of a surface to resist being worn away by rubbing or friction
 - » Paste hardness, aggregate hardness and aggregate/paste bond
- » Vehicular traffic – bends and corners
- » Surface properties are important
 - » Porosity of top layer
 - » Surface finishing
- » Low paste content
- » Hard and strong aggregates



Scrivener et al. (2004), Safiuddin (2015)


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Erosion

- » Action of flowing water or wind
- » Rain and flowing water in hydraulic structures
- » Abrasion due to solid particles influences erosion - usually a part
- » Surface properties are important
 - » Porosity of top layer
 - » Surface finishing
- » Precautions
 - » Reduce velocity of water flow
 - » Slope should be low



University of Sciences and of Technology Houari
Boumediene, Algeria

Hadja and Kharchi (2017)

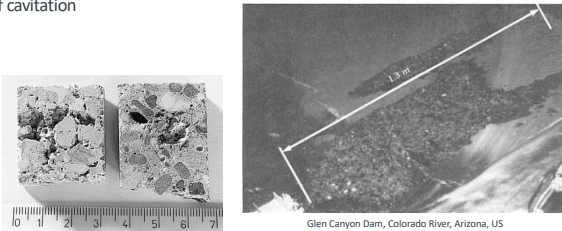
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Cavitation

- » Low pressure region – water vapour
- » High pressure region – vapour collapse causing extreme pressures
- » Collapse of vapour bubbles impacts surface
- » Elimination of location of cavitation
- » Concrete
 - » Low w/c ratio
 - » High strength



Glen Canyon Dam, Colorado River, Arizona, US

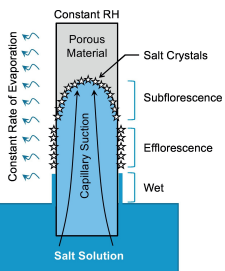
Momber (2000)

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Physical salt attack

- » One side in contact with salt solution
- » Evaporation on another side
- » Rate of evaporation > rate of supply for salt solution
 - » Crystallization of salts in pore – stresses
- » Rate of evaporation > rate of supply for salt solution
 - » Efflorescence on the surface



The diagram illustrates the physical salt attack mechanism. A porous material is shown with a salt solution at the bottom. A capillary suction arrow points upwards from the salt solution into the porous material. On the left side, a constant rate of evaporation is indicated by upward arrows. On the right side, a constant relative humidity (RH) is indicated. The diagram shows salt crystals forming within the pores, leading to subflorescence (crystals on the internal surface) and efflorescence (crystals on the external surface). The bottom of the material is labeled 'Wet' and 'Salt Solution'.



A photograph showing concrete blocks submerged in a salt solution, with visible white crystalline deposits (efflorescence) on the surface.

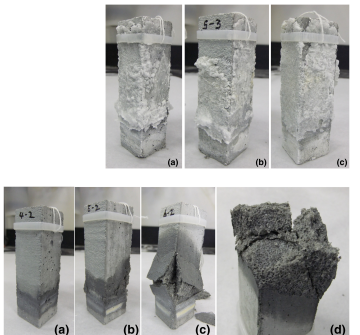
Lee and Kurtis (2017)

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Physical salt attack

- » Type of salt
- » Prevention
 - » Reduce connected porosity
 - » Allow flow of water
 - » Use of SCMs
 - » Surface treatments



Four photographs (a, b, c, d) showing concrete blocks affected by salt attack. (a) and (b) show blocks with significant surface erosion and white crystalline deposits. (c) shows a block with a large, irregular crack. (d) shows a block with a large, irregular crack and significant surface erosion.


Lee and Kurtis (2017)

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Freeze-thaw deterioration

- » Concrete is susceptible to cracking and even crumbling when subjected to cyclic freezing and thawing
- » Necessary conditions:
 - » Saturated or nearly-saturated concrete
 - » Freezing and thawing cycles



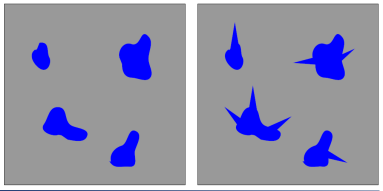
Two photographs showing concrete deterioration. The left image shows a concrete surface with a large, irregular crack and crumbling. The right image shows a concrete structure with multiple arched openings, where the concrete around the openings is crumbling and spalling.

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Mechanism of freeze thaw

- » Ice occupy approximately 8% higher volume
- » Freezing – ice forms – higher volume – movement of water
 - » No cracks – if increase in volume accommodated
 - » Cracks – insufficient pore volume
- » Thawing – ice melts and reduces volume – empty pore or crack
 - » External water enters concrete
- » Repetition of cycle



A diagram illustrating the mechanism of freeze-thaw deterioration. It shows two stages: the left stage shows water (blue) filling a pore, and the right stage shows ice (blue) forming within the pore, causing the pore to expand and crack.

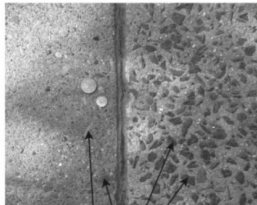
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Identification of freeze thaw


- » D-line cracking or disintegration
- » Scaling – de-icing salts and zonal freezing
- » Popouts

(a) Severely Scaled Sidewalk





Coarse Aggregate

(b) Sidewalk Destroyed by Scaling and Subsequent Internal Frost Action



Valenza and Scherer 2006



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Factors affecting deterioration

- » Degree of saturation
- » Available water volume
- » Pore structure
- » Concrete age
- » Climatic conditions
- » Aggregate characteristics
- » De-icing salts
- » Air entrainment



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Fire damage

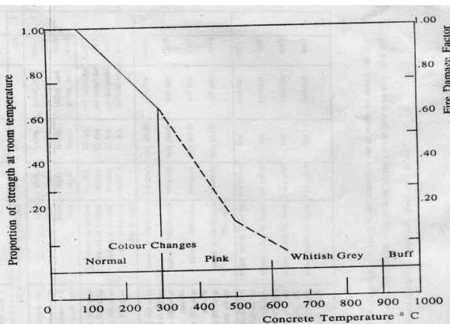
- » At high temperature concrete tends to lose strength
- » Above 200°C strength loss can start to be significant
- » Colour changes from grey to pink to buff
- » Aggregates may start to decompose
- » Higher strength concretes spall more
- » Concrete generally good insulator
- » Steel loses strength at high temperature
- » Characterisation can be used to determine temperature reached

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Fire damage





Concrete Temperature (°C)	Proportion of strength at room temperature	Color Change
0 - 200	1.00	Normal
200 - 300	~0.80	Normal to Pink
300 - 400	~0.60	Pink
400 - 500	~0.40	Pink to Whitish Grey
500 - 600	~0.20	Whitish Grey
600 - 1000	~0.10	Buff

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Chemical attack

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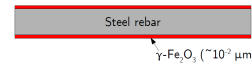
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Corrosion of reinforcement in concrete

- » Reinforcement – tensile strength
- » Steel – produced from iron ore
- » Corrosion of steel reinforcement
- » How reinforcement in concrete can be stable?
 - » Passivating layer
 - » Concrete cover depth

Steel rebar
 $\gamma\text{-Fe}_2\text{O}_3$ ($\sim 10^{-2} \mu\text{m}$)

Thomas, Folliard and Scrivener, 2008

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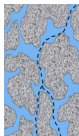
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Mechanism of corrosion

- » Electrochemical process – anode and cathode & electrolytic solution
- » Concrete
 - » Breakdown of passive layer or presence of two different type of metals
 - » Solution available in the pores of concrete



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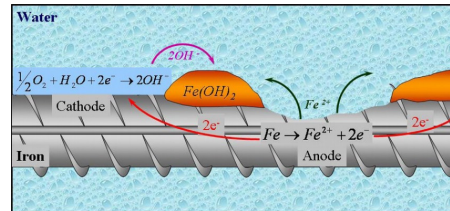
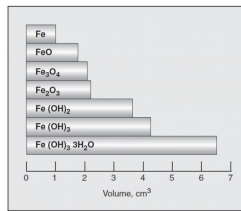
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Mechanism of corrosion

- » Corrosion reaction

Water

Cathode: $\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$

Anode: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$

Products: $\text{Fe}(\text{OH})_2$, Fe^{2+} , $\text{Fe}(\text{OH})_3$

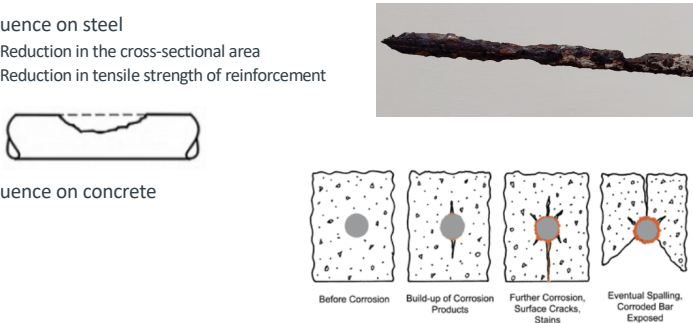
Volume, cm^3

Thomas, Folliard and Scrivener (2008)
Mehta and Monteiro, 2006

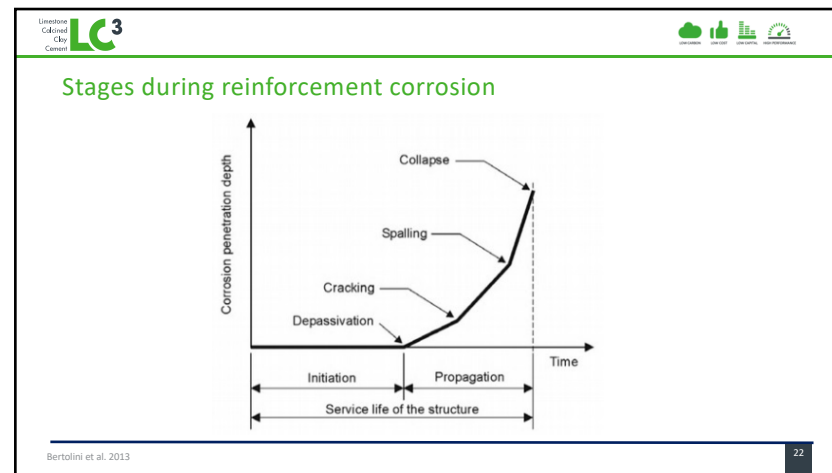
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Influence of corrosion


- » Influence on steel
 - » Reduction in the cross-sectional area
 - » Reduction in tensile strength of reinforcement
- » Influence on concrete



Bertolini et al. 2013





The result



concrete.org.uk

Major reason of corrosion

- » Carbonation
 - » CO_2 in environment
 - » Disruption of passivating film due to lowering of pH
- » Chloride attack
 - » Deicing salts, sea water, sand etc.
 - » Disruption of passivating film at high pH
- » Hydrogen embrittlement
- » Stray currents

Carbonation

- Carbon-dioxide reacts with alkalis to carbonate them, this reduces the pH of the solution



$$\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$$

$$2\text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$$

$$2\text{KOH} + \text{CO}_2 \rightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$$


$$(\text{CaO})_x \cdot (\text{SiO}_2)_y \cdot (\text{H}_2\text{O})_z + x\text{CO}_2 \rightarrow x\text{CaCO}_3 + y\text{SiO}_2 \cdot (\text{H}_2\text{O})_t + (z-yt) \text{H}_2\text{O}$$
- Carbonation of CH increases solid volume
- Carbonation of C-S-H reduces solid volume

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Testing carbonation

- Phenolphthalein test
- Phenolphthalein solution is pink at pH > 9.2 and colourless below 9.2
- pH
- Reserve alkalinity



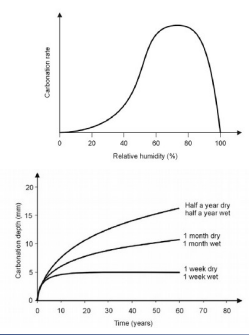
Thomas, Folliard and Scrivener, 2008

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Carbonation

- Rate of carbonation depends on diffusivity/permeability
- Reserve alkalinity
- Environmental CO_2 concentration
- Temperature
- Relative humidity
- Exposure condition



Pedferri et al. 2013

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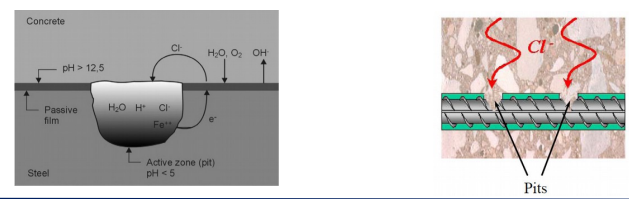
Chloride

- Ferrous ions combine with the chloride ions to form ferrous chloride

$$2\text{Fe}^{2+} + 4\text{Cl}^- \rightarrow 2\text{FeCl}_2$$
- Self-propagating due to acidic conditions created

$$2\text{FeCl}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_2 + 4\text{H}^+ + 4\text{Cl}^-$$

$$2\text{FeOCl} + 2\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_2 + 2\text{Cl}^-$$




Thomas, Folliard and Scrivener, 2008
Bertolini et al. 2013

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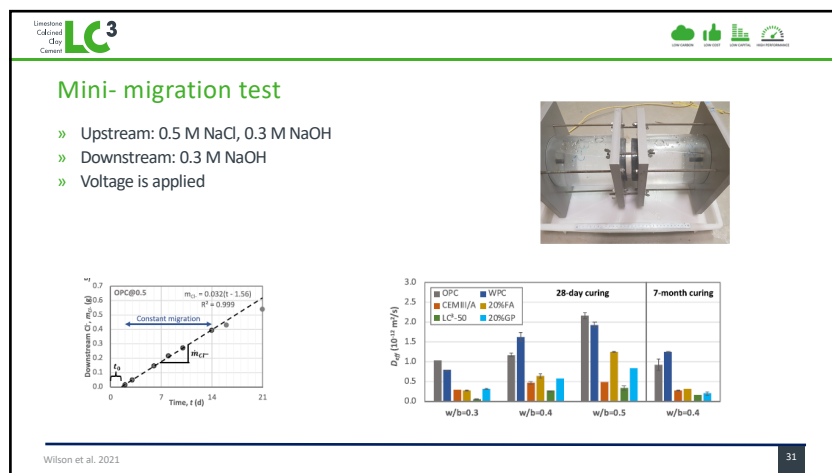
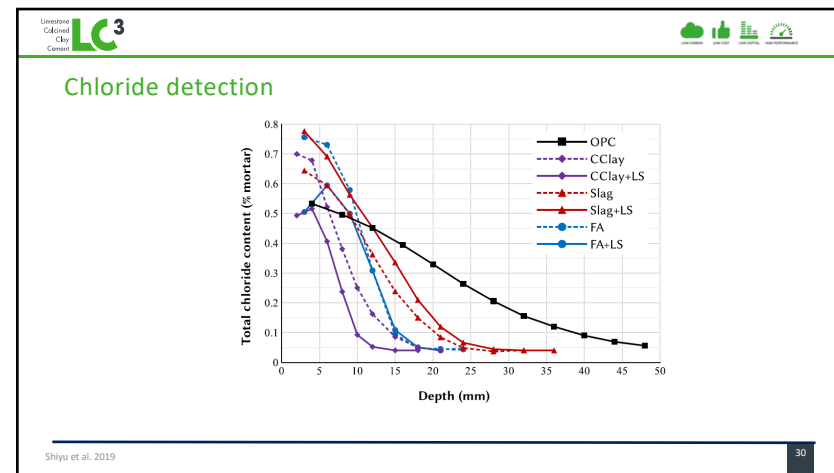
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Chloride detection – bulk diffusion



From: Georget 2020

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Alkali aggregate reaction

- » Aggregates can react under certain conditions
 - » Aggregates can imbibe water
 - » Swelling and cracking occurs
- » Usually a slow process
- » Less often cause of failure than other mechanisms
- » Alkali silica reaction (ASR)
- » Alkali silicate reaction
- » Alkali carbonate reaction (ACR)

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Mechanism of ASR

- » Reactive silica from aggregates + alkalis from cement – gel
- » Gel – imbibe water – volume increase – expansion
- » Restraint – stresses due to ASR expansion

$$4\text{SiO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{Si}_2\text{O}_5 + \text{H}_2\text{O}$$



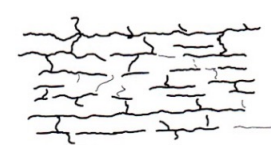
- » SiO_2 ions formed in the aggregates diffuse out slowly
- » Na^+ , K^+ , Ca^{2+} , OH^- ions from solution attracted into the aggregates
- » Pressure builds in the aggregate
- » Surface reaction slow in quartz
- » Penetration of ions if poorly crystalline

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Alkali silica reaction

- » Crack depth – 25 to 50mm
- » Unreinforced concrete
 - » Manx cracks
 - » Crack join
- » Reinforced concrete
 - » Manx cracks
 - » Regular cracks

Richardson 2002

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Alkali silica reaction

- » Identification
 - » Presence of gel in cracks
 - » Presence of potentially reactive aggregates
 - » Crack pattern
- » Crack pattern
 - » Similar to drying shrinkage and freeze-thaw deterioration
- » Gel
 - » Transparent or brownish
 - » Carbonates and turns white on exposure to the atmosphere
 - » Similar to leaching of calcium hydroxide or efflorescence



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Prevention of ASR

- » Reduction in alkalinity can reduce expansion:
 - » Supplementary cementitious materials
- » Chemical effects on gel
 - » Lithium salts: replacement of Na & K in gel
- » Air entrainment
- » Low alkali content: less gel
- » High alkali content: vigorous reaction before hardening?
- » Pessimism effect of aggregates



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Sulphate attack

- » Excess sulphates in concrete can lead to excessive expansion
- » Internal attack ($>5\%$ SO_3 by wt)
 - » Over-sulphated cement
 - » Sulphate contamination of aggregates
 - » High temperature curing
- » External attack
 - » Ingress of sulphates from external sources like ground water, soil, industrial waste, sewage, etc.



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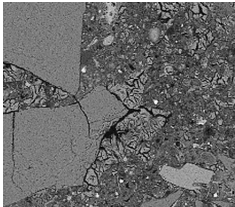
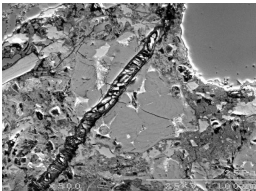

Mechanism of sulphate attack

- » Chemical reactions leading to formation of:
 - » Ettringite, e.g.
 - » Monosulphate + Sulphate + Water \rightarrow Ettringite
 - » Gypsum, e.g.
 - » Portlandite + Sodium Sulphate \rightarrow Gypsum + Sodium Hydroxide + Water
 - » Portlandite + Magnesium Sulphate \rightarrow Gypsum + Magnesium Hydroxide + Water
 - » Thaumasite ($\text{CaSiO}_3 \cdot \text{CaCO}_3 \cdot 15\text{H}_2\text{O}$)
 - » Sulphates + Calcium Silicates + Calcium Carbonate \rightarrow Thaumasite

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The result

Mistaken identity

Thomas, Follard and Scrivener, 2008
Sibbick, 2007

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Protection against sulphate attack

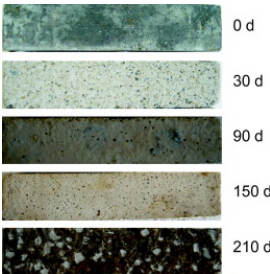
- » Improve quality of concrete
- » Use of surface protection
- » Sacrificial layer of concrete
- » Sulphate resistant cements (e.g. Types II and V)
- » Supplementary cementitious materials
- » Air entrainment
- » Air temperature during hydration
- » Size and geometry of pour
- » Cement content
- » Cement fineness

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Acid attack

- » Acids attack CH and C-S-H
- » Source of acids:
 - » Acid-rain
 - » Industrial sources, etc.
- » Etching to complete breakdown of concrete
- » Rate of attack depends on H⁺ concentration
- » Prevention
 - » Reduce direct exposure to acid
 - » Surface protection
 - » Low permeability concrete
 - » Aggregate type



Chen, Wang and Xie 2013

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Biogenic attack



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Unimatrix Coloured Clay Cement **LC³**

Biogenic attack

- » Sulphate attack
 - » Anaerobic conditions
 - » Conversion of sulphate to H₂S (Desulfovibrio)
 - » Conversion of H₂S to H₂SO₄ by aerobic bacteria on surface
 - » Thiobacillus thiooxidans (concretivorus), produces upto 10% sulfuric acid (pH < 1)
- » Acid attack
- » Ammonium attack
 - » NH₄⁺ reacts with OH⁻ producing NH₃
 - » Green Fungus (Fusarium) produces acids
 - » pH reduction and acid attack
 - » Corrosion of reinforcement

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Biogenic sulfuric acid attack

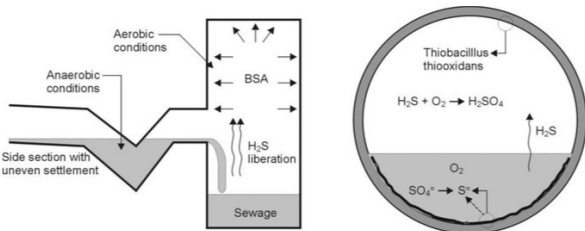


Figure 3.3 Biogenic sulfuric acid attack: a) conditions in sewer system that promote BSA; b) main reactions involved

Bertolini et al. 2013

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