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

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

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

Physical and cracks
Chemical and cracks
Physical attack
Chemical attack
Physical attack

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

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

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

Erosion
- Scrivener et al. (2004), Safiuddin (2015)
- Hadja and Kharchi (2017)
- Glen Canyon Dam, Colorado River, Arizona, US
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

Lee and Kurtis (2017)

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

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
Identification of freeze thaw

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

Factors affecting deterioration

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

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
Chemical attack

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

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

Mechanism of corrosion

- Corrosion reaction
Influence of corrosion

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

Stages during reinforcement corrosion

The result

Major reason of corrosion

- Carbonation
  - CO₂ 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
  
  \[
  \text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}\]
  
  \[2\text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}\]
  
  \[2\text{KOH} + \text{CO}_2 \rightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O}\]
  
  \[(\text{CaO})_x(\text{SiO}_2)_y(\text{H}_2\text{O})_z + x\text{CO}_2 \rightarrow x\text{CaCO}_3 + y\text{SiO}_2(\text{H}_2\text{O})_z + (z-yt)\text{H}_2\text{O}\]

- Carbonation of CH increases solid volume
- Carbonation of C-S-H reduces solid volume

Testing carbonation

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

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
  
  \[2\text{FeCl}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_2 + 4\text{H}^+ + 4\text{Cl}^-\]
  
  \[2\text{FeCl}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_2 + 2\text{Cl}^-\]
Chloride detection – bulk diffusion

From: Shiyu et al. 2019

Mini-migration test

- Upstream: 0.5 M NaCl, 0.3 M NaOH
- Downstream: 0.3 M NaOH
- Voltage is applied

From: Wilson et al. 2021

Chloride detection

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)
Mechanism of ASR
- Reactive silica from aggregates + alkalis from cement → gel
- Gel – imbibes water – volume increase – expansion
- Restraint – stresses due to ASR expansion
  \[ 4\text{SiO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{Si}_4\text{O}_9 + \text{H}_2\text{O} \]
- SiO\text{-} ions formed in the aggregates diffuse out slowly
- Na\text{\textsuperscript{+}}, K\text{\textsuperscript{+}}, Ca\text{\textsuperscript{+}}, OH\text{\textsuperscript{-}} ions from solution attracted into the aggregates
- Pressure builds in the aggregate
- Surface reaction slow in quartz
- Penetration of ions if poorly crystalline

Alkali silica reaction
- Crack depth – 25 to 50mm
- Unreinforced concrete
  - Manx cracks
  - Crack join
- Reinforced concrete
  - Manx cracks
  - Regular cracks

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?
- Pessimum effect of aggregates

Alkali silica reaction
- Identification
  - Presence of gel in cracks
  - Presence of potentially reactive aggregates
  - Crack pattern
  - Gel
  - Transparent or brownish
  - Carbonates and turns white on exposure to the atmosphere
  - Similar to leaching of calcium hydroxide or efflorescence
**Sulphate attack**
- Excess sulphates in concrete can lead to excessive expansion
- Internal attack (>5% SO\textsubscript{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.

**Mechanism of sulphate attack**
- Chemical reactions leading to formation of:
  - Ettringite, e.g.
    \[
    \text{Monosulphate} + \text{Sulphate} + \text{Water} \rightarrow \text{Ettringite}
    \]
  - Gypsum, e.g.
    \[
    \text{Portlandite} + \text{Sodium Sulphate} \rightarrow \text{Gypsum} + \text{Sodium Hydroxide} + \text{Water}
    \]
    \[
    \text{Portlandite} + \text{Magnesium Sulphate} \rightarrow \text{Gypsum} + \text{Magnesium Hydroxide} + \text{Water}
    \]
  - Thaumasite (CuSiO\textsubscript{3}.CaCO\textsubscript{3}.CaSO\textsubscript{4}.15H\textsubscript{2}O)
    \[
    \text{Sulphates} + \text{Calcium Silicates} + \text{Calcium Carbonate} \rightarrow \text{Thaumasite}
    \]

**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
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

Biogenic attack
- Sulphate attack
  - Anaerobic conditions
  - Conversion of sulphate to H2S [Desulfovibrio]
  - Conversion of H2S to H2SO4 by aerobic bacteria on surface
  - Thiothrix thesoioids (concretivorus), produces up to 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

Biogenic sulfuric acid attack
- Conversion of H2S to H2SO4 by aerobic bacteria on surface
- Thiothrix thesoioids (concretivorus), produces up to 10% sulfuric acid (pH < 1)
- Acid attack
Corrosion of reinforcement by bacteria

Factors affecting biogenic attack
- Cement composition
- Permeability of concrete
- Temperature
- Sewage characteristics
- Prevention
  - Surface protection – low w/c concrete

Concrete in sea

Thank You!
Half cell potential

Reference electrode touched down at suitable intervals on concrete surface to measure potential difference of reinforcing steel.

Electrical resistivity

\[
\begin{align*}
\text{When } \rho \geq 120 \, \Omega \cdot \text{m} & \quad \text{corrosion is unlikely} \\
\text{When } 80 \leq \rho \leq 120 \, \Omega \cdot \text{m} & \quad \text{corrosion is possible} \\
\text{When } \rho \leq 80 \, \Omega \cdot \text{m} & \quad \text{corrosion is fairly certain}
\end{align*}
\]

Bungey et al. 2006