Understanding chemical attacks and permeation properties of concrete

1st Saudi Concrete Conference,
1-4 May 2016 Riyadh, Jeddah and Khobar KSA

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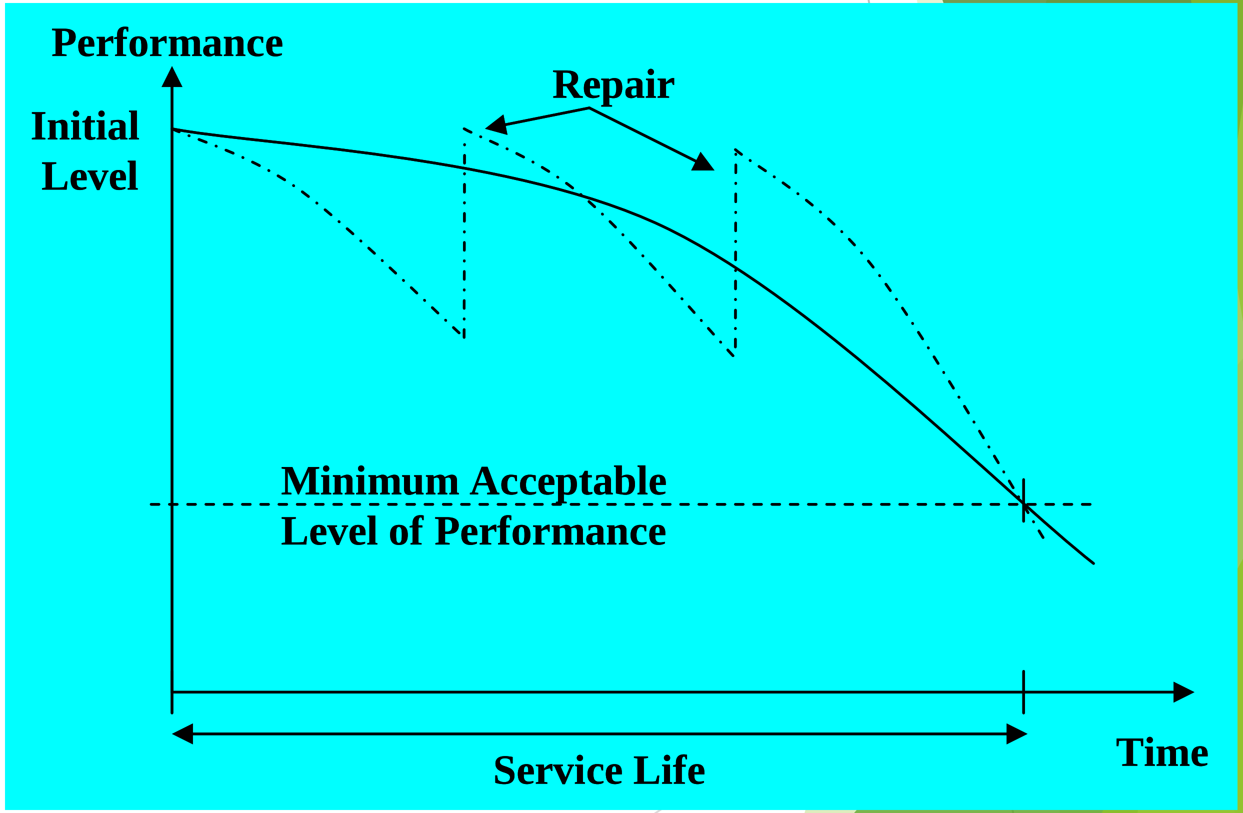
Durability and permeation properties

What is durability?

"The ability of concrete to withstand the damaging effects of the environment and of its service conditions until it reaches a minimum level of performance"



Type of attacks on concrete durability In the Middle East

- Corrosion of reinforcement by:
  - Chloride ingress
  - Carbonation
- Sulfate attack
- Delayed Ettringite Formation (DEF)
- Physical salt weathering
- Acid attack
- Multi-aggressive sea water attack

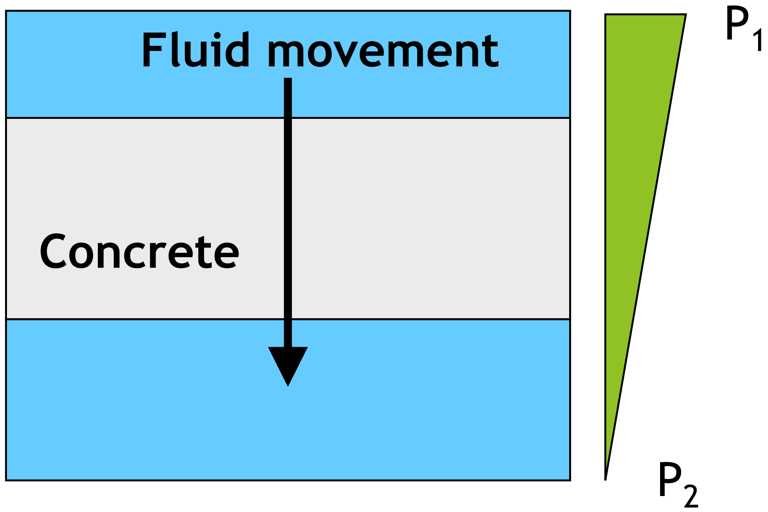
The common factor

Permeation Mechanisms

Permeation of water and gasses can be divided into three distinct phenomena:

- **Permeability**
- **Absorption**
- **Diffusion**

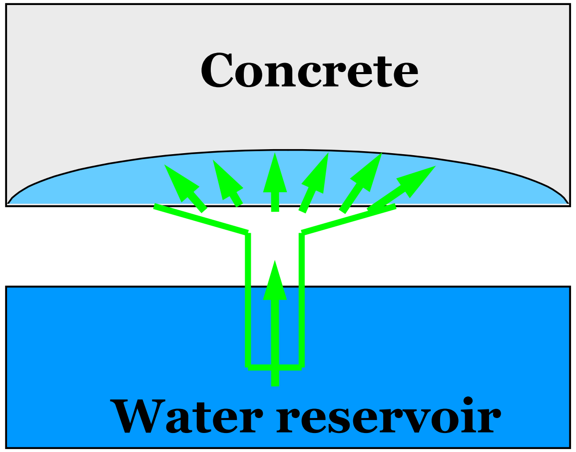
Permeability



The flow property of concrete by which water will pass through it, under a pressure differential

Typically affects: dams, tunnel linings, liquid retaining structures, submerged offshore structures

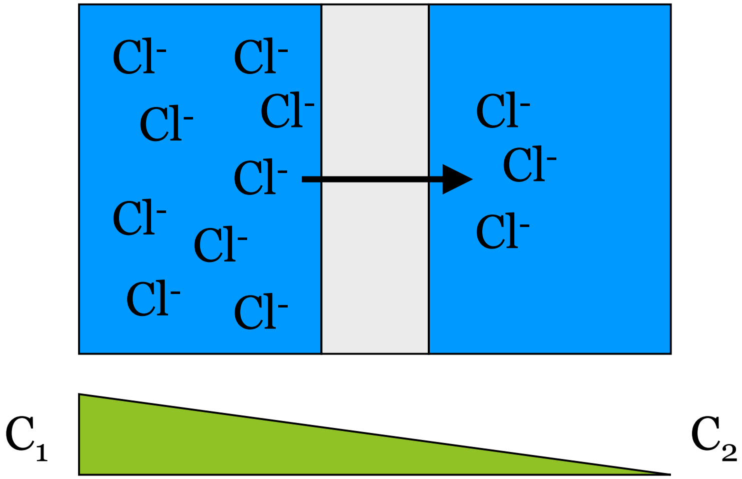
Absorption



The process by which concrete takes in water by capillary action.

Typically affects: Structures subjected to cyclic wetting and drying e.g. marine structures in the tidal zone

Diffusion



The process by which a vapour, gas or ion can pass through concrete under the action of a concentration gradient

Typically affects: Foundation elements , Highway structures, sub-merged marine structures

Hydrophobic & Pore-blocking admixture to enhance permeation properties

What is Hydrophobic & Pore-blocking Admixture

A hydrophobic & pore blocking admixture, which is cementitious and in powder form, additionally alters the microstructure of concrete to stop water and moisture transport mechanisms, thus increasing the long term durability of concrete.

CI/SfB
Yu2

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BBA BRITISH BOARD OF AGRÉMENT
TECHNICAL APPROVALS FOR CONSTRUCTION

Agrément Certificate
No 01/3843

PRODUCT SHEET 1 — PUDLO CWP (CEMENT WATERPROOFING POWDER)

PRODUCT SCOPE AND SUMMARY OF CERTIFICATE

This Certificate relates to Pudlo CWP (Cement Waterproofing Powder), a hydrophobic, pore-blocking admixture to provide watertight concrete or render.

AGRÉMENT CERTIFICATION INCLUDES:

- factors relating to compliance with Building Regulations where applicable
- factors relating to additional non-regulatory information where applicable
- independently verified technical specification
- assessment criteria and technical investigations
- design considerations
- installation guidance
- regular surveillance of production
- formal three-yearly review.

KEY FACTORS ASSESSED

Resistance to water penetration — concrete and render containing the product will have reduced permeability when compared to the equivalent plain concrete (see sections 4 and 5).

Reinforcement protection — concrete containing the product will have enhanced resistance to reinforcement corrosion when compared to the equivalent plain concrete (see section 6).

Mechanical properties — the mechanical properties of the concrete and render will not be adversely affected by the incorporation of the product (see section 7).

Durability — concrete containing the product is more durable than the equivalent plain concrete mix due to its reduced permeability (see section 15).

The BBA has awarded this Agrément Certificate for Pudlo CWP (Cement Waterproofing Powder) to David Ball Group plc as fit for its intended use provided it is installed, used and maintained as set out in this Agrément Certificate.

On behalf of the British Board of Agrément

Date of First issue: 8 August 2001
Date of Third issue: 19 February 2008

Head of Approvals — Materials

Chief Executive

The BBA is a UKAS accredited certification body — Number 113. The schedule of the current scope of accreditation for product certification is available in pdf format via the UKAS link on the BBA website at www.bbacerts.co.uk

Readers are advised to check the validity and latest issue number of this Agrément Certificate by either referring to the BBA website or contacting the BBA direct.

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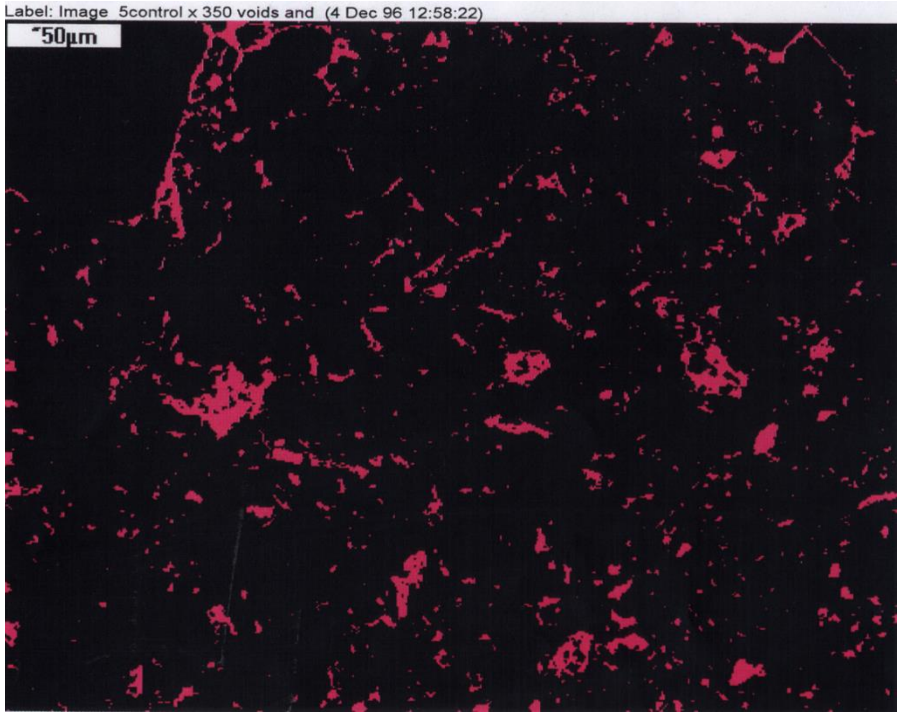
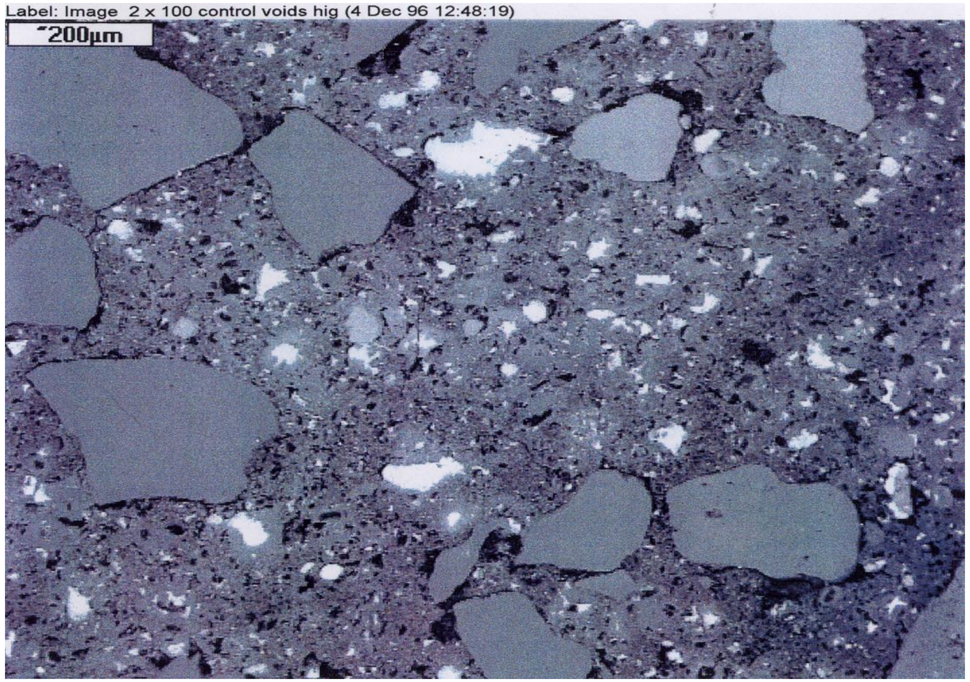
Comparison between control & HPA concrete

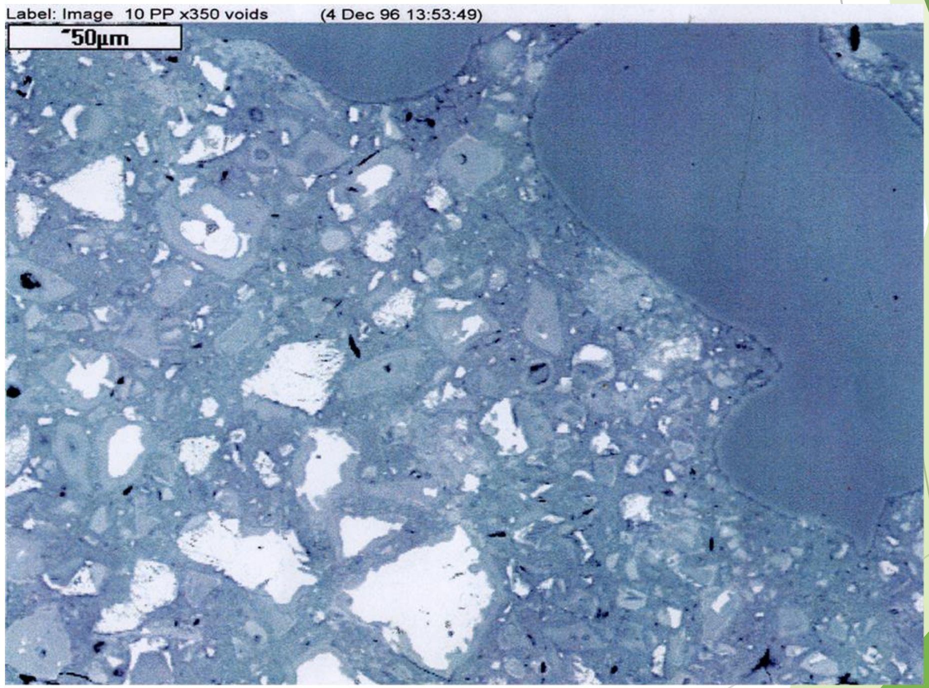


Porosity highlighted in red scale

Comparison between control & HPA concrete

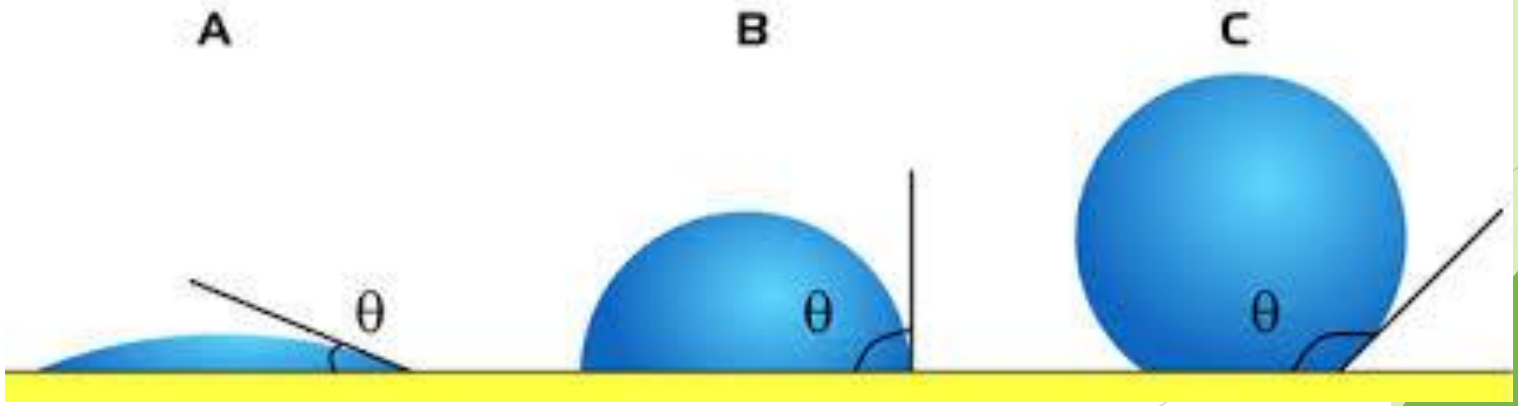


100 times magnification – low w/c ratio control concrete

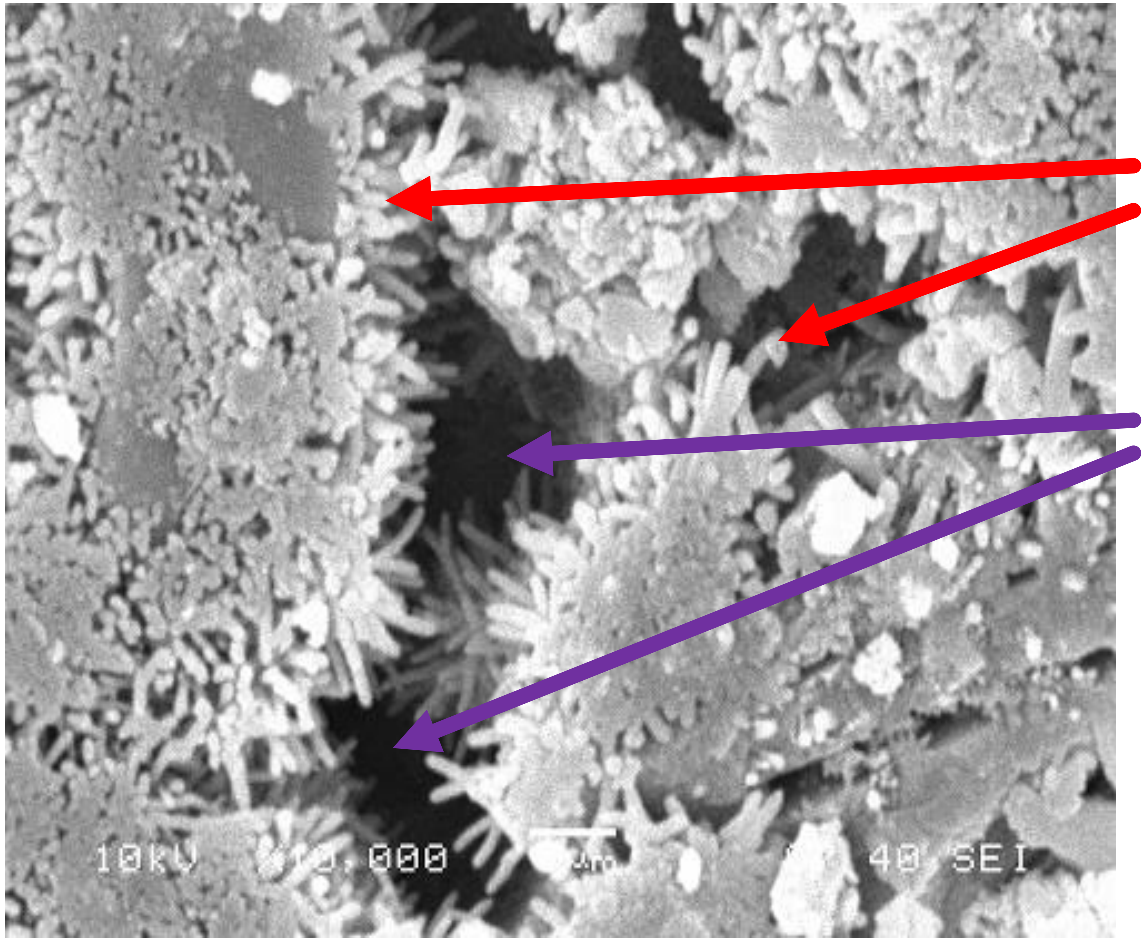


350 times magnification – low w/c ratio HPA modified concrete

Hydrophobic characteristics of HPA concrete



Cement Particle Hydration Process



Development of the hydration process by producing hydration products

The process alone does not eliminate the presence of **voids** within the concrete matrix

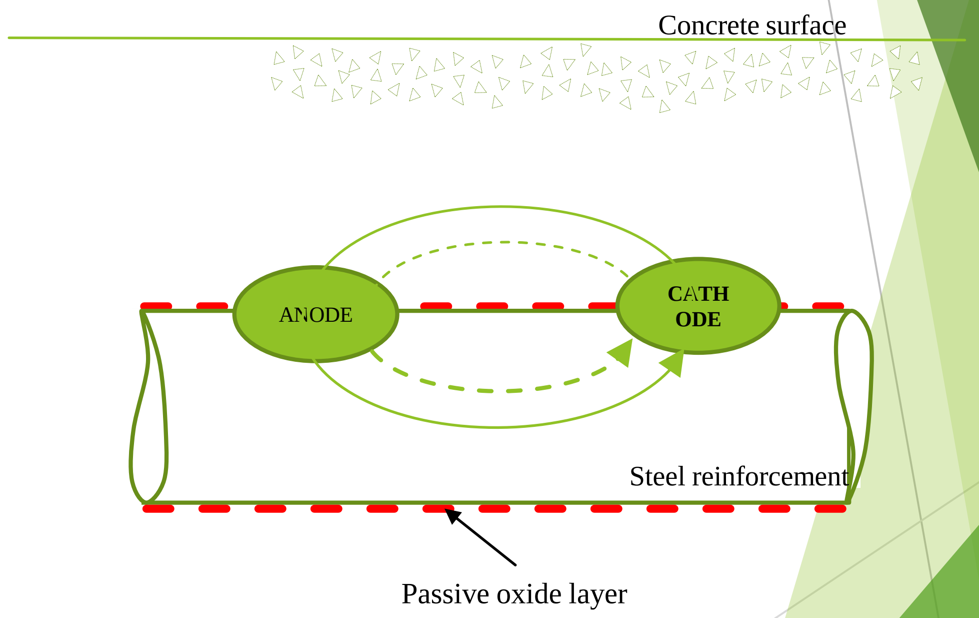
HPA blocks the pores by densifying the cement matrix to eliminate the voids

Attacks on concrete durability

Corrosion

Corrosion of steel

- Corrosion of steel is an **electro-chemical process**
- It starts once the **passive oxide layer** of steel bar is broken down, creating microcells of :
  - Anode
  - Cathode



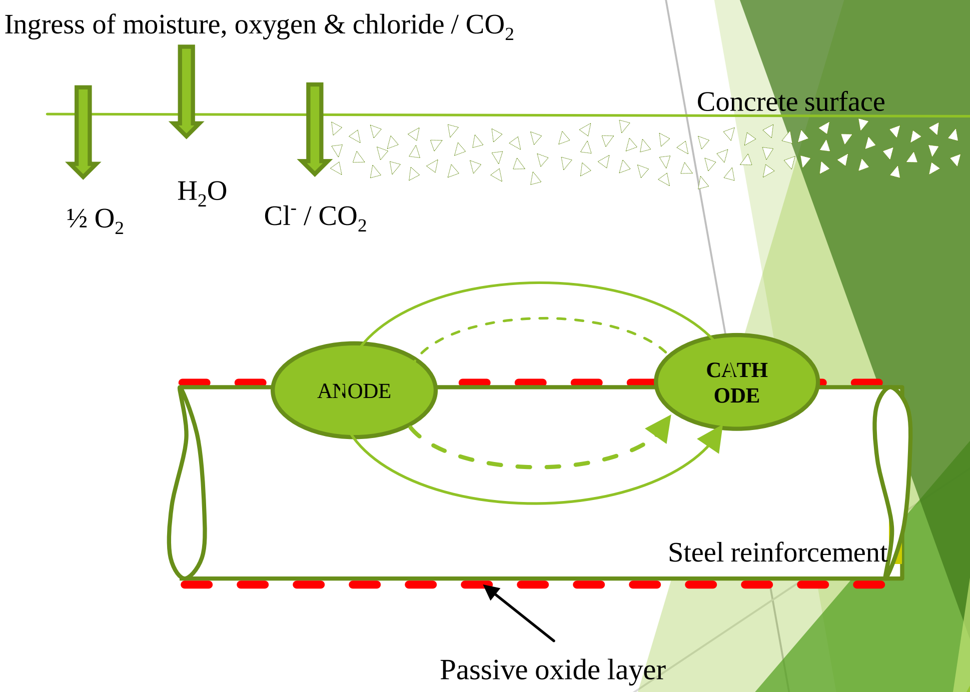
Corrosion of steel

The passivating layer could be broken down mainly due to the:

- Ingress of chloride ions

  or

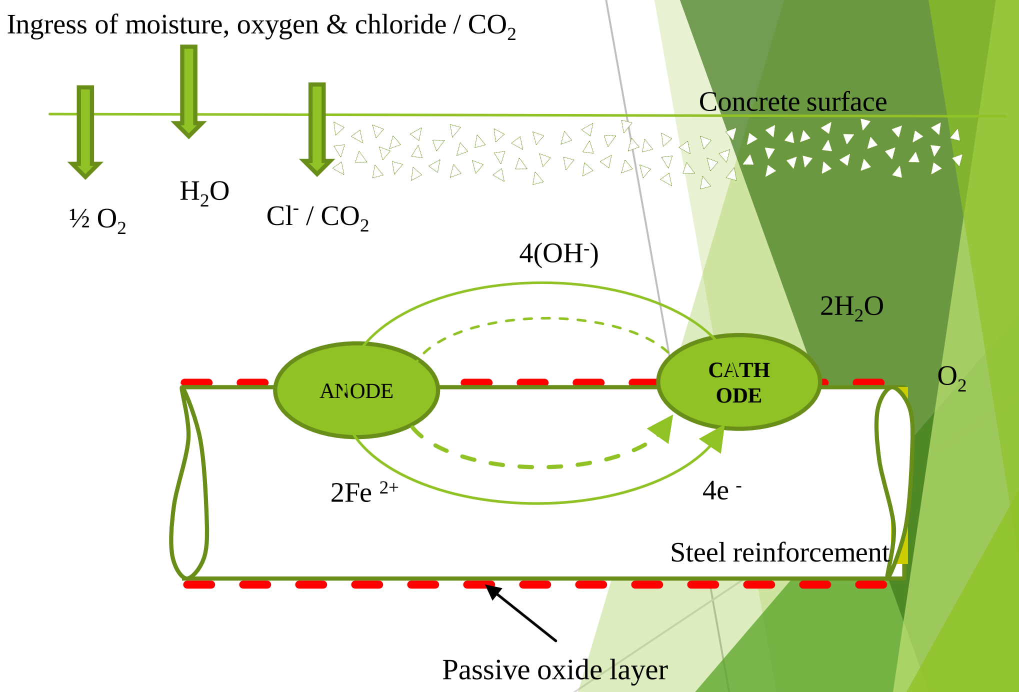
- Carbonation



Corrosion of steel

At anode, once the passivating layer is broken down, **dissolution of steel** is taken place.

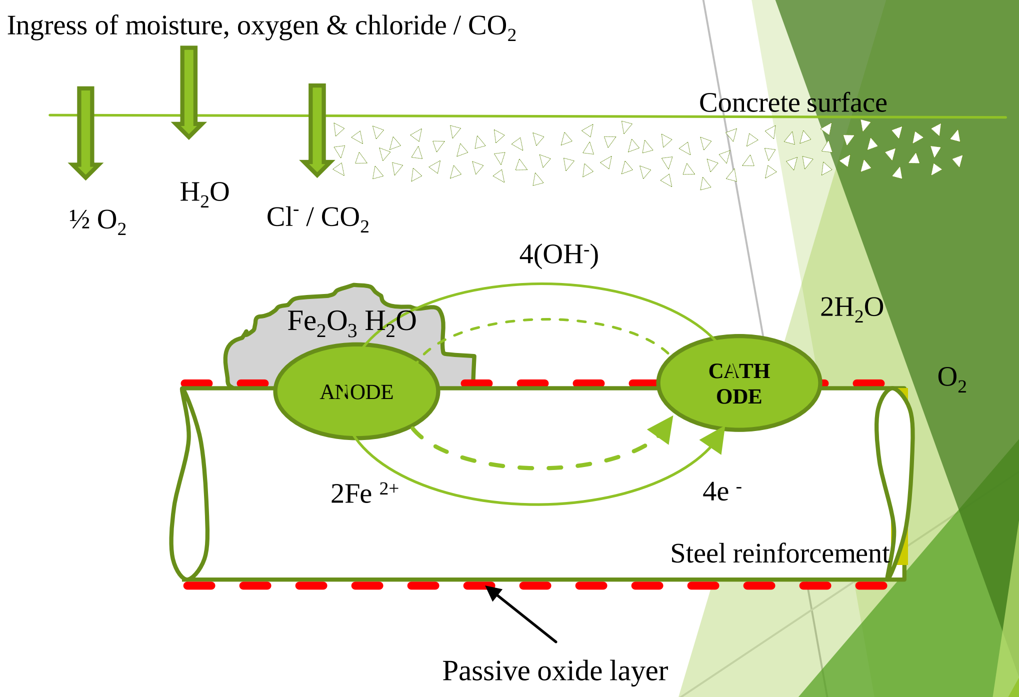
Producing into the solution positive **Fe^{2+}** and negative electrons



Anode $Fe \longrightarrow Fe^{2+} + 2e^-$

Corrosion of steel

- At the cathode the liberated negative electrons combine with H_2O and O_2 to form -ve OH^- ion
- These -ve OH^- ions then travel to the anode to add with +ve Fe^{2+} ions to form $Fe_2O_3.H_2O$ or rust

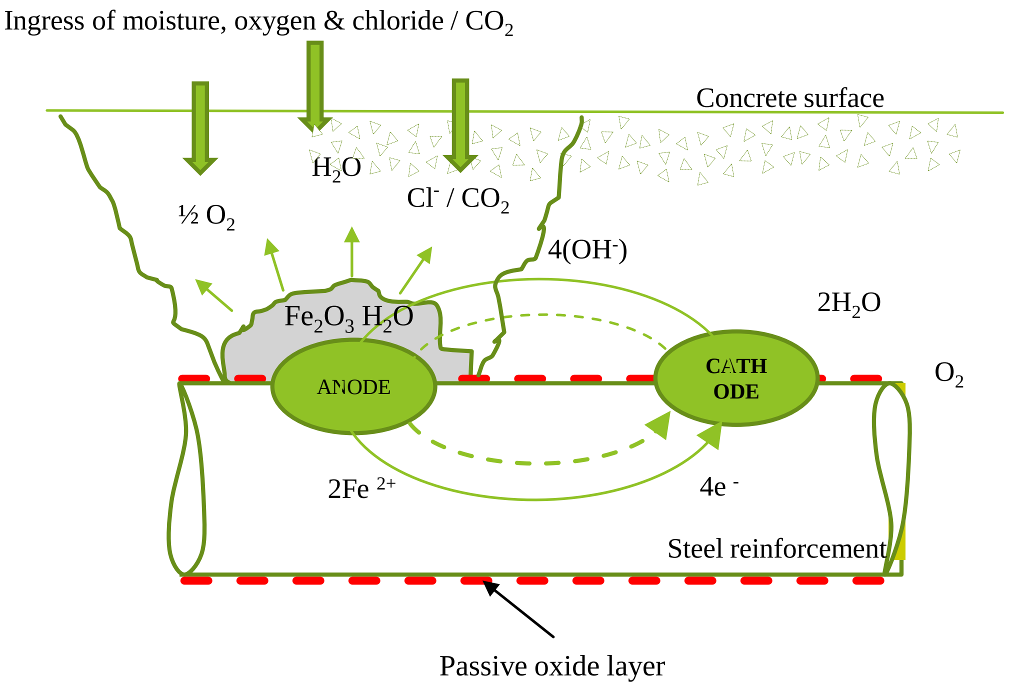


Cathode $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

Overall = $Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2 \xrightarrow{O_2} Fe_2O_3 \text{ x } H_2O$

Corrosion of steel

- The volume of rust is **3 to 6 times** more than the original volume of steel
- Thus the formation of rust resulting into an expansive pressure to the concrete
- Concrete cracks when this pressure exceeds the tensile strength capacity of concrete



Chloride-induced corrosion

- It is a very specific type of 'pitting' corrosion
- Characterised by galvanic action between
    - relatively large areas of passive steel acting as cathodes and
    - very small, local anodic pits connected by means of an electrolyte (pore fluid)

Examples of pitting corrosion induced by chloride ingress after 5 years

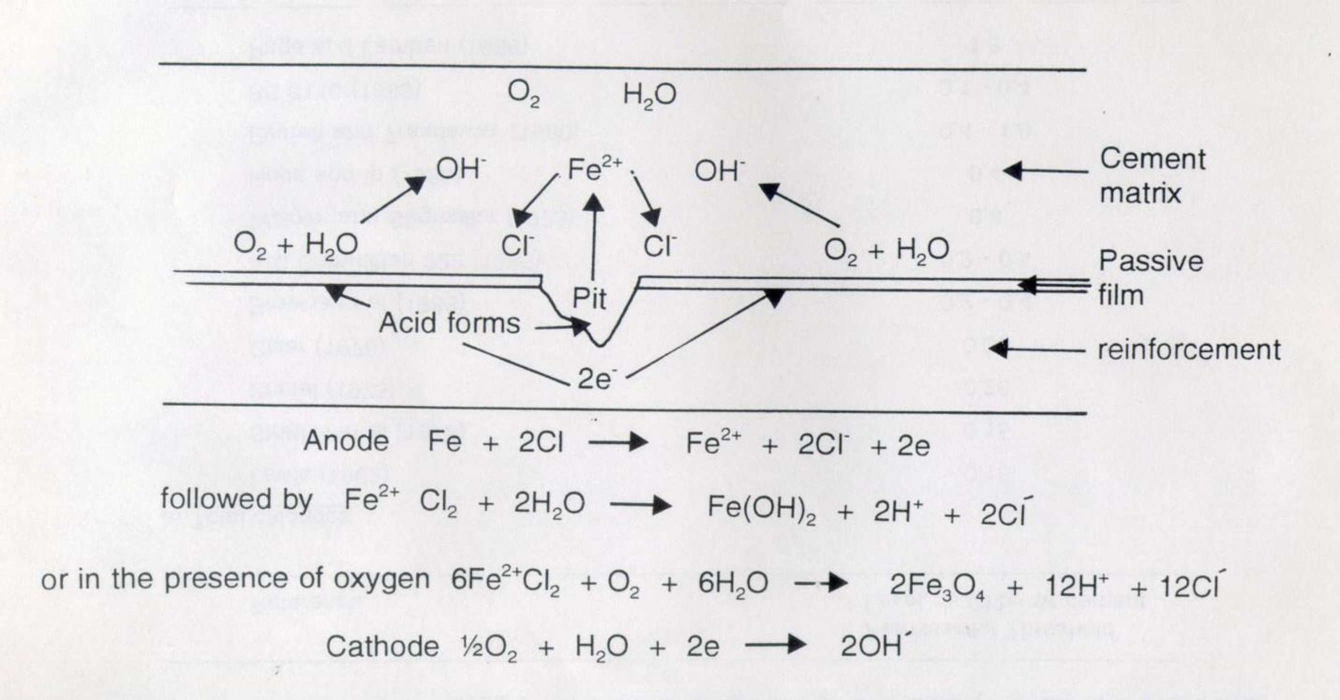
Chloride-induced corrosion

For initiation of corrosion, the passive oxide layer must be broken down and chloride ions must activate the steel surface to form an anode, with the passive surface being the cathode:

$Fe + 2Cl \rightarrow Fe^{++} + 2Cl^{-} + e^{-}$

$Fe^{++} + 2Cl^{-} \rightarrow FeCl_2$

$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl$



Corrosion due to carbonation

Carbonation is a diffusion controlled chemical reaction and can be divided into three simplified stages.

Stage 1 – Ingress of CO_2

CO_2 will move into the concrete pores by the process of diffusion due to a concentration difference between internal and external pore atmosphere.

Stage 2 – Reaction of CO_2 with pore fluids

CO_2 is then dissolved by the alkaline pore fluids (consisting mainly of water) to form carbonic acid.

$$CO_2 + H_2O \rightarrow H_2CO_3$$

Corrosion due to carbonation

Stage 3 – Formation of carbonates (carbonation) and neutralisation

The carbonic acid will then react with the alkaline constituents of the hydrate structure ($Ca(OH)_2$) to form carbonates and in the presence and continued supply of CO_2, carbonic acid reacts with the carbonates to form bicarbonates

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3$$

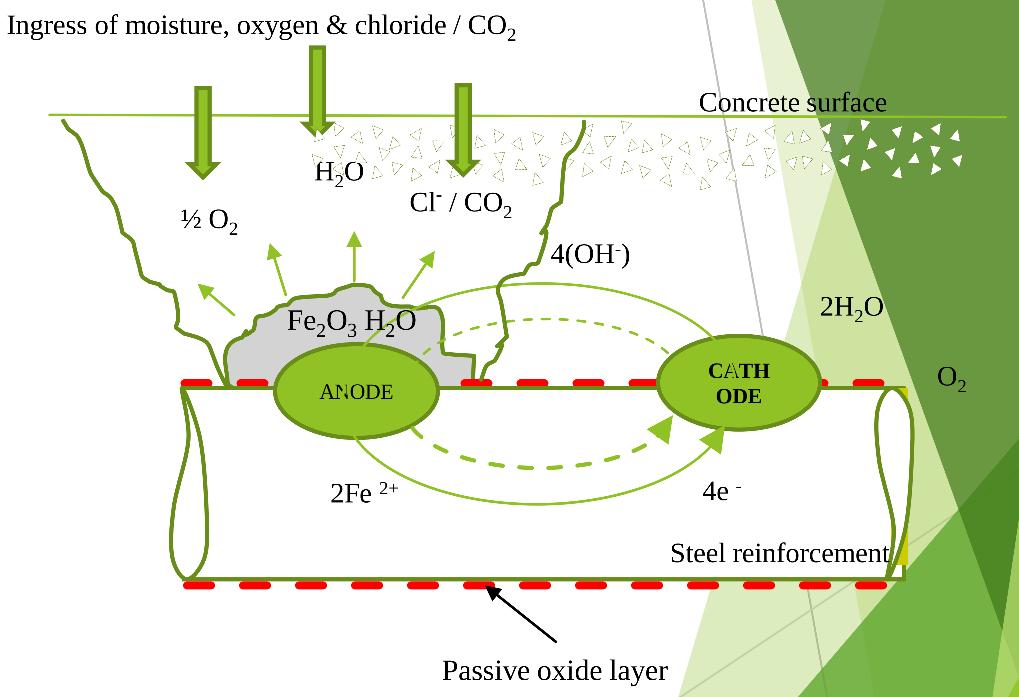
$$H_2CO_3 + CaCO_3 \rightarrow Ca(HCO_3)_2$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O$$

<u>Neutralisation will lead to a reduction of the highly alkaline nature of concrete and the breakdown of the passivating oxide layer protecting the steel reinforcement.</u>

Resisting Corrosion by enhancing concrete performance

- Enhancing permeation properties of concrete / covercrete
  - Type of cement/cementitious
  - Reduced w/c
  - Admixtures to improve the properties of concrete
  - Good concrete practice
- Increase the depth of cover



Sulfate attack

Sulfate Attack of Concrete

Dissolved sulfate in ground water can react with certain components of the cement paste leading to expansion, cracking and spalling of concrete

Sulfate Attack of Concrete

The most common forms of sulfate are:

Sodium sulfate	Na_2SO_4
Potassium sulfate	K_2SO_4
Magnesium sulfate	$MgSO_4$
Calcium sulfate	$CaSO_4$

Mechanism of Sulfate Attack

Sulfates will attack some or all of the three main hydrate components of hardened concrete:

Calcium hydroxide	$Ca(OH)_2$
Calcium aluminate hydrate	$CaO.Al_2O_3.H_2O$
Calcium silicate hydrate	$CaO.SiO_2.H_2O$

depending on the type of sulfate in solution involved.

$C_2S/C_3S + H_2O$ → C-S-H + $Ca(OH)_2$

$C_3A + H_2O$ → C-A-H + $Ca(OH)_2$

Mechanism of Sulfate Attack

Attack of $Ca(OH)_2$ components

$$Ca(OH)_2 + Na_2SO_4.10H_2O \rightarrow CaSO_4.2H_2O + 2NaOH + 8H_2O$$

$CaSO_4.2H_2O$: gypsum

$2NaOH$: soluble hydroxide

Mechanism of Sulfate Attack

Attack of calcium aluminate hydrate ($CaO.Al_2O_3.H_2O$) components

$$2(3CaO.Al_2O_3.12H_2O) + 3(Na_2SO_4.10H_2O) \longrightarrow 3CaO.Al_2O_3.3CaSO_4.31H_2O$$

ettringite

+

$$2Al(OH)_3 + 6NaOH + 17H_2O$$

soluble hydroxides

Mechanism of Sulfate Attack

Attack of calcium silicate hydrate ($CaO.SiO_2.H_2O$) components

$$3CaO.2SiO_2.aq + MgSO_4.7H_2O \longrightarrow CaSO_4.2H_2O + Mg(OH)_2 + SiO_2.aq$$

$Mg(OH)_2$: low solubility hydroxide

Factors Influencing Sulfate Attack

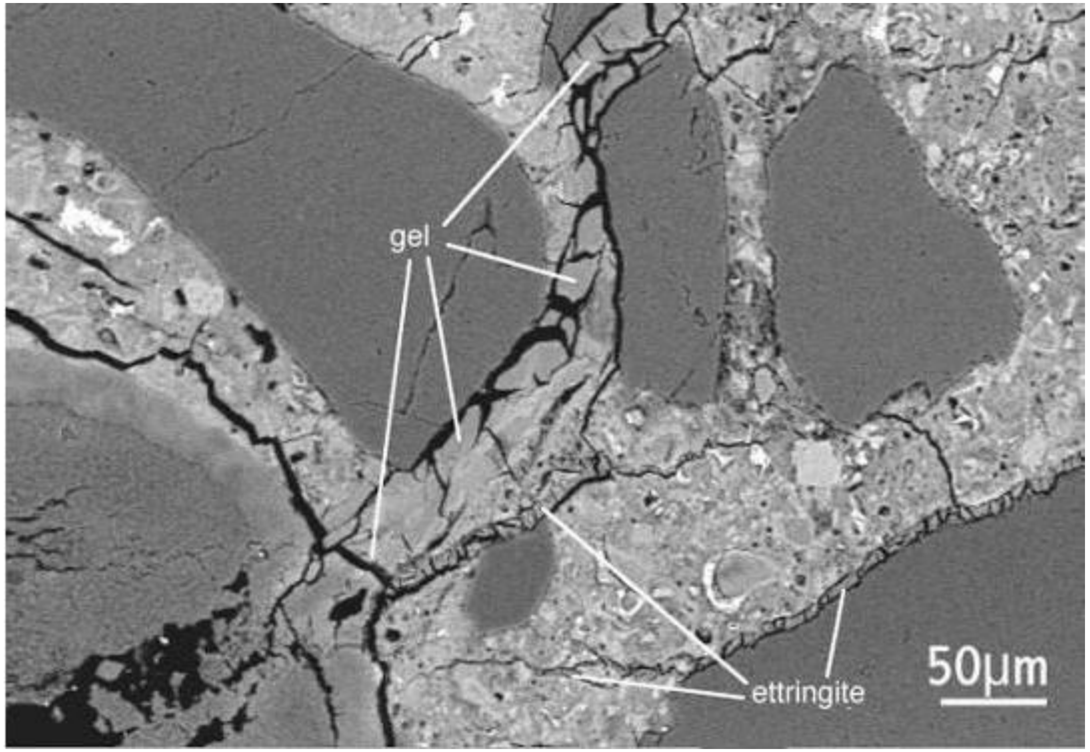
The main parameters which influence sulfate attack are:

1. Type of sulfate
2. Concentration
3. Permeation properties of concrete
4. Cement Type
5. Mobility Rate
6. Section size
7. Environment

Minimising the Effects of Sulfate Attack

- Enhancing permeation properties of concrete
- Use of supplementary cementitious materials
- Use of Sulfate Resisting Portland Cement
- Appropriate mix design
- Provide physical barrier against sulfates

Delayed Ettringite Formation (DEF)



Delayed Ettringite Formation (DEF)

As a part of the hydration process, ettringite, is normal to produce at the early stage due to the reaction of C_3A with gypsum

$C_3A + 3CaSO_4.2H_20 + 26H_2O$
Gypsum

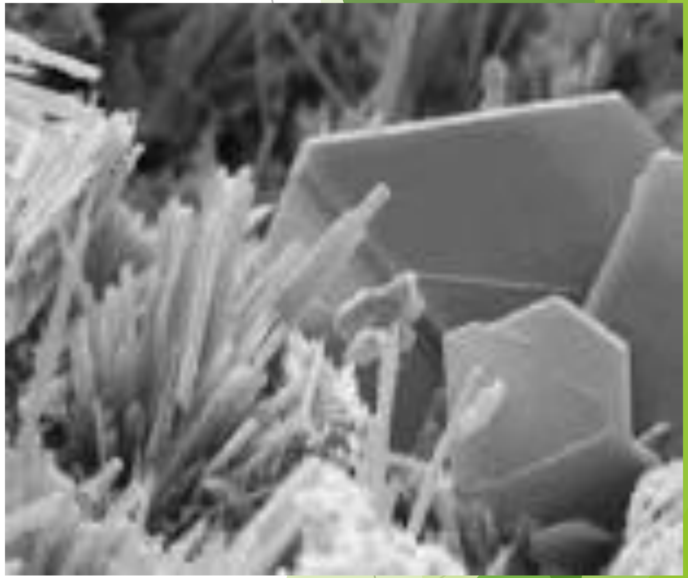
→

$C_3A.3CaSO_4.32H_20$
Ettringite

$C_3A.3CaSO_4.32H_20$
Ettringite

→

$C_3A.CaSO_4.12H_20$
Monosulfate

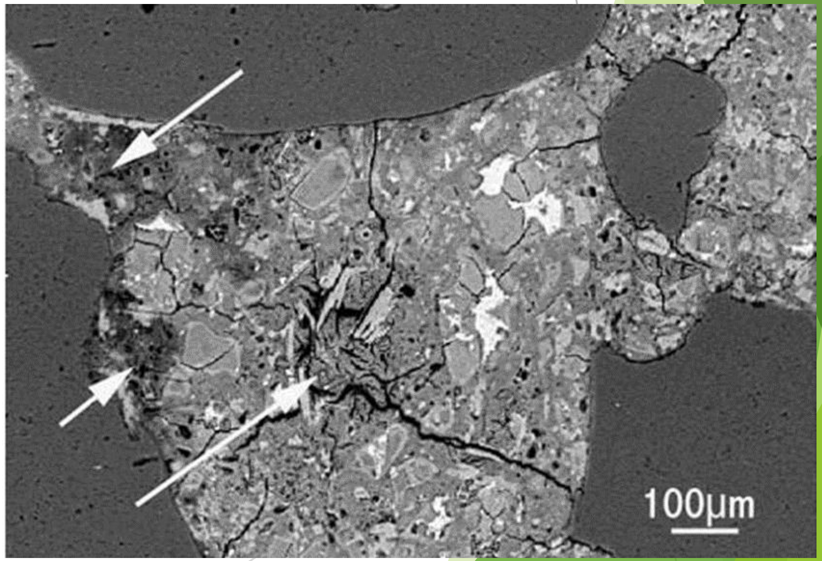


Delayed Ettringite Formation (DEF)

- If the concrete temperature exceeds 70°C, the early formation of ettringite does not occur
- The delayed formation of ettringite could be formed:
  - after hardening of concrete
  - in the prolonged presence of water
  - when the temperature cooled down

Delayed Ettringite Formation (DEF)

- As the volume of ettringite is larger than its original hydration product, it would produce internal stress, and induce cracks
- The most common factors of DEF are:
  - elevated temperature
  - prolonged exposure to water



Factors responsible for DEF

- Other factors:
  i) Composition of concrete
  ii) Aggregate type
  iii) Aggregate paste bond
  iv) Cement type and chemical composition of cement
  v) Exposure condition
  vi) Presence of high sulfate and alkali content in the original mix is also contributed to the DEF

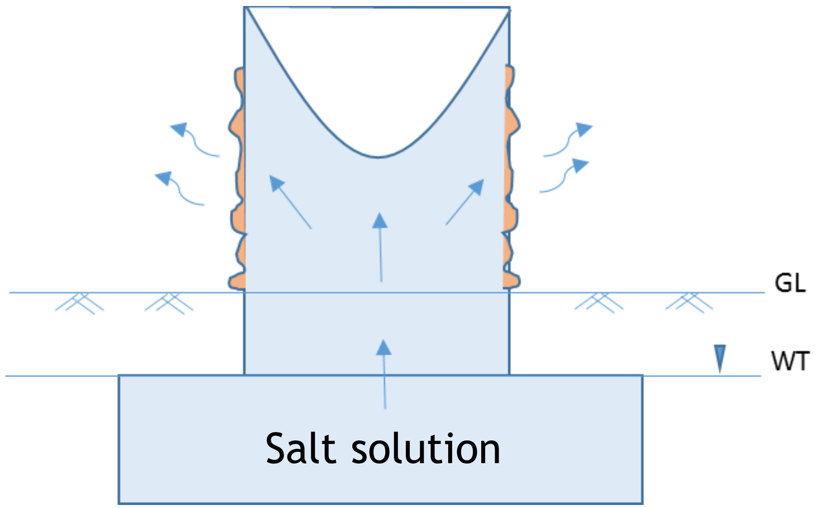
Combatting DEF

- Controlling the concrete temperature
- Use of high volume GGBS to reduce the heat of hydration
- Use of pozzolanic materials or reduced C_3A content cement
- Enhancement of permeation properties
- Use of water resisting admixture such as Pudlo

Salt Weathering

Salt Weathering

- Salt in solution from groundwater / damp soil can be transported by capillary action vertically through a concrete member.
- Above ground level, the moisture is drawn to the surface and evaporates, leaving crystals of salt growing in the near surface pores.



Salt Weathering

- This results in an area of deterioration just above ground level.
- This form of attack is common in hot, dry areas and may also occur in marine structures.

Combatting Salt Weathering

- More pronounce on porous structure by capillary rise mechanism
- Reduction of porosity by densifying the concrete microstructure
- Enhancing permeation properties by means of lower absorption of concrete
- Hydrophobic & pore-blocking admixture densify the concrete matrix by producing more C-S-H and reduce the absorption by creating a hydrophobic lining


Acid Attack

Acid Attack on Concrete

Concrete containing Portland cement, being highly alkaline in nature (pH>11), have little inherent resistance to attack from strong acids or compounds which may convert to acids (pH<3).

Mechanism of Acid Attack on Concrete

1. Acids decompose the hydrates of cement paste to form soluble calcium salts

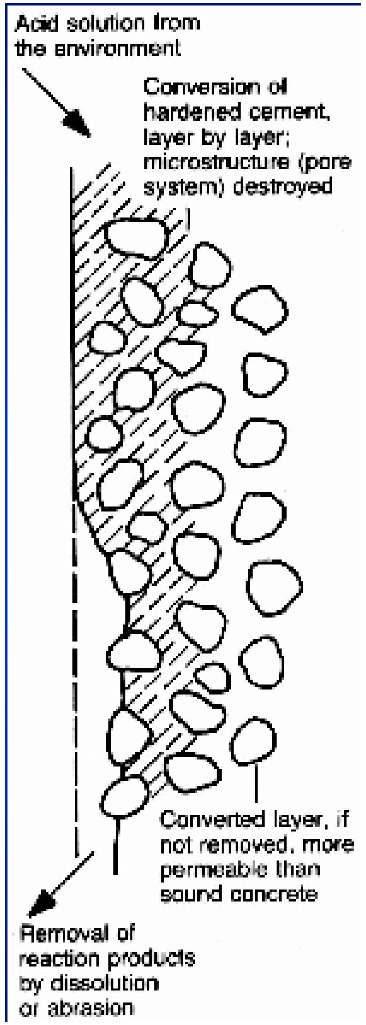
2. These soluble calcium salts will leach out in the presence of water

Acids in solution
(typically pH<5)

Hydrates of hardened concrete:
Calcium hydroxide: $Ca(OH)_2$
Calcium silicate hydrate: C-S-H
Calcium aluminate hydrate: C-A-H

Calcareous aggregates (limestone)

Mechanism of Acid Attack on Concrete



The most pronounced form of acid attack is the dissolution of calcium hydroxide which occurs:

$$2\ HX + Ca(OH)_2 \rightarrow CaX_2 + 2\ H_2O$$

(X is the negative anion of the acid)

Types and Sources of Acids

Acids can be present in many forms and may attack concrete such as:

- Agricultural environments
- Industrial environments
- Concrete airport pavements
- Sewer systems
- Moorland water systems
- Chemical storage tanks
- Gas arising from sewage or exhaust fumes may also acid attack concrete.

Types and Sources of Acids

Inorganic Acids
Carbonic
Hydrochloric
Hydrofluoric
Nitric
Phosphoric
Sulfuric

Organic Acids
Acetic
Citric
Formic
Humic
Lactic
Tannic

Other acidic substances:
Aluminium chloride
Hydrogen sulfide
Vegetable oils
Ammonium salts
Vegetable and animal fats
Lubricating oils

How to resist acid attack?

- Enhancing its permeation properties of concrete
- Reduced absorption
- Enhancing paste-aggregate bond
- Physical barrier for strong acidic situation

Multi-aggressive Seawater Attack

Multi-Aggressive Seawater Attack

Seawater contains a complexity of ions which will be detrimental to concrete in marine structures

The salts which are most common in seawater are:

- Sodium chloride ($NaCl$)
- Magnesium chloride ($MgCl_2$)
- Magnesium sulfate ($MgSO_4$)
- Calcium sulfate ($CaSO_4$)
- Potassium chloride (KCl)
- Potassium sulfate (K_2SO_4)

Multi-chemical Action

<u>Action of CO_2</u>

- Ingress of dissolved CO_2 will react with the $Ca(OH)_2$ and water to form aragonite and calcite ($CaCO_3$).
- This will precipitate to form a coating on the surface of the structure.

Multi-chemical Action

<u>Action of Sulfates</u>

- Sulfates will have a limited action due to the formation of non-expansive Friedell's salts (Calcium chloro-aluminate) in the presence of chlorides.
- However, gypsum will form leading to expansion, precipitation and the further formation of expansive ettringite.

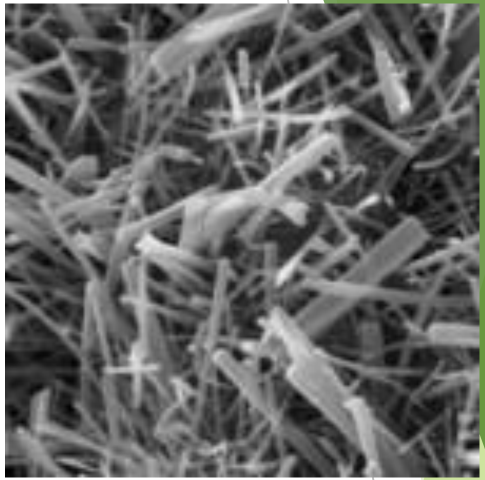
Friedell's salt

Gypsum

Multi-chemical Action

Action of Chlorides

- The presence of chlorides react with calcium hydroxide to form soluble calcium chloride ($CaCl_2$)
- A secondary reaction of $CaCl_2$ with the C-A-H in the hydrated cement leads to the formation of expansive chloro-aluminate, ettringite and thaumasite



Ettringite

Thaumasite

Mitigating multi-chemical action

- All deleterious chemical and gaseous ions enter into the concrete microstructure through **diffusion** mechanism
- Enhancing permeation properties of concrete by means of
  - reduced w/c ratio,
  - use of SCMs and
  - specific water resisting admixtures such as HPA
- Good concrete practice
- Curing and protection

Examples of Durable structures

Maple Lodge Sewage Treatment Works, UK

Construction began 1938 as above and after 70 years continuous wet/dry use no sign of corrosion

Southwark's Integrated Waste Management Facility, UK

- Chemical leachate
- High temperature up to 85 deg C
- No coating
- Extreme chemical environment
- Beside chemical resistant Pudlo provided higher initial and final compressive strength in high volume GGBS concrete

London borough waste and recycling centre, UK

- Resistance to the chemical residues - mostly acidic -leached by the waste.
- Floor needed to withstand substantial wear and tear from heavy vehicles and plant
- HPI modified durable concrete with the addition of steel and PPE fibres provided the solution

Examples of Truly Durable Structures

Photograph by Permission of "The Builder."

IN the design of the new Reptile House at the London "Zoo," the architect—Mr. E. Guy Dawber, A.R.A., P.R.I.B.A., made use of the basement structure of a building that previously occupied the site. When the progress of the work showed that the ground was waterlogged, the floor of the altered basement was covered with cement concrete, and the walls were rendered with cement mortar, both made impervious by the addition of 'PUDLO' Brand Cement Waterproofer. This inner lining forms a tank that keeps the water out of the basement. The general contractors, Messrs. Prestige & Co., Ltd., did the work by mixing the waterproofing powder with ordinary good Portland cement that was already on the job. The usual skill of the ordinary workman is quite sufficient to ensure successful results with

'PUDLO'
BRAND
CEMENT WATERPROOFER

KERNER-GREENWOOD & CO., LIMITED
CIRCUS STREET KING'S LYNN
Sole Proprietors and Manufacturers.

London Zoo Reptile House

Designed and built in 1926-27 by Joan Beauchamp Proctor and Sir Edward Guy Dawber, the reptile house opened in 1929.

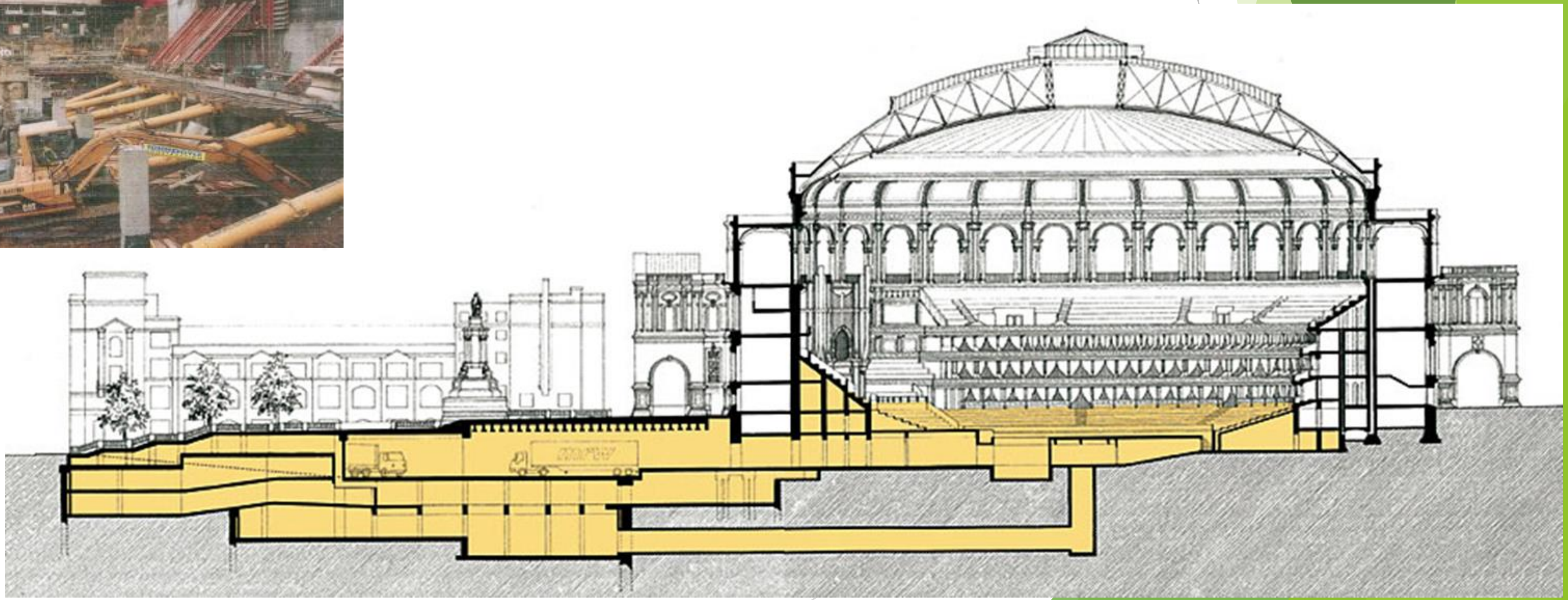
Examples of Truly Durable Structures

Church at Turner's Cross, Cork, Ireland

1931

Now

Royal Albert Hall, London

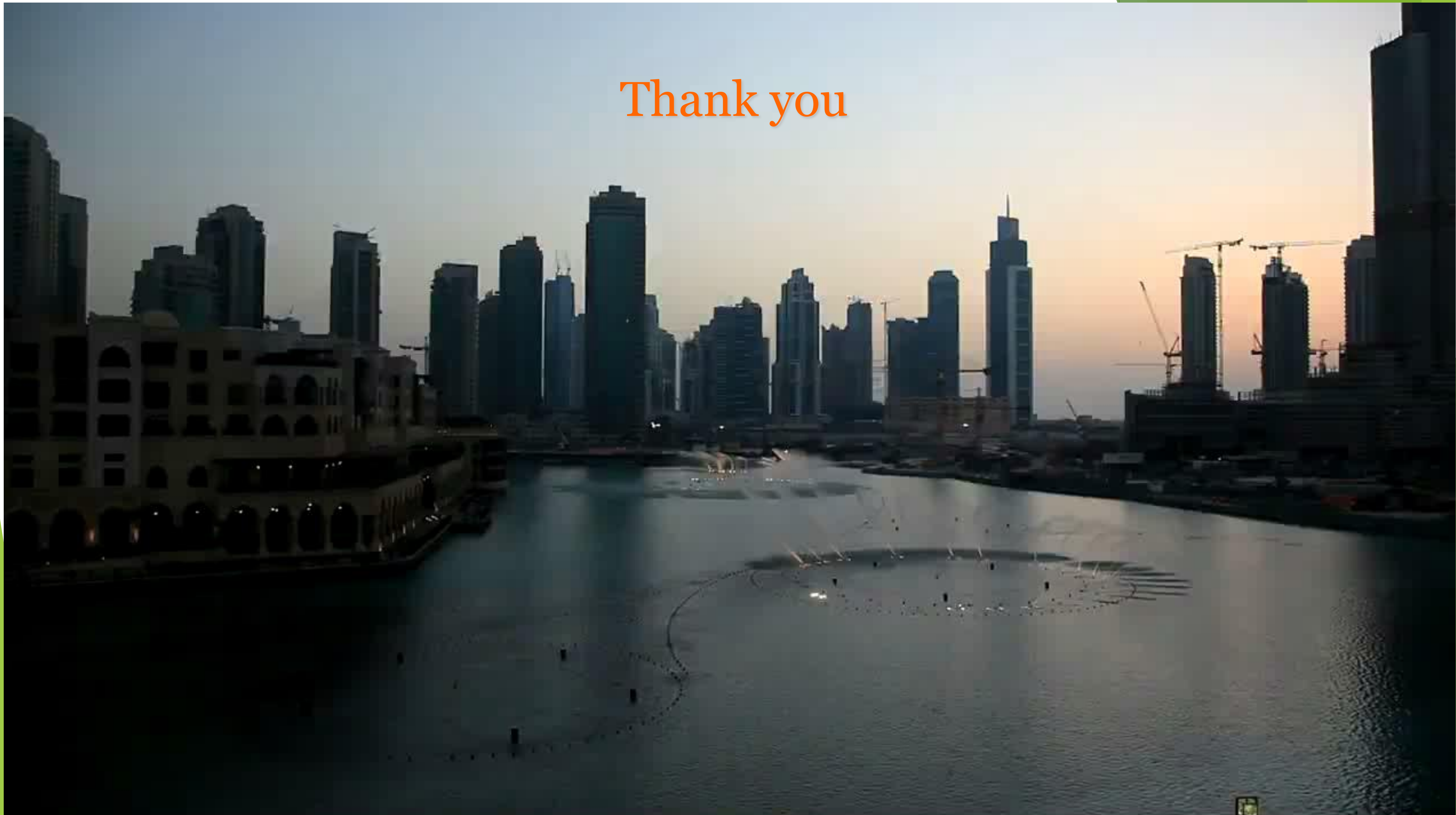


Royal Albert Hall, London

Building Design Partnership / Taylor Woodrow

Burj Khalifa Fountains

- 2½ kilometres of under-ground tunnels
- Housing cables and pipe racks to facilitate over 6,600 lights and 50 colour projectors to create a visual spectrum of over 1,000 different water expressions
- Fountain rises to a height of 500ft, equivalent of a 50 storey building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