Lecture 03: Corrosion protection of reinforced concrete

Mon 11.01.2016
Previous lecture summary

- Demolition planning
- Demolition methods applicable for concrete repair
- Demolition equipment
- Demolition of structural components
- Demolition procedures for reinforced concrete structures
- Controlling risks in demolition work
- Asbestos removal
- Other hazardous materials
Course content

Rak-43.3301 Repair Methods of Structures I

Deterioration mechanisms
Condition assessment
Repair analysis
Recommended repair methods

Rak-43.3312 Repair Methods of Structures II

Removal of deteriorated structures
Repair and protection of Reinforcing steel
Repair of facade structures
Repair of service systems
Repair of moisture problems

Service life evaluation

Rak-43.3312 Repair Methods of Structures II (4 cr)
Esko Sistonen & Fahim Al-Neshawy
Learning Café: Background

1. Factors influencing corrosion of reinforcement

2. Consequences of corrosion
Outlines

• Corrosion
  o Basic corrosion processes of steel in concrete
  o Corrosion cell
  o Phases

• POURBAIX-DIAGRAM

• Corrosion protection techniques
  o Cathodic protection
  o Chemical inhibitors
  o Re-passivation (Patch repairs)
  o Protection by alkalization
  o Coating systems
  o Electrochemical chloride removal
Basic corrosion processes of steel in concrete

1. **Depolarization reagent**, i.e. O₂ arrives at the surface through the medium surrounding it, dissolved in the medium.

2. **Electrochemical reactions** at the interface of metal

   **Cathodic reaction**
   (Oxygen) : \( O_2 + 2H_2O + 4e^- = 4OH^- \)
   (Chloride) : \[ Fe + 2Cl^- = \text{Complex (Fe}^{2+} + 2\text{Cl}^-) + 2H_2O + 2e^- \]

   **Anodic reaction**
   (Oxygen) : \( Fe = Fe^{2+} + 2e^- \)
   (Chloride) : \[ Fe + 2Cl^- = \text{Complex (Fe}^{2+} + 2\text{Cl}^-) + 2H_2O + 2e^- = Fe(OH)_2 + 2H^+ + 2Cl^- \]

Fe²⁺ can be further oxidized to Fe³⁺ under oxidizing conditions and can be accumulated at the surface of steel rebar or be dissolved into the pore solution.
Basic corrosion processes of steel in concrete

Cathode Site: \[ 2 \text{H}_2\text{O} + \text{O}_2 + 4 \text{e}^- \rightarrow 4 \text{OH}^- \]
[Water + Oxygen + Electron (Iron) = Hydroxyl Ions]

Cathode Site: \[ 2 \text{Fe}^{++} + 4 \text{OH}^- \rightarrow 2 \text{Fe(OH)}_2 \]
[Iron Ions + Hydroxyl Ions = Ferrous Hydroxide]

(Chloride):
\[ \text{Fe} + 2\text{Cl}^- = \text{Complex} \left( \text{Fe}^{2+} + 2\text{Cl}^- \right) + 2\text{H}_2\text{O} + 2\text{e}^- \]

Anode Site:
\[ 2 \text{Fe(OH)}_2 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \rightarrow 2 \text{Fe(OH)}_3 \]
[Iron Hydroxide + Water + Oxygen = Iron Hydroxide (RUST)]

(Chloride):
\[ \text{Fe} + 2\text{Cl}^- = \text{Complex} \left( \text{Fe}^{2+} + 2\text{Cl}^- \right) + 2\text{H}_2\text{O} + 2\text{e}^- = \text{Fe(OH)}_2 + 2\text{H}^+ + 2\text{Cl}^- \]
**Video:** Basic corrosion processes of steel in concrete
Four parts of a corrosion cell

Cathode
(no corrosion)
Reduction Half-Reaction

Anode
(location where corrosion takes place)
Oxidation Half-Reaction

Electrolyte
(Water, Moisture, etc.)

Electrical Connection between anode and cathode
(Metal)

Electrochemical corrosion can be stopped by eliminating any one of the four components
Phases of corrosion damage

**An initiation period**
- activated by
  - carbonation
  - chloride attack

**A propagation period**
- formation of expansive corrosion products at the steel surface
- cracking of the cover concrete

**An acceleration period**
- corrosion increases due to easy access of oxygen and water through cracks
- resulting in spalling of concrete.

Iron equilibrium diagram (POURBAIX-DIAGRAM)

• **Region 1: Corrosion**
  - At potentials more positive than -0.6 and at pH values below about 9, ferrous ion (Fe\(^{2+}\) or Fe II) is the stable substance.
  - This indicates that iron will corrode under these conditions.

• **Region 2: Active corrosion by Ferric ions Fe\(^{3+}\)**
  - At higher potentials and acidic pH values ferrous ions will form giving rise to active corrosion. **Ferric ions Fe\(^{3+}\)** are produced only at high potentials above 0.7 V.

Region 1: Corrosion, no passivity possible
Region 2: Active corrosion by Ferric ions Fe\(^{3+}\)
Region 3: Immunity, no corrosion possible
Region 4: Possible passivity by stable Fe2O3 and metastable Fe3O4
Iron equilibrium diagram (POURBAIX-DIAGRAM)

- **Region 3: Immunity**
  - At negative potentials iron Fe itself is the stable form hence in this region no corrosion is possible (immunity condition)
- **Region 4: Possible passivity by stable Fe₂O₃ and metastable Fe₃O₄**
  - If the pH > 7, then insoluble surface oxides will form.
  - Magnetite or black iron oxide Fe₃O₄ is produced at low electrode potentials.
  - At more positive potentials the iron oxide Fe₂O₃ is formed at the surface as a thin adherent film (passive layer)
  - Fe₂O₃ acts to block the surface reactions and hence corrosion rates are reduced.
  - The corrosion rate is very low in the passivation region of the diagram.
Learning Café: Corrosion protection

1. Protection associated with reinforcement steel

2. Protection associated with interface of steel / concrete (concrete cover)
Corrosion control using Pourbaix diagram

For the corrosion state point (A) in Pourbaix diagram for iron is controlled by:

1. Increase pH
   - Re-passivation (Patch repairs)
   - Protection by alkalization
2. Decrease the potential (E) to immunity region
   - Cathodic protection
3. Increase the potential (E) at the same pH
   - Addition of inhibitors
   - Special coating on the reinforcement surface to avoid the direct contact between the steel and concrete medium
Cathodic protection

Cathodic protection systems
- Galvanic systems (Sacrificial anode)
- Impressed current

**PRINCIPLE:**

- The material to be protected is supplied with an external cathodic current
- The electrochemical potential of the protected material is moved in a negative direction to the immune area
- The material is completely protected when it reaches the Protection Potential
Cathodic protection: Galvanic systems (Sacrificial anode)

- Sacrificial less noble metal corrodes to provide protective current
- There is no external control
- Anode material
  - Alloys of Mg, Al, Zn
- The cathode ↔ anode current is a function of:
  - the potential difference and
  - the electrical resistance.
- The potential difference between anode and cathode is a function of:
  - the environment
  - the relative electrode potentials of the anode and cathode materials.

http://www.jpbroomfield.co.uk/pages/galvanic-cathodic-protection.php
Cathodic protection: Impressed Current

- Impressed Current consists of an anode system, a DC power supply and monitoring probes, with associated wiring.
- ICCP has been applied to most types of reinforced concrete structures, such as buildings (blocks of flats, offices, hospitals, schools etc.), bridges (decks and substructures), tunnels etc.

http://www.jpbroomfield.co.uk/pages/impressed-current-cathodic-protection.php
Cathodic protection: Impressed Current

- For steel in concrete, one of the most important decisions is the choice of anode.
- Anodes consist of:
  - Conductive coating
    - Sprayed, rolled or brushed over a niobium wire (300 um thickness)
  - Arc sprayed zinc
    - Spraying metal on concrete with compressed air (300-400 um)
  - Titanium anode mesh
  - Titanium anode mesh jackets
  - Titanium ribbon
  - Discrete anodes
  - Thermally sprayed titanium

- Current requirements
  - Atmospheric zones (5 to 15 mA/m²)
  - Under water (0.2 to 2 mA/m²)
  - Decreases with time

http://www.jpbroomfield.co.uk/pages/impressed-current-cathodic-protection.php
Cathodic protection: Impressed Current
## Comparison of Cathodic Protection systems

<table>
<thead>
<tr>
<th>Pros</th>
<th>Impressed current system</th>
<th>Galvanic system (Sacrificial anode system)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Longer anode life</td>
<td>Inherently simple</td>
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<td></td>
<td>Current can be controlled</td>
<td>No monitoring and maintenance</td>
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<tr>
<td></td>
<td></td>
<td>No requirement for electrical isolation</td>
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<td></td>
<td></td>
<td>Risk of hydrogen embrittlement on high strength steel is minimal</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Saw cutting and concrete encapsulation for anodes is not required</td>
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</tbody>
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<table>
<thead>
<tr>
<th>Cons</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Requires monitoring and maintenance</td>
<td>Short anode life</td>
</tr>
<tr>
<td></td>
<td>Electrical isolation required between anode and steel</td>
<td>Anode current delivery is dependent on anode chemistry and surrounding environment</td>
</tr>
<tr>
<td></td>
<td>Conduit and wiring required</td>
<td>Current cannot be adjusted or controlled</td>
</tr>
</tbody>
</table>
Corrosion Inhibitors

- Inhibitors are substances that:
  - decrease reactivity
  - slow oxidation/reduction reactions by removing reactants like O2 gas by reacting it with an inhibitor
- A corrosion inhibitor may act in a number of ways:
  - blocking active sites on the metal surface.
  - increasing the potential of the metal surface
  - formation of a thin layer on the surface

- The range of inhibitors presently available can be summarized as follows:
  - vapour phase inhibitors, based on volatile amino alcohols which create a molecular layer on the steel to stop corrosion
  - Calcium nitrite, an anodic inhibitor in a mixture to aid penetration into concrete
  - Monofluorophosphate which seems to create a very alkaline environment as it hydrolyses in the concrete.

http://cdn.intechopen.com/pdfs-wm/46243.pdf
Likely performance of migrating corrosion inhibitors in concrete

The effectiveness of migrating corrosion inhibitors is generally controlled by environmental, material and structural factors.

<table>
<thead>
<tr>
<th>Likely inhibition</th>
<th>Corrosive conditions</th>
<th>Concrete conditions</th>
<th>Severity of corrosion</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Good</strong></td>
<td>Mildly corrosive, low chlorides or carbonation</td>
<td>Dense concrete with good cover depths (&gt; 50 mm)</td>
<td>Limited corrosion with minor pitting of steel</td>
</tr>
<tr>
<td><strong>Moderate</strong></td>
<td>Moderate levels of chloride at rebar (i.e. &lt;1%)</td>
<td>Moderate quality concrete, some cracking</td>
<td>Moderate corrosion with some pitting</td>
</tr>
<tr>
<td><strong>Poor</strong></td>
<td>High chloride levels at rebar (i.e. &gt; 1%)</td>
<td>Cracked, damaged concrete, low cover to rebar</td>
<td>Entrenched corrosion with deep pitting</td>
</tr>
</tbody>
</table>
Patch repair

- Localized patch repairs of areas of corrosion damage
- Restoring passivating conditions to the reinforcement
- Patch repairs consist of:
  1. removal of cracked and delaminated concrete to fully expose the corroded reinforcement
  2. cleaning of corroded reinforcement
  3. application of a protective coating to the steel surface
  4. application of repair mortar or micro-concrete to replace the damaged concrete
  5. possible coating or sealant applied to the entire concrete surface to reduce moisture levels in the concrete
Re-alkalization

- Used primarily on **carbonated building facades**
- The re-alkalization process **restores the alkalinity of carbonated concrete and return the passivity of the steel reinforcement**
- During this process, an electric field is applied between the reinforcing steel and an externally mounted anode mesh.
- Alkaline electrolyte provides a connection between the concrete and the embedded anode mesh.
- The electric field produces a high pH environment at the steel surface as electrolysis occurs.

- The alkaline electrolyte conducts electricity and provides alkalis to the carbonated concrete.

![Diagram of re-alkalization process](http://wisdotresearch.wi.gov/wp-content/uploads/06-06corrosionconcretebridges-f1.pdf)
Coating systems: Epoxy-coated reinforcement

Epoxy coatings protect the steel from corrosion in two ways.

1. First, coatings are nonconductive, preventing an electrical connection from forming between bars.

2. Second, epoxy coatings act as a barrier to oxygen, moisture, and chlorides, preventing them from reaching the underlying steel.

Advantage of epoxy coated rebar

- Strong adhesive force to the steel.
- Good chemical stability.
- High insulation and anti-cathode decomposability.
- High adhesive force with the concrete.
- Used in the building with high demand and under the corrosive Environment, it can lengthen the use life of the building for more than 50 years.
Coating systems: Epoxy-coated reinforcement

\[ \text{ANODE: } Fe \rightarrow Fe^{2+} + 2e^- \]

\[ \text{CATHODE: } \frac{1}{2} H_2O + \frac{1}{4} O_2 + e^- \rightarrow OH \]
Coating systems: Galvanized reinforcement

- zinc acts as a barrier to moisture and chlorides
- In a corrosive environment, zinc will act as a sacrificial anode, providing cathodic protection to the steel
- In concrete, zinc reacts with the highly alkaline pore solution in concrete, forming a calcium zincate salt and hydrogen gas.

\[
Zn + Ca(OH)_2 + 2H_2O \rightarrow CaZn(OH)_4 + H_2
\]

- Below a pH of 13.3, the zincate salt forms a stable passive layer
- Evolution of hydrogen gas can increase the permeability of the surrounding concrete

- Most galvanized bars are treated with:
  - chromate or
  - coated with an organic coating
  both to prevent hydrogen formation and to protect the zinc in high pH environments
Coating systems: Galvanized reinforcement

Corrosion of ordinary and hot-dip galvanised reinforcement bars in carbonated concrete (initiation and propagation period).

![Graph showing corrosion of galvanized reinforcement bars over time](image)
Coating systems: Galvanized reinforcement

Galvanic corrosion of zinc coating in chloride-contaminated and carbonated concrete.
Electrochemical chloride extraction (ECE)

- The technique uses a temporary anode and passes a high current (about 1A/m² of steel or concrete surface area) to pull the chlorides away from the steel.

http://www.jpbroomfield.co.uk/pages/electrochemical-chloride-extraction.php
Electrochemical chloride extraction (ECE)

- high current (1A/m² of steel or concrete surface area)
- Usually around 50 to 90% of the chloride can be completely removed
- It is at its best where the steel is closely spaced and the chlorides have not penetrated too much beyond the first layer of reinforcing steel and future chlorides can be excluded.
- It has been applied to highway structures, car parks and other structures in Europe and North America.
- The treatment typically takes six to eight weeks.

http://www.jpbroomfield.co.uk/pages/electrochemical-chloride-extraction.php
Electrochemical chloride extraction (ECE)

**Benefits**
- Non-Destructive Repair Method
- Removes the Cause of Corrosion
- Lower Cost
- Permanent Advantages
- Protection for Entire Structure
- Extended Service Life
- Fast Installation and Removal
- No Permanent Maintenance Required
- More Environmentally Friendly
- Hydroxyl ion formation increases pH around reinforcement

http://www.jpbroomfield.co.uk/pages/electrochemical-chloride-extraction.php
## Comparison of corrosion protection techniques

<table>
<thead>
<tr>
<th>Technology</th>
<th>Effective Life</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathodic Protection</td>
<td>&gt; 100 years</td>
<td>• Permanent protection.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Proven track record.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Longest effective life.</td>
</tr>
<tr>
<td>Stainless Steel Bars</td>
<td>Not known</td>
<td>• Expensive option.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Lifetime unproven.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Possible issues with galvanic couples.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Not suitable for hot marine environments.</td>
</tr>
<tr>
<td>Coated Reinforcement</td>
<td>Highly variable</td>
<td>• Very sensitive to contractor handling.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• There is inevitably coating damage during the fabrication and concrete pouring.</td>
</tr>
<tr>
<td>Chemical Inhibitors</td>
<td>Highly variable</td>
<td>• Limited “active” life.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Conflicting data as to effectiveness.</td>
</tr>
<tr>
<td>Patch Repair</td>
<td>&lt; 5 to 10 years</td>
<td>• Incipient anode effect renders corrosion</td>
</tr>
<tr>
<td></td>
<td>years</td>
<td>• Inevitable in adjacent parts of the structure</td>
</tr>
</tbody>
</table>

[http://www.cathodic.co.uk/files/1246457276Steel%20In%20Concrete%20Overview.pdf]
Summary

Teaching event summary

- Corrosion
- Approaches to prevent corrosion of steel reinforcement
- Corrosion prevention measures for reinforced concrete systems
  - Cathodic protection systems
  - Coating systems
  - Electrochemical chloride removal
  - Corrosion inhibitors
  - Patch repair
  - Re-alkalization

Next teaching event

Thu 14.01.2016 Repair of concrete and rendered structures