Corrosion Protection

Basic Corrosion Theory and Protection Method
Part 1

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Universiti Teknologi Malaysia
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Survey 1

"What should be the primary degree of a corrosion engineer?"
Survey 2

"What did you graduate in yourself?"
Corrosion & Corrosion Control

- What is Corrosion
- How/Why Does Corrosion Occur
- Corrosion Costs
- Forms of Corrosion
- Corrosion Control Methods
  - Coatings
  - Painting
  - Cathodic Protection (CP)
Corrosion cost in US and MY

Total cost = 137 billion USD (2001)

Malaysia corrosion cost is ~ RM 462 Million (1996)
What is Corrosion

Corrosion (n)
- The chemical or electrochemical reaction between a material and its environments that produces a deterioration of the material and its properties
Impact of Corrosion

Corrosion is a major Economic, Environmental, and Safety Problem which adversely affects our Nation, as well as many of everyday facilities.
Impact of Corrosion

Losses due to Corrosion

Consequences of Corrosion

- Reduction of metal thickness leading to mechanical strength and structural failure and breakdown

Corrosion impact on gas pipeline
Consequences of Corrosion

- Hazard or injuries to people arising from structural failure or breakdown e.g. bridge, cars and aircraft
Consequences of Corrosion

- reduced value of goods due to deterioration of appearance
Consequences of Corrosion

- Contamination of fluid in vessel and pipe
- Mechanical damage to pump, valves etc or blockage of pipe by corrosion product
Corrosion Costs

Direct Costs
- NACE, CCTechnologies & FHWA jointly produced a report in 2001 detailing the costs of corrosion
  - $276 billion USD annually
  - 3.1% of US GDP (1998)

Indirect Costs
- Catastrophe
  - Public safety, property damage, environmental contamination
- Natural Resources
  - Waste production, increase energy consumption
- Public Oursey
  - Traffic, Inconvience
Electrochemistry - Corrosion Cell

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \] (anodic reaction)

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \] (cathodic reaction)
Electrochemistry of Corrosion

\[ 2\text{Fe} \rightarrow 2\text{Fe}^{2+} + 4\text{e}^- \text{ (anodic reaction)} \]
\[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \text{ (cathodic reaction)} \]

\[ 2\text{Fe} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_2 \]

Iron + Water with oxygen dissolved in it \rightarrow Iron hydroxide

\[ 4\text{Fe(OH)}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O} \]

Iron hydroxide + Oxygen \rightarrow Water + Hydrated iron oxide (brown rust)
Bare Steel Corrosion

- Microscopic anodic and cathodic areas exist on a single piece of steel.

- As anodic areas corrode, new material of different composition is exposed and thus has a different electrical potential.
Three required ingredients for rust formation

1. Water (solvent and reactant)
2. Oxygen (oxidizer reactant)
3. Electrolyte (ion transport in water)

- Paint or polymer coatings protect the metal and prevent corrosion
- Even pinhole can lead to breakdown
The Galvanic Series

ZINC – Anode
STEEL - Cathode

This arrangement of metals determines what metal will be the anode and cathode when the two are put in a electrolytic cell (arrangement dependent on salt water as electrolyte).
How different types of atmosphere affect corrosion rates with two years of exposure

<table>
<thead>
<tr>
<th>Metal</th>
<th>Industrial Air (microns/year)</th>
<th>Marine Air (microns/year)</th>
<th>Rural Air (microns/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>0.81</td>
<td>0.71</td>
<td>0.025</td>
</tr>
<tr>
<td>Copper</td>
<td>1.19</td>
<td>1.32</td>
<td>0.58</td>
</tr>
<tr>
<td>Lead</td>
<td>0.43</td>
<td>1.41</td>
<td>0.48</td>
</tr>
<tr>
<td>Zinc</td>
<td>5.13</td>
<td>1.60</td>
<td>0.86</td>
</tr>
<tr>
<td>Mild Steel</td>
<td>13.72</td>
<td>6.35</td>
<td>5.08</td>
</tr>
<tr>
<td>Weathering steel</td>
<td>2.54</td>
<td>3.81</td>
<td>1.27</td>
</tr>
</tbody>
</table>
Forms of Corrosion

- General
  - Identified by uniform formation of corrosion products that causes an even thinning of the substrate steel

- Localized
  - Caused by difference in chemical or physical conditions between adjoining sites

- Bacterial
  - Caused by the formation of bacteria with an affinity for metals on the surface of the steel

- Galvanic/Dissimilar Metal
  - Caused when dissimilar metals come in contact, the difference in electrical potential sets up a corrosion cell or bimettalic couple
Bimetallic Corrosion

- Severe problems are often encountered where different metals are joined together. If their corrosion potentials are different a cell is formed with electrons passing between them – one is anode (attacked) the other is cathode.

- Let’s see what happens:
Bimetallic Couple
Case study for bimetallic corrosion

• In a plumbing system a mild steel pipe had to be couples to a copper one. A ceramic insulator was used to insulate the pipes from each other. However, the carefully engineered assembly as attached by a metal brackets to a wall panel made of sheet metal. The panel bypassed the insulated joint and allowed electrons to flow from the steel to the copper. The steel pipe leaked in a very short time.
# Electrochemical Series

<table>
<thead>
<tr>
<th></th>
<th>Ag</th>
<th>Cu</th>
<th>Sn</th>
<th>Fe</th>
<th>Zn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E^0$ ($V_{she}$)</td>
<td>0.8</td>
<td>0.3</td>
<td>-0.1</td>
<td>-0.4</td>
<td>-0.8</td>
<td>-1.7</td>
</tr>
</tbody>
</table>

- **noble**
- **base**
Atmospheric Corrosion

How does corrosion take place in air?
-due to moisture and contaminants!

Rate increases for Relative Humidity > 60-70%
Chlorides (from sea) or sulphur dioxide (from power stations etc) accelerate, also particulates.
The Delhi pillar
Delhi pillar inscription
Corrosion of Steel H Piling Embedded in Concrete
Pitting Corrosion

- Passive alloys resist corrosion, but are subject to various problems:
- In the presence of aggressive ions, notably halides, local breakdown of the oxide film occurs with consequent attack.
- Surrounding passive areas act as the cathode.
What is pitting?

- Metal dissolves in pit and hydrolysis lowers pH

![Diagram showing aluminium, Al^{3+}, oxygen, passive film, and 3e](image)
Ionic current drives chloride ions into pit → high \([\text{Cl}^-]\) (plus low pH)
Effects of flow

PITTING

WALL THINNED
Removed & Leaking

Tank Wall Completely Penetrated Due to Pitting Corrosion
Why corrosion?

Thermodynamics tells us that $\Delta G$ for the formation of oxides, sulphides etc is negative for most metals used in engineering; only gold, platinum etc are stable.

We are concerned with *kinetics* – how fast is corrosion?
What is the mechanism?

Some types of corrosion involve gas-phase reactions e.g. high temperature oxidation, controlled by transport within the growing solid oxide.

Most corrosion ("aqueous corrosion") requires the presence of water to allow reactions to occur (or another ionising liquid).
What is the mechanism?

Corrosion is electrochemical – the metal surface acts as an electrode with two reactions:

Anodic – oxidation (releases electrons)
Cathodic – reduction (consumes electrons)

No external current is needed: electrons from anode are consumed by cathode.

Because metal conducts, the anode and cathode can be in different places.
Corrosion in acids

\[ M + 2\text{HCl} \rightarrow M\text{Cl}_2 + \text{H}_2 \]

Is really:

\[ M + 2\text{H}^+ \rightarrow M^{++} + \text{H}_2 \]

(sporntaneous?)
Anode:

$$\text{Fe} \rightarrow \text{Fe}^{++} + 2e$$

Cathode:

$$2 \text{H}^+ + 2e \rightarrow \text{H}_2 \quad \text{(in acid)}$$

Or in neutral aerated solutions:

$$\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2e \rightarrow 2 \text{OH}^-$$
When anode and cathode are separate, ionic current must flow in solution.
## Pipeline Failure Causes

![Pipeline Failure Causes Table](image)

### Natural Gas Transmission Pipeline Incident Summary by Cause 1/1/2002 - 12/31/2003

<table>
<thead>
<tr>
<th>Reported Cause</th>
<th>Number of Incidents</th>
<th>% of Total Incidents</th>
<th>Property Damages</th>
<th>% of Total Damages</th>
<th>Fatalities</th>
<th>Injuries</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excavation Damage</td>
<td>32</td>
<td>17.8</td>
<td>$4,583,379</td>
<td>6.9</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Natural Force Damage</td>
<td>12</td>
<td>6.7</td>
<td>$8,278,011</td>
<td>12.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Other Outside Force Damage</td>
<td>16</td>
<td>8.9</td>
<td>$4,688,717</td>
<td>7.1</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>Corrosion</td>
<td>46</td>
<td>25.6</td>
<td>$24,273,051</td>
<td>36.6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Equipment</td>
<td>12</td>
<td>6.7</td>
<td>$5,337,364</td>
<td>8.0</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>Materials</td>
<td>36</td>
<td>20.0</td>
<td>$12,130,558</td>
<td>18.3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Operation</td>
<td>6</td>
<td>3.3</td>
<td>$2,286,455</td>
<td>3.4</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Other</td>
<td>20</td>
<td>11.1</td>
<td>$4,773,647</td>
<td>7.2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>180</td>
<td></td>
<td>$66,351,182</td>
<td></td>
<td>2</td>
<td>13</td>
</tr>
</tbody>
</table>

Note that corrosion (external and internal) is the most common cause of natural gas transmission pipeline incidents in 2002-2003.
Corrosion Can Be Controlled

Corrosion Control must be properly addressed during the design, installation, and subsequent operation of systems adversely affected by the corrosion process.
Venn diagram

The relationship between corrosion management, corrosion control, materials, environments and people
CORROSION and DESIGN

Specification ➔ Design ➔ Materials Selection

Corrosion Protection?

- Paint?
- Metallic Coating?
- Inhibitors?
- Cathodic Protection?

Maintenance?

- Inspection and Monitoring
Corrosion Control

- Modification to the design
- Modification to the environmental
- Application of barrier coats
  - Barrier protection
- Selection of materials
  - Corrosion Resistance Material
- Electrical Method
  - Cathodic protection
Corrosion Control by Design

Principle of good design is to minimize corrosion problem;

- Ensure structure has adequate safety margin
- Allowing overdesign to minimise, resulting in thinner section, lower weight and reduced capital cost
Corrosion Control by Design

Case 1 – Corrosion occurred in a buried oil pipeline 360 km long, which has a 200 mm external diameter. A wall thickness of 6.3 mm was adequate to cope with the stress levels imposed on the pipe, but to allow for corrosion it was increased to 8.3 mm. This corrosion allowance used an extra 3000 tonnes of steel and caused a loss of 4% carrying capacity in the line.
Corrosion Control Methods

- **Barrier Protection**
  - Provided by a protective coating that act as a barrier between corrosive elements and the metal substrate

- **Cathodic Protection**
  - Employs protecting one metal by connecting it to another metal that is more anodic, according to the galvanic series

- **Corrosion Resistance Materials**
  - Materials inherently resistant to corrosion in certain environments
Barrier Protection

- Paint
- Powder Coatings
- Galvanizing
Surface Preparation

For painting or coating performance it is most essential that the surface to be painted or shell be adequately prepared.

Therefore all surface to be coated shell be clean by abrasive blasting to near white metal in accordance to SSPC-SP 10 (sa 2 ½) or NACE -01 specification:

- To remove the loose material
- To increase the surface area of the substrate by increasing the roughness and anchor pattern of the surface
Coatings

Protective coatings are the most commonly used method of corrosion control.

The air conditioner on the left is starting to show rust stains due to problems with protective coating.

The same types of problems are starting to appear on the aluminum airplane wing shown on the right.
Coatings

Type of coating mainly depend on

- method of coating
- the suitability of the environment
- type of structure to be protected
How do Coatings Protect?

- Protect metal from corrosion by acting as a barrier
- Reducing transport of \( \text{H}_2\text{O}, \text{O}_2 \) and ions
- Coating high resistance → low corrosion rate
# Coating types and their lives

<table>
<thead>
<tr>
<th>Protection duration needed</th>
<th>Requirement for coating type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short term</td>
<td>Single pack materials such as alkyds, emulsions and acrylics are usually this category</td>
</tr>
<tr>
<td>1-5 years</td>
<td></td>
</tr>
<tr>
<td>Medium term</td>
<td>Two component materials such as zinc-rich primers, epoxies, polyurethanes, usually at lower thickness</td>
</tr>
<tr>
<td>5-10 years</td>
<td></td>
</tr>
<tr>
<td>Long term/high performance</td>
<td>Two-component materials such as metal spray, epoxies, polyurethanes, glass flake and FRP</td>
</tr>
<tr>
<td>10+ years</td>
<td></td>
</tr>
</tbody>
</table>
Corrosion Protection by Organic Coating

- Absorption of water by organic coating is related to the concentration of water in the electrolyte.

- Water permeability to the coating is controlled by the concurrent process of water absorption and diffusion. The present of the defect such as pores, holiday and fissures will effect the coating quality.

- The entire coated surface of each pipe shall be inspected with Holiday Detector before lower in to the trench.
Above Ground Corrosion Control by Coating
Station Corrosion Prevention by Coating
Station Corrosion Prevention

Methods – Applying Paint onto Corroded Surface

- Corroded surface are cleaned with water and solvent to remove any oil and grease traces
- Corroded/rusty portion are removed using wire brush
- The surface are cleaned and dried using cotton rag
- A layer of primer coating coating paint are applied e.g. Zinc Rich Primer, Micaceous Iron Oxide (MIO), Red Oxide Primer (ROP)
- A layer of finished polyurethane base paints are applied according to standard colour
Station Corrosion Prevention

Methods – Applying Antiseize Grease onto Corroded Surface

- Corroded metal surface from any rust, grease and dirt are removed with clean water
- Rust are removed with wire brush and the surface is left dry
- Antiseize compound are applied onto the bare metal
- Antiseize commonly used to apply on screw bolts and nuts to protect from corrosion as a lubricant
Under Ground Corrosion Control by Coating
Question?