Anodic Protection Systems

Corrosion Protection for Sulfuric Acid Tanks

Hugo Chagas
hugo.chagas@clark-koch.com

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SUMARY

Direct and Indirect Costs of Corrosion Worldwide

- Study conducted by US federal highway administration showed the following figures:
  - Direct and indirect corrosion costs nowadays
    - US$ 1.8 trillion WORLDWIDE
    - 276 Billion US dollars (For US)
    - Representing 3-4% of the Gross Domestic Product
- According to the Hoar Report 25% of the annual cost of corrosion could be saved!
  - Which Means: US$ 450 billions worldwide!!!!

It is clear that Corrosion must be avoided and well controlled.

The Challenge is to identify and apply the optimal Corrosion Control Method for each specific case.

Virmani, Paul, Corrosions Costs and Preventive Strategies in the US 2002
An Option to Minimize and control Corrosion in Sulfuric Acid Storage Tanks.

Reducing Risks, Capital investments, and maintenance costs.
Topics

• Sulfuric Acid Corrosion
• Principles of Anodic Protection – Main Concepts
• Equipment for Anodic Protection
• Design Operation and Maintenance of Anodic Protection Systems
• Sulfuric Acid Storage Equipment’s Protection
• Economical Advantages of Anodic Protection Systems for Sulfuric Acid Storage Tanks
Sulfuric Acid Corrosion

Boundary-Work – Equipment, Material and Conditions

• Carbon Steel Storage Tanks
• Under ambient Conditions
• Mainly with 80 – 100% acid concentration

What governs Carbon Steel corrosion rates in sulfuric Acid:

• Temperature;
• Acid concentration
• Ferrous Sulfate Diffusion Velocity

Understanding how these Physical Properties impacts on Corrosion Rates will help to understand how Anodic Protection works
Temperature & Concentration – At which condition Corrosion Rate increases?

If no other properties vary, Carbon Steel Corrosion will increase with temperature increase.
Sulfuric Acid Corrosion

**Diffusion Velocity**
During the Corrosion Reaction a soft film of FESO4 is formed on the surface and works as a physical barrier for the diffusion of the reactants (H⁺; SO₄²⁻)

**Corrosion Reaction**

\[ \text{H}_2\text{SO}_4 + \text{Fe} \rightarrow \text{FESO}_4 + \text{H}_2 \]

**Diffusion Barrier**
Soft Film of FeSO₄ is formed on the metal surface.

**FESO₄ Film Disintegration**

- Natural FESO₄ Diffusion
- Erosion Corrosion Effect

**Mechanism**

- FESO₄ Diffusion
- Inlet Nozzles
- Hydrogen Grooving
- Splashing acid

FESO₄ Film is a protection and can be really effective for Storage Tanks since the types of Erosion-Corrosion Effects are not related to the main function of the equipment and thus can be avoided.
How does Anodic Protection Works?

- Anodic Protection is a Method to achieve an electrochemical barrier between the corrosive electrolyte and metal base by forming an oxides thin layer.
- Passivity is attributed to the formation of a protective Layer, at the metal-electrolyte interface. This “Passive” Layer Prevents the contact between the metal and the electrolyte reducing corrosion rate at a minimum value.
- Metal Tendency to be passivated can be measure and this measures provides an representation of the electrochemical corrosion characteristics. Measurements can be represented by a Anodic polarization curve.

<table>
<thead>
<tr>
<th>Zones</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Passive</td>
<td>Passive Film Acts as a Barrier</td>
</tr>
<tr>
<td></td>
<td>No Corrosion Reaction</td>
</tr>
<tr>
<td></td>
<td>Thus Very Small Current Density</td>
</tr>
<tr>
<td>Active</td>
<td>Corrosion Occurrence</td>
</tr>
<tr>
<td></td>
<td>Current Density is constantly increasing with</td>
</tr>
<tr>
<td></td>
<td>the Potential increasing</td>
</tr>
<tr>
<td></td>
<td>Passive Film Formation</td>
</tr>
</tbody>
</table>
Principles of Anodic Protection – Main Concepts

- Responsible for the system control.
- Receives FEEDBACK from the Potential Sensing and responds with direct current actual value.
- Provides direct current for the System.
- Connected to the (−) pole of power supply.
- Can be one or multiple depending on design/tank size.

Diagram:

- Potential Sensing
- Potential Controller
- Direct Current Power Source
- Reference Electrode
- Cathode
How Anodic Protection Works

- Ref. Electrode
- Cathode
- Coupon

Elevation 1:250
Cathodes

- Cathode shall be stable and resist attack by impressed cathodic current.
- Cathode should have a high conductivity that does not contribute to the overall circuit resistance.
- The Cathode Area determines the contact resistance between Cathode and Anode solution. So cathode area should be as high as is economically and physically to keep power requirements low.
- Usually for Sulfuric Acid Storages Cathodes Material is HASTELOY C

SPARK PREVENTION

- In order to avoid spark in cases of minimum level switch failure a silicon rope is used to make sure that there are solution to conduct electrical current between the cathode and the tank wall.
Reference Electrodes

- Potential of the Tank wall must be measure and controlled
- Reference Electrode gives a comparison of tank wall potential.
- It senses the solution potential with an minimum error.
- For Acid Tanks most common material used is Platinum/Platinum (Inert Metal).
Equipment for Anodic Protection

**Coupons**

- Coupons are used for visual verification of the Anodic Protection Effectiveness.
- While one metal sample (same material of the tank) is connected to the tank sidewall, and the other one not.
- Result it is possible to compare the corrosion rate between them.
Positive Tank Connection

- Detail of the Positive side connected to the tank sidewall.
Equipment for Anodic Protection

Rectifier Panel

- Power Distribution
  - Transformers
- Control
  - TPCC
- Monitoring
  - Alarms
  - Remote Monitoring
  - LCD Displays
- Panel Conditioning
  - Inner Temperature Control
  - Shield and Earth grounding
Rectifier Panel

Potential Controller
- It is proven that precision of the control potential in field instruments need not to be as high as that of laboratory potentiostat. Satisfactory Control were achieved if the potential were maintained within ± 5mV.
- This Permits the use of on-off controls
- The other possibility is Proportional Control
- In the past most of the applications in USA and CANADA used ON-OFF Control. Proportional would be used only for critical nature in which the potentials would instantly shift to corrosive value when the current was off.

Power Supply
- Usually transforming AC Current on DC as demanded.
Design Operation and Maintenance of APS

Simplified Process Trough Design

- Experiments in the Laboratory
- Result: Anodic Polarization Behavior Curve
- Particular Attention to simulate process conditions
- Ref. Electrode and Cathode Selection
- Size Power Supply
- Establish Electrochemical Parameter
- Size and number of Cathodes
- Electronic Hardware Selection
- Power Supply Criteria
Usual Electrochemical Parameters (Theory)

<table>
<thead>
<tr>
<th>Solution</th>
<th>Concentration %</th>
<th>Temperature oC</th>
<th>Passivate mA/cm²</th>
<th>Maintain mA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oleum</td>
<td>-</td>
<td>25</td>
<td>2.64</td>
<td>0.00380</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>93-98</td>
<td>25</td>
<td>2.64</td>
<td>0.0398</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>78</td>
<td>25</td>
<td>3.08</td>
<td>0.0550</td>
</tr>
</tbody>
</table>

REF: Riggs, OL; Locke, CE; Anodic Protection

Common Values Found in industry

- For a Tank of aprox. 7000 m³ with Sulfuric Acid at aprox. 94-96% and T=25oC (for this case )
- Current to Passivate → aprox. 350A
- Current to Maintain → aprox. 0.6 A

General Comments

- Generally design phase takes up to 180 days.
- Documentation received by the Client is similar to a common Electrical Panel and cable routing;
- IT is possible to remotely monitor some parameters of the AP System such as direct current supply, ref electrodes, AC power supply.
Installation and Startup

- There are some criteria's to position the Cathode and Electrode in the Tank.
- If more than one Cathode is used; they should be installed evenly in the radius orientation.
- There is no critical issues related to the distance between the cathode and the tank wall, but generally they should be at the middle of the distance between the center and the wall of the tank.
- Cathode should reach 1 feet above the bottom of the tank.
- Reference Electrode should be spaced radially as far from the cathodes as possible.
- Reference Electrode should be at 18” from the bottom of the tank.

Operation and Maintenance

- Does not require excessive amount of attention from operating personnel.
- Keep a record of current demand as function of time and operating conditions.
- Limits are setup and when achieved alarm is activated and unit turned off.
Reduction of Iron Content Verification

Minimum 40 ppm After a week

Effectiveness of Anodic Protection Tanks
REF: Riggs, OL; Locke, CE; Anodic Protection

- Data Shows that Anodic Protection can reduce the Iron content from 1273 ppm to less than 40 ppm.
- At lower temperature effectiveness is even better

Table – Average Iron Content before and after Anodic Protection of Storage Tanks, 100% Sulfuric Acid

<table>
<thead>
<tr>
<th>Location</th>
<th>Iron Cont. (ppm) BEFORE</th>
<th>Iron Cont (ppm) After</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharge</td>
<td>145</td>
<td>35</td>
</tr>
<tr>
<td>Feed</td>
<td>31</td>
<td>26</td>
</tr>
<tr>
<td>Iron Pickup</td>
<td>114</td>
<td>9</td>
</tr>
</tbody>
</table>

Rate of accumulation of iron in Sulfuric Acid
REF: Riggs, OL; Locke, CE; Anodic Protection
Principles of Anodic Protection – Main Concepts

Reduction of Corrosion Rate Verification

<table>
<thead>
<tr>
<th>Dist. of the Coupon From Tank Bottom (ft)</th>
<th>Corrosion Rates (mpy) Unprotected</th>
<th>Corrosion Rates (mpy) Protected</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>35.3</td>
<td>3.6</td>
</tr>
<tr>
<td>1</td>
<td>34.1</td>
<td>3.4</td>
</tr>
<tr>
<td>2</td>
<td>31.2</td>
<td>3.1</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>3.2</td>
</tr>
<tr>
<td>4</td>
<td>29.9</td>
<td>3.5</td>
</tr>
<tr>
<td>5</td>
<td>22.1</td>
<td>5.8</td>
</tr>
<tr>
<td>6</td>
<td>4.3</td>
<td>5.4</td>
</tr>
<tr>
<td>7</td>
<td>6.3</td>
<td>5.3</td>
</tr>
<tr>
<td>8</td>
<td>3.8</td>
<td>4.1</td>
</tr>
<tr>
<td>9</td>
<td>2.2</td>
<td>1.4</td>
</tr>
<tr>
<td>10</td>
<td>0.8</td>
<td>0.9</td>
</tr>
<tr>
<td>11</td>
<td>0.8</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table: Results of test on Anodically Protected and Unprotected Coupons exposed 50 Days in 100% Sulfuric Acid Storage Tank.


Data Taken using Corrosion Coupons in a 10,000 ton 93% Sulfuric acid tank

REF: D. Fyfe, Chem Eng Proc, 73, 65 (1977)
Economical Advantages of Anodic Protection Systems for Sulfuric Acid Storage Tanks

Anodic Protection as an Option

- Reduction of Product Contamination
- Increase of Tank Life Cycle
- Reduction of Corrosion allowance
  - Reduction of plates thickness, which impacts on materials and fabrication costs
- Low Maintenance Costs
- Minimum intervention during operation;
• Tanks - Cathodes
• Tanks - Cathodes
• Tanks - Cathodes
Rectifier Panel

Pictures – PERU DOE RUN/ Southern Copper Peru/ Corrosion Service
• Rectifier Panel
• Tanks - Cathodes
- Tanks - Cathodes
• Tanks - Cathodes
• Tanks – Reference Electrodes
Tanks – Reference Electrodes
References

- O, L, Riggs, JR. M. Hutchson and NL Conger, Corrosion 16(2), 1960
- YAM Kolotyrkim et al
- D Fyfe, Chem ENG PROG, 73, 65, 1977

Contato:
Hugo Chagas
hugo.chagas@clark-koch.com