ICorr Corrosion Awareness Day (Aberdeen)

Mitigation by Chemicals
Chemical Corrosion Control Techniques

Chemical treatment involves injecting chemicals that retard the corrosion of a metal.

Types of Treatment for oilfields include:

- Neutralization (pH control)
- Removal of dissolved gases (scavengers)
- Corrosion inhibitors
- Biocides
Chemical Corrosion Control Techniques

A. pH Control

Steel corrosion rate related to hydrogen ion concentration in electrolyte

To avoid acid corrosion, the pH of the medium shall be raised up to about 7 by injection of

- Caustic Soda NaOH
- Amines NH₃

Periodical check on pH by means of pH probes
B. Removal of Dissolved Gases - Dissolved Oxygen

Dissolved oxygen can be removed from seawater injection systems

- Normally mechanical de-aerator is used to remove $O_2$ in conjunction with oxygen scavengers (normally sulphite, bisulphite based)

- Minox units, initially developed during the 80s by Minox and Norsok Hydro’s Research Centre, mainly for de-oxygenation of seawater injection systems

Based on stripping oxygen from water with a closed loop circulated nitrogen in which the oxygen is being removed in a low temperature catalytic process

The Ultra Compact Minox 2-stage edition
Chemical Corrosion Control Techniques

B. Removal of Dissolved Gases – H₂S

- **Regenerable Systems (Re-circulated)**
  - Tail Gas Treating (TGT)
  - Amine Unit (MDEA)
  - High Capital Cost
- **Oxidative Processes**
  - Catalytic Oxidation
  - Zinc Oxide
  - Nitrite Solution
- **Non-Regenerable Systems (Once-through)**
  - water-soluble (i.e. triazines) and oil-soluble scavengers
  - Low Capital Cost
C. Corrosion Inhibitors

NACE definition: “Chemicals which reduce the corrosion rate when added to a normally corrosive medium in small concentrations.”

Inhibitors selection is based on:
- metal
- environmental chemical composition
- service condition
  - temperature
  - flow rate
  - Delivery method (e.g. gas lift, capillary, umbilical)
  - Produced fluid
  - secondary properties (e.g. compatibility, emulsion, foaming, flash point)

With the type of selection test work tailored to these requirements.
Corrosion found in the Oil Field
Chemical Corrosion Inhibitor Applications

Batch:
• Oil and gas wells
• Pipelines

Continuous:
• Oil and gas wells
• Production facilities
• Water Systems
• Pipelines

Squeeze:
• Oil and gas wells
Types of corrosion inhibitors 1

- **Anodic inhibitors**
  - Also called passivators
  - Act by forming a protective oxide film on the surface of the metal causing a large anodic shift of the corrosion potential.
  - The shift forces the metallic surface into the passivation region.
  - Chromates, nitrates, tungstate, molybdates are some examples of anodic inhibitors.

- **Cathodic inhibitors**
  - Act by either slowing the cathodic reaction itself or selectively precipitating on cathodic areas to limit the diffusion of reducing species to the surface.
  - The rates of the cathodic reactions can be reduced by the use of cathodic poisons.
  - However, cathodic poisons can also increase the susceptibility of a metal to hydrogen induced cracking since hydrogen can also be absorbed by the metal during aqueous corrosion or cathodic charging.
Types of corrosion inhibitors 2

- **Mixed Inhibitors**
  - Work by reducing both the cathodic and anodic reactions.
  - Typically film forming compounds that cause the formation of precipitates on the surface blocking both anodic and cathodic sites indirectly.
  - Most common mixed inhibitors are the silicates and the phosphates.
  - Sodium silicate, for example, is used in many domestic water softeners to prevent the occurrence of rust water.
  - In aerated hot water systems, sodium silicate protects steel, copper and brass. However, protection is not always reliable and depends heavily on pH.
  - Phosphates also require oxygen for effective inhibition.
  - Silicates and phosphates do not afford the degree of protection provided by chromates and nitrites; however, they are very useful in situations where non-toxic additives are required.
Types of corrosion inhibitors 3

- **Volatile Corrosion Inhibitors (VCI)**
  - Also called Vapour Phase Inhibitors (VPI)
  - Compounds transported in a closed environment to the site of corrosion by volatilization from a source
  - In boilers, volatile basic compounds, such as morpholine or hydrazine, are transported with steam to prevent corrosion in the condenser tubes by neutralizing acidic CO₂ or by shifting surface pH towards less acidic and corrosive values
  - In closed vapour spaces, such as shipping containers, volatile solids such as salts of dicyclohexylamine, cyclohexylamine and hexamethylene-amine are used
  - When these inhibitors come in contact with the metal surface, the vapour of these salts condenses and is hydrolysed by any moisture to liberate protective ions.
  - It is desirable, for an efficient VCI, to provide inhibition rapidly while lasting for long periods. Both qualities depend on the volatility of these compounds; fast action requires high volatility while enduring protection requires low volatility.
Usually organic compounds with long hydrocarbon chains with polar (charged) head
Emphasize it is the class of filming corrosion inhibitor in upstream oilfield systems.

Mok, Wai Y, 24/07/2014
Chemical Corrosion Inhibitors

Film forming theory

Mechanism:

- Formation of physical barrier, thus blocking the reaction sites (anode and cathode sites)

- The inhibitor can be adsorbed onto corrosion product layer to block the transportation of corrosive species.
Biocide Application Overview

- Bacterial Control
- Chemical Biocides
- Application
An estimated 20% of all Corrosion damage to metals and building materials are microbial influenced or enhanced.
Biocide Bacterial Control

• Stair stepped
  ➔ Typical of SRB

• Drill hole, cavernous or worm hole
  ➔ Typical of APB

• Slime usually cover corroded areas
Chemical Biocides

- INORGANIC CHEMICALS (oxidising)
  - Chlorine
  - Chlorine dioxide (ClO₂)

- ORGANIC CHEMICALS (non oxidising)
  - Aldehydes (glutaraldehyde / formaldehyde)
  - Quaternary ammonium compounds
  - Quaternary phosphonium compounds
  - Amines

- Many finished products are a blend of different chemistries
Biocide Application Chemicals

- Chlorine – inexpensive, effective treatment (usually generated by hypochlorite generators or sodium hypochlorite)
  - Chlorine hydrolyzes to form hypochlorous and hydrochloric acid
    \[ \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{Cl}^- + \text{HOCl} \]
    - Ionizes to form hydrogen ions and hypochlorite ions
      \[ \text{HOCl} \rightarrow \text{H}^+ + \text{OCl}^- \]
    - Effectiveness depends on pH, a chlorine residual is required to ensure control

<table>
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<td>6-8</td>
<td>0.2</td>
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<tr>
<td>8-9</td>
<td>0.4</td>
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<tr>
<td>9-10</td>
<td>0.8</td>
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- Strong oxidizer so there will be a demand by the system and some incompatibility
Chemical Biocides

- Aldehydes – mainly glutaraldehyde used
  - Very good at killing bacteria
  - Poor penetration of biofilm

- Quat’s / Amines – very surface active
  - Good at penetrating biofilm and cleaning action

- Use of blended chemistry final products

- Specific biocides for boiler waters and drinking waters
Biocide Application

- **Continuous Treatment**
  - Appropriate for chlorination
  - Inappropriate for non-oxidising biocides
  - Not cost effective compared to slug treatments

- **Squeeze Treatment (short term success)**
  - Biocide
  - Overflush
  - Shut - in period (24 hours )
  - Dosage >1000 ppm
  - Reflow well
Biocide modes of action

- QUATS
- ISOThIAZOLIN
- AMINES
- FORMALDEHYDE

- OUTER MEMBRANE
- PERIPLASM
- CYTOPLASMIC MEMBRANE

- OXIDIZERS
- ALDEHYDES
- OXIDIZERS

- ISOTHIAZOLIN
- ALDEHYDES
- OXIDIZERS

- -SH GROUPS

- -COOH GROUPS

- -NH₂ GROUPS

- e- TRANSPORT

- DNA

- QUATS
- AMINES