Corrosion

• Corrosion Basics
  – General corrosion theory
  – Corrosion examples

• Specialty Problems
  – CO$_2$ and H$_2$S
  – O$_2$ in sea water injection
  – Acid Treatment
  – Packer Fluids
Major Causes of Corrosion

- Salt water (excellent electrolyte, chloride source)
- H$_2$S (acid gas with iron sulfide the by-product)
- CO$_2$ (Major cause of produced gas corrosion)
- O$_2$ (key player, reduce any way possible)
- Bacteria (by products, acid produced)
Other Factors

- pH
- Chlorides (influences corrosion inhibitor solubility)
- Temperature (Increase usually increases corrosion)
- Pressures (CO$_2$ and H$_2$S more soluble in H$_2$O)
- Velocity - important in stripping films, even for sweet systems
- Wear/Abrasion (accelerates corrosion)
- Solids – strips film and erodes metal
Chemical Corrosion

- H2S
  - weak acid, source of H+
  - very corrosive, especially at low pressure
  - different regions of corrosion w/temp.
- CO2
  - weak acid, (must hydrate to become acid)
  - leads to pitting damage
- Strong acids - HCl, HCl/HF, acetic, formic
- Brines - chlorides and zinc are worst
Corrosion - Best Practices

- Adopt a corrosion management strategy.
- Be aware of corrosion and erosion causes.
- Completion planning must reflect corrosion potential over well’s life.
- Develop maintenance programs, measure corrosion.
- Know the corrosion specialists.
- Ensure inhibitors are compatible with materials and the reservoir!
- If tubing corrosion is suspected, DO NOT bullhead fluids in the formation.

Corrosion in tubing exacerbated by abrasion from wireline operators.
# 1970’s Industry Study of Failures

<table>
<thead>
<tr>
<th>Method</th>
<th>% of Failures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion (all types)</td>
<td>33%</td>
</tr>
<tr>
<td>Fatigue</td>
<td>18%</td>
</tr>
<tr>
<td>Brittle Fracture</td>
<td>9%</td>
</tr>
<tr>
<td>Mechanical Damage</td>
<td>14%</td>
</tr>
<tr>
<td>Fab./Welding Defects</td>
<td>16%</td>
</tr>
<tr>
<td>Other</td>
<td>10%</td>
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</tbody>
</table>
## Causes of Petroleum Related Failures (1970’s study)

<table>
<thead>
<tr>
<th>Cause</th>
<th>% of Failures</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ Corrosion</td>
<td>28%</td>
</tr>
<tr>
<td>H$_2$S Corrosion</td>
<td>18%</td>
</tr>
<tr>
<td>Corrosion at the weld</td>
<td>18%</td>
</tr>
<tr>
<td>Pitting</td>
<td>12%</td>
</tr>
<tr>
<td>Erosion Corrosion</td>
<td>9%</td>
</tr>
<tr>
<td>Galvanic</td>
<td>6%</td>
</tr>
<tr>
<td>Crevice</td>
<td>3%</td>
</tr>
<tr>
<td>Impingement</td>
<td>3%</td>
</tr>
<tr>
<td>Stress Corrosion</td>
<td>3%</td>
</tr>
</tbody>
</table>
Corrosion can be considered a natural result of energy stored in the metal when it was refined and fabricated.

Iron ore (Oxides) Corrosion products

Energy added by refining

Energy release by corrosion

"Pure" metal or alloy
The size and number of the crystals present in metals are a function of the cooling process (quenching).
Corrosion Types

- **Galvanic** – a potential difference between dissimilar metals in contact creates a current flow. This may also occur in some metals at the grain boundaries.

- **Crevice Corrosion** — Intensive localized electrochemical corrosion occurs within crevices when in contact with a corrosive fluid. Will accelerate after start.

- **Pitting** – Extremely localized attack that results in holes in the metal. Will accelerate after start.

- **Stress Corrosion** – Occurs in metal that is subject to both stress and a corrosive environment. May start at a “stress riser” like a wrench mark or packer slip mark.
Corrosion Types

- **Erosion Corrosion** – Passage of fluid at high velocity may remove the thin, protective oxide film that protects exposed metal surface.

- **Hydrogen Sulfide Corrosion** – $\text{H}_2\text{S}$ gas a water creates an acid gas environment resulting in $\text{FeS}_x$ and hydrogen.

- **Hydrogen Embrittlement** – Atomic hydrogen diffuses into the grain boundary of the metal, generating trapped larger molecules of hydrogen molecules, resulting in metal embrittlement.

- **Hydrogen Corrosion** – Hydrogen blistering, hydrogen embrittlement, decarburization and hydrogen attack.
CO2 Partial Pressure

- Severity is a function of the partial pressure
  - 0-3 psi - very low – non chrome use possible
  - 3-7 psi – marginal for chrome use
  - 7-10 psi – medium to serious problem
  - >10 psi – severe problem, requires CRA even for short term application.

Partial pressure is the mole fraction of the specific gas times the total pressure. If the CO2 mole concentration is 1% and the pressure is 200 psi, the partial pressure is $0.01 \times 200 = 2$ psi.
$\text{CO}_2$ corrosion

$\text{CO}_2$ localised attack in 7” production tubing
The corrosion rate of CO₂ is a function of partial pressure, temperature, chloride presence of water and the type of material.

Corrosion rate in MPY – mills per year is a standard method of expression, but not a good way to express corrosion where pitting is the major failure.
Note the effect of the temperature on the corrosion rate.

Cost factors between the tubulars is about 2x to 4x for Chrome-13 over low alloy steel and about 8x to 10x for duplex (nickel replacing the iron).
Severe CO$_2$ corrosion in tubing pulled from a well. One reason for the attack was that the tubing was laying against the casing, trapping water that was replenished with CO$_2$ from the gas flow.
Thinned and embrittled tubing twisted apart when trying to break connection during a tubing pull.
CO₂ CORROSION ISOPLOT

pH 5

Corrosion Rate, mm/y

Temperature, degC

Log(Pco2)

-4

-3

-2

-1

0

1

0.0 - 0.1 mm/y

0.1 - 0.2 mm/y

0.2 - 0.3 mm/y

0.3 - 0.4 mm/y

0.4 - 0.5 mm/y

0.5 - 0.6 mm/y

0.6 - 0.7 mm/y

0.7 - 0.8 mm/y

0.8 - 0.9 mm/y

0.9 - 1.0 mm/y
Corrosion weakened pipe – large areas can be affected.
Mills/per year or mm/yr may not be a good indicator when the metal loss is in pitting.

Trench corrosion common from CO2 attack.
Chloride Stress Cracking

- Starts at a pit, scratch or notch. Crack proceeds primarily along grain boundaries. The cracking process is accelerated by chloride ions and lower pH.
Stress Sulfide Corrosion

- Occurs when metal is in tension and exposed to $\text{H}_2\text{S}$ and water.
# API/SPEC 5A, 5AC, 5AX Tubing and Casing

<table>
<thead>
<tr>
<th>Grade</th>
<th>Yield</th>
<th>Tensile</th>
<th>H₂S</th>
<th>Spec.</th>
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<tbody>
<tr>
<td></td>
<td>Min.</td>
<td>Max.</td>
<td>Min.</td>
<td></td>
</tr>
<tr>
<td>H-40</td>
<td>40,000</td>
<td></td>
<td>60,000</td>
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<tr>
<td>J-55</td>
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<td>80,000</td>
<td>75,000</td>
<td>Yes</td>
</tr>
<tr>
<td>K-55</td>
<td>55,000</td>
<td>80,000</td>
<td>95,000</td>
<td>Yes</td>
</tr>
<tr>
<td>N-80</td>
<td>80,000</td>
<td>110,000</td>
<td>100,000</td>
<td>?</td>
</tr>
<tr>
<td>C-75</td>
<td>75,000</td>
<td>90,000</td>
<td>95,000</td>
<td>Yes</td>
</tr>
<tr>
<td>L-80</td>
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<td>95,000</td>
<td>95,000</td>
<td>Yes</td>
</tr>
<tr>
<td>C-95</td>
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<td>110,000</td>
<td>105,000</td>
<td>?</td>
</tr>
<tr>
<td>P-105</td>
<td>105,000</td>
<td>135,000</td>
<td>120,000</td>
<td>No</td>
</tr>
<tr>
<td>P-110</td>
<td>110,000</td>
<td>140,000</td>
<td>125,000</td>
<td>No</td>
</tr>
</tbody>
</table>
Domain Diagram for C110

Sulphide Stress Cracking Performance Domain of "Sour Resistant" Grade 110ksi Steel

- **Acceptable** region
- **Unacceptable** region

Parameters:
- Solution pH
- \( \text{pH}_2 \text{S} \) (bara)
Hydrogen Sulfide Corrosion

• $\text{Fe} + \text{H}_2\text{S} + \text{H}_2\text{O} \iff \text{FeS}_x + \text{H}_2 + \text{H}_2\text{O}$
• FeS - cathode to steel: accelerates corrosion
• FeS is a plugging solid
• Damage Results
  – Sulfide Stress Cracking
  – Blistering
  – Hydrogen induced cracking
  – Hydrogen embrittlement
H₂S corrosion is minimized by sweetening the gas (knocking the H₂S out or raising pH.)
Domain Diagram for Super 13Cr

Domain Diagram For The Sulphide Stress Cracking Limits
Of 95ksi Super 13Cr Alloys In High Chloride (120,000 ppm Cl⁻) Waters
SSC Failure of Downhole Tubular String in Louisiana

Video
Crevice Corrosion

• The physical nature of the crevice formed by the tubing to coupling metal-to-metal seal may produce a low pH aggressive environment that is different from the bulk solution chemistry – hence a material that looks fine when tested as a flat strip of metal can fail when the test sample (or actual tubing) includes a tight crevice.

• This damage can be very rapid in water injection wells, wells that produce some brine or in wells where there is water alternating gas (WAG) sequencing – causing failure at the metal-to-metal seals in a matter of months.
Crevice Corrosion

Note the seal crevice corrosion – this caused a leak to the annulus.
Crevice Corrosion

Note the pit that started the washout – seal crevice corrosion.
O₂ Corrosion

There is no corrosion mechanism more damaging on a concentration basis than oxygen – small amounts of oxygen, water and chlorides can ruin a chrome tubing completion in a few months. Injection wells are the most severely affected – minimise oxygen and don’t use chrome pipe in injectors.

20 ppb O₂ limit for seawater in carbon steel injection tubulars. 13Cr is CO₂ resistant but very susceptible to pitting corrosion in aerated brines. 5 ppb O₂ is suggested as a limit, but even these levels have not been confirmed.
Oxygen in Surface Waters

- 32ºF - 10 ppm (saturation)
- 212ºF - 0 ppm

\[
\text{ppm O}_2 = 10 - 0.055 (T - 30^\circ)
\]

T = water system temperature, ºF
A split in the side of 5-1/2” casing. Cause was unknown – mechanical damage (thinning by drill string abrasion) was suspected.
Abrasion by solids, gas bubbles or liquid droplets may significantly increase corrosion by continuously removing the protective oxide or other films that cover the surface following the initial chemical reaction.
Most graphs do not show the effect of too low a velocity on the corrosion rate. When the surface is not swept clean, biofilms can develop or the surface liquid layer may saturate with CO2 or other gas, increasing corrosion. Minimum rates are about 3.5 ft/sec for clean fluids.
Note the effect of increasing flowing fluid density on corrosion rate.

Also – presence of solids in the flowing fluids very significantly lowers the maximum permissible flow rate.
Erosion - All Liquid Flow

• Described by API Equation 14E

\[ V_c = C \times (\text{density})^{1/2} \]

where:  
- \( V_c \) = critical flow velocity, ft/sec  
- density = fluid density in g/cc  
- \( C = 100 \) for long life projects  
- \( C = 150 \) for short life project  
- \( C = >200 \) for peak flows
Corrosion increases after water cut reaches 10 to 20%. The cause is removal of the protective oil film. In the third phase, the pipe is completely water coated and corrosion rate becomes more constant.
Acid Corrosion Rates on Alloys

N-80

410-Stainless
Top, Left: Chrome pipe after acidizing with the proper inhibitor and inhibitor intensifier.

Bottom, Left: Chrome pipe after acidizing with a marginal inhibitor.

Bottom, Right: Chrome pipe after acidizing without an inhibitor.

15% HCl, 2 hour exposure
Increasing Rate of Penetration with Pit Development

Large anodic area, rate of metal loss and pit penetration is slow.

Anodic area decreases, cathodic area extends down side of pit. Rate of penetration increases.

Anodic area confined to bottom of pit. Rapid rate of metal loss and wall penetration.

NOTE: Corrosion product normally coating or filling pits not shown.
Welds

The heating that occurs during the welding process will cause the weld metal and the heat affected zone around the weld to be physically different from the surrounding, original metal.

An **anode** is created by this difference.

An anode can start here or here.

Base metal

[Diagram showing the welding process with labeled parts: Base metal, Heat affected zone, Weld metal (added and different from original base metal).]
Bacterial deposits on injection tubing. Pitting under the bacterial colony can be severe.

Anaerobic
SRB’s -sours the well/reservoir
Iron Fixers - slime and sludge
Slime Formers - formation damage
Sulfate Reducing Bacteria

• SRB’s anaerobic bacteria
  – colony growth most numerous
  – low pH below colony

• Generates high H$_2$S concentration in small area

• worst where velocity $<$ 3-1/2 fps
Many of the super alloy failures have been linked backed to the brines used for completions.
High Island – Failure of 13Cr Alloy
Cracking initiated at a stress riser – impact or wrench mark.
CO2 corrosion on pin end of tubing, above the coupling.

Solutions:
1. Use a 13 Chrome tubing
2. Eliminate the coupling - (may work for short term projects)
1496.3'
210 F
11:28:39

5” casing collar

Note corrosion
Sacrificial Anodes - Galvanic Series in Sea Water

1. Magnesium
2. Zinc
3. Soft aluminum
4. Cadmium
5. Hard aluminum
6. Steel
7. Stainless steel (300 series)
8. Lead
9. Brass and bronze
10. Inconel
11. Hasteloy C 276
Sacrificial anode (magnesium) from an offshore platform. This was a round bar stock anode.
Controlling Corrosion

1. Maintain high pH
2. Control gas breakout
3. Use passive metals
4. Remove Oxygen
5. Control velocities
6. Lower chlorides
7. Bacteria control
8. Acid/brine use considerations and alternatives
9. Liquid removal
10. Inhibitor injection
11. coatings
Typical Corrosion Inhibitors

oleic
imidazoline

alkyl ethoxy phosphate
How do Corrosion Inhibitors Work?

- Metal Surface
- Water and Oil
- Polar Group
- Alkyl chain
- Oil film
- Metal Surface
Inhibitor Deployment

- inject via quill
- counter-current to flow
- atomising quill for gas systems

- continuous injection (10 - 50 ppm) better than batch
- keep feed tank full and pump operating
- corrosion inhibitor squeeze can affect reservoir wettability and the return concentration is often too low to be useful (ca 5 ppm)