

Aegis Tech Line

Aegis Chemical Solutions

Technical Newsletter

Volume 09, February 2019



CORROSION FAILURE ANALYSIS

CO₂ Corrosion – Sweet Corrosion

Corrosion that develops in oilfield wells and surface equipment in the presence of carbon dioxide gas (CO₂) is referred to “sweet corrosion”. Failures that result from sweet corrosion are characterized by:

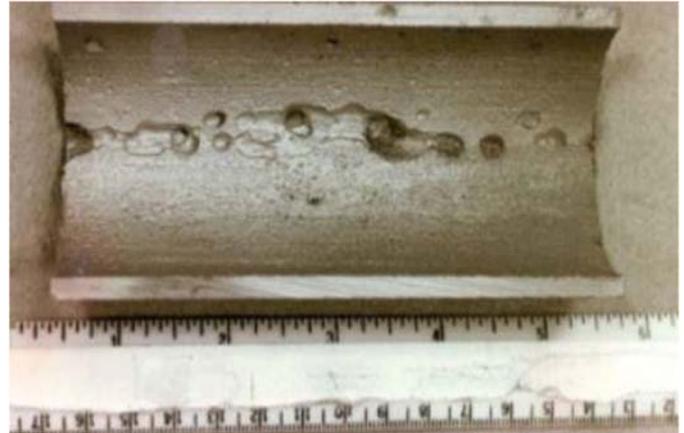
- Interconnected pits
 - Described as wormhole or honeycomb pitting
- Sharp edges and undercutting at low velocity
 - At higher velocities and/or presence of sand, sharp edges may be worn away
- Mesa which is a small area of uncorroded steel surrounded by corroded areas
- Failure may have FeCO₃ corrosion product which can be detected with 15% HCl. Deposit will fizz and turn pale green if Fe is present. With air contamination, solution will turn yellow or reddish-yellow due to iron oxidation. Absence of green color means the deposit is likely CaCO₃.

Included below are photographs of steel tubulars or other oilfield steel structures that show the characteristics of sweet corrosion listed above.

Interconnected Pits or Wormhole Pattern in Pipe



Wormhole in Pipe

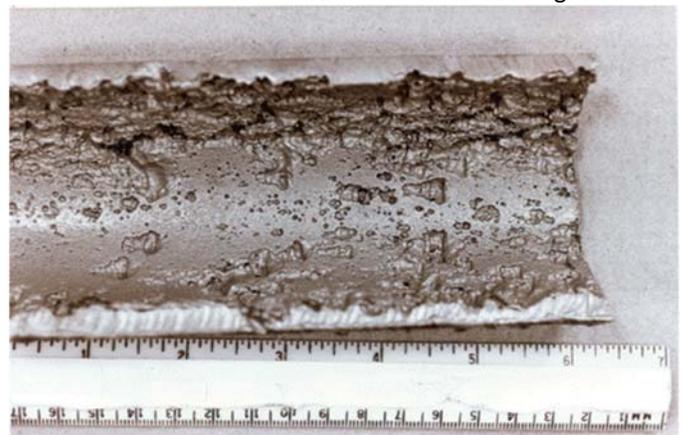


Wormhole on Sucker Rod



Sharp Edges

Corrosion occurred where water condensed in gas well



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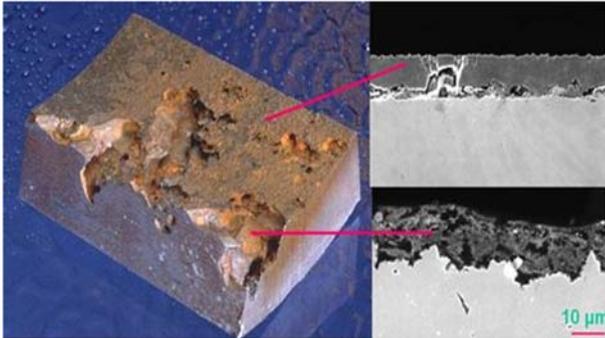
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Technical Newsletter

Volume 09, February 2019



Sharp Edges, Interconnected Pits, and Undercutting



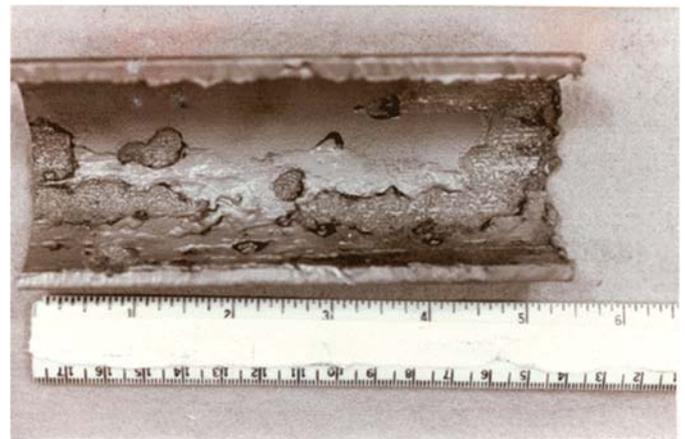
High Velocity
Sharp edges worn away



Heat Affected Zone (HAZ) – Sharp edges and Undercutting



Mesa Corrosion



High Velocity
Sharp edges worn away



Penetrating Localized Attack

An oil well developed a penetrating localized attack of CO₂ corrosion. The leak occurred after 18 months of service. The well began producing formation water well in advance of the well design predictions. Water cut increased from 5% after two months to 80% after 17 months. The CO₂ molar fraction in the gas phase was 30%, and the bubble point pressure was 5.2 bar. The wellhead pressure was always higher than this, so this was a liquid-only oil well with a CO₂ partial pressure of 1.6 bar. The calculated pH was 5 – 5.5. Both detailed caliper data over the whole well depth and detailed inspection of the recovered well string were available. The tubing had penetrating mesa attack close to the top of the well, at around 100m depth corresponding to 4.6mm/yr. corrosion

Aegis Tech Line

Aegis Chemical Solutions

Technical Newsletter

Volume 09, February 2019



rate based on the total production period. A section of the tubing where penetrating localized attack was found is shown in the photograph below. Further down in the well, the corrosion rate was measured at 0.3 – 0.9mm/yr. by caliper data.

Penetrating Localized Attack in Oil Well



Isolated Pitting on Sucker Rod



H₂S Corrosion – Sour Corrosion / Sulfide Corrosion

Corrosion that develops in oilfield wells and surface equipment in the presence of hydrogen sulfide gas (H₂S) is referred to “sour or sulfide corrosion”. Failures that result from sour corrosion are characterized by:

- Isolated pitting
- Large, rounded deep pits
- May have cracks or ruptures in steel due to hydrogen induced cracking
- Bubbles may form on the outside wall of steel
- Failure may have FeS corrosion product which can be detected with 15% HCl. Deposit will dissolve in acid and give a rotten egg odor (H₂S). Solution will turn pale green as FeS dissolves. With air contamination, solution will turn yellow or yellowish red.
- In high H₂S environments (>1% or 10,000 ppm) FeS₂ is formed which will not dissolve in 15% HCl.

Included below are photographs of steel tubulars or other oilfield steel structures that show the characteristics of sour corrosion listed above.

Large, Round Deep Pits on Inside of Pipe



Large, Rounded Pits



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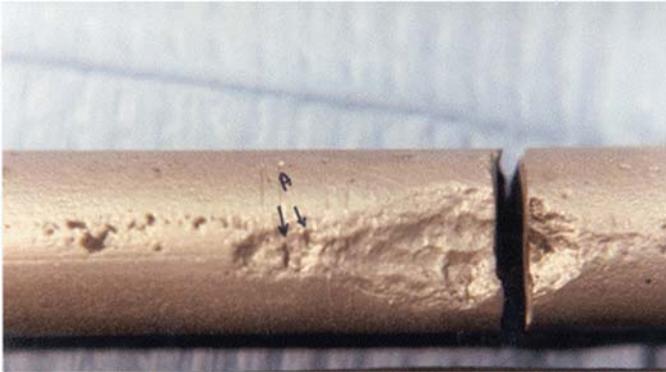
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Technical Newsletter

Volume 09, February 2019



Cracking at Pit



Hydrogen Embrittlement

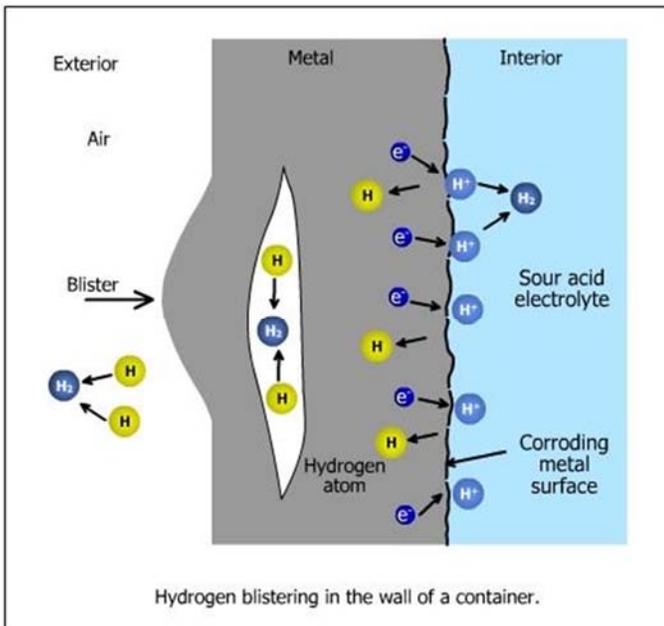
Cracking due to H₂S corrosion of high strength steel



Hydrogen Cracking

H₂S is associated with Hydrogen cracking of high strength steels. Hydrogen atoms produced in corrosion easily penetrate to interior of pipe. If 2 hydrogen atoms meet, a molecule of H₂ is formed which occupies a larger volume than the separate H atoms. This causes a bubble to form in the steel, eventually causing a crack and failure. Hydrogen atoms will penetrate all the way through the steel wall and can be detected with a hydrogen patch detector.

Hydrogen Induced Cracking



Hydrogen Crack



Aegis Tech Line

Aegis Chemical Solutions

Technical Newsletter

Volume 09, February 2019



MIC Corrosion – due to SRB

Corrosion that develops in oilfield wells and surface equipment in the presence of sulfate reducing bacteria (SRB) is referred to “microbial induced corrosion (MIC)”. Failures that result from MIC corrosion are characterized by:

- Layered or concentric pits
- Range from large isolated pits to small connected pits
- May have sharper edges than H₂S corrosion, but not as sharp as low velocity CO₂ corrosion
- Failure may have FeS corrosion product which can be detected with 15% HCl. Deposit will dissolve in acid and give a rotten egg odor (H₂S). Solution will turn pale green as FeS dissolves. With air contamination, solution will turn yellow or yellowish red.
- Verify by SRB culturing techniques from uncontaminated deposits in the failure

Included below are photographs of steel tubulars or other oilfield steel structures that show the characteristics of MIC corrosion listed above.

Concentric or Layered Pits



Layered Pits



Concentric Pits



Oxygen Corrosion

Corrosion can develop in oilfield wells and surface equipment due to the presence of oxygen (O₂). Failures that result from O₂ corrosion are characterized by:

- Wide shallow pits
- Presence of yellow, red, or brown Fe₂O₃ (iron oxide)
- Tubercles may form
- Check water stream or gas phase for O₂

Included below are photographs of steel tubulars or other oilfield steel structures that show the characteristics of O₂ corrosion listed above.

Aegis Tech Line

Aegis Chemical Solutions

Technical Newsletter

Volume 09, February 2019



Wide Shallow Pits



Tubercles



Reddish Yellow Fe_2O_3



Miscellaneous Corrosion

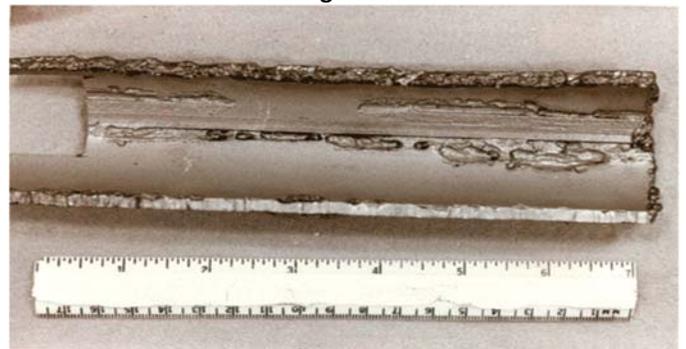
Corrosion in Heat Affected Zone

Corrosion can develop in oilfield wells and surface equipment at heat affected zones (HAZ). Photographs of steel tubulars or other oilfield steel structures that show the characteristics of HAZ are included below.

Fe_2O_3 Deposits



Pitting at Seam



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Technical Newsletter

Volume 09, February 2019



Galvanic Corrosion

Galvanic Corrosion Cell between Weld Material and Pipe



Ringworm Corrosion

Poorly Normalized Upset Tubing



Failure Analysis

It is important to document details of the failure and sample being analyzed including:

- **Type of Equipment:** Pipeline, Tubing, Sucker Rod, Pump, Tank, etc.
- **Description of Equipment (examples):** 1" Sucker Rod, 15th from top; 2 7/8" tubing at 6000 ft. from surface; 4" Flowline at 15 feet downstream of wellhead horizontal section; etc.
 - A sketch of the equipment and its location in reference to other equipment or landmarks is recommended especially for surface failures.

- For surface failures, document elevation changes, bends, changes in pipe diameter, and presence of welds or seams in pipe.
- **Description of Failure (examples):** Isolated pitting at the 5 o'clock position on flowline; Pin break on 1" sucker rod; Sucker rod body break 4" from end; etc. (photographs recommended).
- **Production data at time of failure:** oil, water, gas, pressure, temperature, etc.
- **Unusual conditions (examples):** Well just acidized; downhole pump just replaced, pipeline pigged the day before, etc.
- **Sample of failure:** If tubing or rod is cut, be sure cut far enough away so that any deposits are not impacted by the heat generated. Wrap failure in plastic to keep air and other contaminants away.
- **Metallurgical analysis:** may be required.
- **Deposits around corrosion failure:** may need to be analyzed by X-Ray diffraction or scanning electron microscopy (SEM), or other techniques.

Field Failure Analysis Strategy

It is a best practice to conduct field analysis as soon as the failure sample is available and before any "cleaning" takes place. Exposure of the failure sample to the elements (rain, air, mud, etc.) may cause chemical changes in the corrosion products or cause contamination. Document any "layering" of deposits on the steel. For instance, intermittent oxygen intrusion can greatly accelerate corrosion, and may show up as a distinct reddish-yellow layer. Take photographs of the failure as soon as possible since these can serve as a visual record for reference. If corrosion products are covered with oil or paraffin, it may be necessary to wash the oil and paraffin from the sample with xylene or gasoline. Addition of a small amount of surfactant or soap to the 15% HCl will help remove the oil from the deposit. If there is an oily, gunky coating on the deposit it is recommended that this be saved for lab analysis. Sometimes a poor corrosion inhibitor will "gunk" up the steel and contribute to under-deposit corrosion. Always collect a separate sample in a plastic bottle that is sealed for more detailed and/or confirmatory laboratory analysis.

Aegis Tech Line

Aegis Chemical Solutions

Technical Newsletter

Volume 09, February 2019



Corrosion By-Products

By-products from the corrosion process can develop (see Aegis Tech Line, Volume 02, September 2017; CORROSION IN OIL & GAS PRODUCTION) as follows:

- Carbon dioxide corrosion results in the formation of iron carbonate (FeCO_3).
- Hydrogen sulfide corrosion results in the formation of iron sulfide (FeS or FeS_2).
 - At low concentrations of H_2S and/or MIC corrosion, FeS is typically formed and easily detectable by adding acid and noting the rotten egg smell of H_2S .
 - At high concentrations of H_2S (10,000 ppm or higher), FeS_2 may be preferentially formed and is called pyrite. It is not soluble in 15% HCl.
- Oxygen corrosion results in the formation of iron oxide (Fe_2O_3).

NOTE: On samples exposed to air for long periods, FeCO_3 , FeS , and FeS_2 all convert to iron oxide (Fe_2O_3).

Field Corrosion By-Product Analysis

If the solid fizzes when acid is applied, this is an indication of a carbonate (CO_3). The fizzing solid could either be FeCO_3 corrosion product from CO_2 corrosion, or CaCO_3 scale. If the solution turns pale green but does not smell of H_2S , there is probably some FeCO_3 present from CO_2 corrosion.

If the acid produces the characteristic rotten egg smell of H_2S , the solid probably contains a form of FeS . This could be due to H_2S corrosion or MIC (Microbial induced corrosion).

An alternative test for FeS that does not require a keen sense of smell involves hydrochloric acid (HCl) solution saturated with a couple of ppm of arsenic trioxide (As_2O_3). This solution produces a bright yellow sulfur color if the deposit is FeS .

When FeS or FeCO_3 dissolve in 15% HCl, the solution will usually turn pale green initially. With some time, the solution will turn yellow or orange as the Fe is oxidized with air.

If the corrosion deposit is reddish-orange or yellow, this is an indication of iron oxide (Fe_2O_3) from oxygen corrosion. However, one must be cautious since FeS or FeCO_3 exposed

to air will eventually turn to iron oxide (Fe_2O_3). Fe_2O_3 is slowly soluble in 15% HCl and does not produce a “fizz” or odor.

If there is concern about MIC due to sulfate reducing bacteria (SRB), it is recommended that a portion of the deposit is placed in a clean/sterile container of distilled water, mixed gently, and then serial dilution bottles be inoculated. Other techniques may also be used, such as Sani-check or Rapid-check. It may also be desirable to test for acid producing bacteria (APB).

NEXT ISSUE

The next volume of the Aegis Tech Line will follow this volume with similar content. Volume 10 will be titled “SUCKER ROD FAILURE ANALYSIS” and will focus on sucker rod failures that are a significant issue in mature fields that produce oil with beam pumps. Watch for Volume 10 that will be out shortly.