The elusive goal of “root cause” failure analysis – the importance of persistence and its application to pitting identification.

(illustrated by O&G case histories: (1) Distinguishing between MIC, CO2 and H2S pitting and, (2) the accelerated corrosion of alloy 625 injection tubing in wet gas production wells.)

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Learning Goals

What you should (hopefully) learn from this presentation:

- What is “root cause” and why is it important.
- How to distinguish between CO₂, H₂S, MIC and Oxygen pitting in O&G environments
- Why correcting identifying pitting cause is important in a failure analysis project.
The Elusive Goal of Root Cause Analysis

The importance of root cause
What is “root cause” in a laboratory failure analysis?

- Laboratory testing and analysis tells one the how something failed.
- Root Cause explains “why” something failed.
- Example: Fatigue failures
  - The physical evidence of flat, brittle appearing fractures transverse to the primary loading axis with macroscopic “beach marks” and microscopic striations identifies fatigue.
  - That information alone is not particularly helpful to the client.
  - Root cause explains whether the fatigue failure was caused by human error, poor design, overloading or manufacturing defects.
Why Root Cause?

- Identifying the correct cause any failure (here O&G pitting failures) is important in the corrective action to properly mitigate the failure and prevent recurrence.
- The remedy for pitting corrosion failures caused by different mechanisms can be different.
- Misidentifying the cause for corrosion failures can cost time and money in treating the problem.
Difficulties in Root Cause Analysis

- Pitting of down hole and surface equipment in well fluids from different corrosive species can look similar.
- Obtaining the needed background and technical information in down hole well component failures can be a problem.
- Identifying the correct corrosive species cannot always be done solely in a laboratory setting vacuum!
  - The failure analyst should always discuss the background and environmental conditions regarding a failure.
Information Needs for Root Cause

- Example background data to obtain that should be available includes:
  - Well workover report
  - Well fluid analysis (usually from the chemical treatment vendor)
  - Well production reports
  - Wellbore design
  - Well stimulation information
    - Fracing
    - Pumping
    - Artificial lift using re injected gas.
Impediments to root cause

- Money
- Interest
- Lack of information
- Lack of support
- Lack of effort
The types of corrosion most often encountered in well down hole and surface equipment includes:

- Pitting
  - DO
  - H₂S
  - CO₂
  - MIC
- Uniform Corrosion
- Erosion-corrosion
- Sulfide SSC
- Fatigue
- Wear
Pitting Corrosion in O&G Production

- We will be reviewing the distinguishing characteristics of corrosive species that cause pitting corrosion in producing wells.
  - It is one of the most difficult types of corrosion to interpret
  - Many people get it wrong
  - The mitigation remedy can be different
  - Pitting appearance alone cannot always distinguish what caused the corrosion.
  - Analysis of corrosion products will not always arbitrate what caused the corrosion.
CO₂ Pitting

Characteristics of CO₂ Pitting
CO₂ Pitting

- The topography of carbon dioxide corrosion pits includes the following characteristics:
  - sharp edges
  - smooth sidewalls
  - smooth bottoms
  - pits tend to run into each other

- The main corrosion by-product that indicates carbon dioxide corrosion is taking place is siderite (FeCO₃). Magnetite (Fe₃O₄) and hematite (Fe₂O₃), both iron oxides, could indicate that carbon dioxide corrosion is occurring.

- Note: oxygen is required to form siderite. Another indication that carbon dioxide corrosion is occurring is the amount of carbonates present in the deposits. If the deposits contain over 3% carbonates, then most likely carbon dioxide is present in the system.

- Ref: www.materialsinspectionassociates.com
**CO₂ Pitting**

- CO₂ corrosion pits are round based, deep with steep walls and sharp edges.
- The pitting is usually interconnected in long lines but will occasionally be singular and isolated.
- The pit bases will be filled with iron carbonate scale, a loosely adhering gray deposit generated from CO₂.
  - HCL chemical spot test

Ref: norrisrods.com
CO2 Corrosion Characteristics

- **Form of Corrosion**
  - Uniform — FeCO$_3$ film
    - Pits — Round to oval shape
    - Sharp edges
    - Round bottoms
    - Smooth sides and bottoms

- **Corrosion Products**
  - Iron carbonate (FeCO$_3$)
  - Siderite
  - Iron oxide (Fe$_3$O$_4$, magnetite)
  - Color — tan, green, brown to black

Ref: Nalco Corrosion in Petroleum Industry
Unique Forms of Corrosion
- Wormhole attack
- Ringworm corrosion
- Heat-affected corrosion
- Mesa attack
- Rain drop
H$_2$S Pitting

Characteristics of H$_2$S Pitting
H₂S Corrosion Characteristics

- **Forms of Attack**
  - Uniform — FeS₂ film
  - Pits — Conical shaped
  - Pit bottoms sharp
  - Edges etched and slightly sloped
  - Sides etched

- **Corrosion Products**
  - Black, blue-black iron sulfide
  - Fe₁₋ₓS pyrite, greigite, mackinwaite Kansite,
  - iron oxide (Fe₃O₄), magnetite

Ref: Nalco Corrosion in Petroleum Industry
Characteristics of H$_2$S Corrosion

- H$_2$S pitting is round based, deep with steep walls and beveled edges.
- It is usually small, random, and scattered over the entire surface of the rod.
- A second corrodenet generated by H$_2$S is iron sulfide scale. The surfaces of both the sucker rod and the pit will be covered with the tightly adhering black scale.

Ref: www.norrisrods.com
Characteristics of $\text{H}_2\text{S}$ Corrosion

- The topography of hydrogen sulfide corrosion pits includes the following characteristics:
  - conically-shaped
  - sloping sidewalls
  - etched bottoms

- The main corrosion by-product that indicates hydrogen sulfide corrosion is taking place is pyrite ($\text{FeS}_2$). Pyrrhotite ($\text{Fe}_7\text{S}_8$) and troilite ($\text{FeS}$), which are iron sulfides, could indicate that hydrogen sulfide corrosion is occurring. The main mechanism occurring is indicated by the following equation:

$$\text{Fe} + \text{H}_2\text{S} \rightarrow \text{FeS} + \text{H}_2$$

- Ref: www.materialsinspectionassociates.com
DO Pitting

Dissolved Oxygen Pitting
Identifying DO

- The rate of oxygen enhanced corrosion is directly proportional to the DO concentration, chloride content and/or presence of other acid gases.

- Pitting is usually shallow, flat-bottomed, and broad-based with the tendency of one pit to combine with another.

- Pit shape characteristics may include sharp edges and steep sides if accompanied by CO$_2$ or broad, smooth craters with beveled edges if accompanied by H$_2$S.

- Ref: norrisrods.com
Oxygen Corrosion Characteristics

- Forms of Attack
  - Uniform
    - With red rust deposit
  - Pits
    - Smooth bottoms
    - Smooth sides
    - Sloped edges
    - Width much greater than pit depth
  - Corrosion Products (similar to CO₂ corrosion)
    - Iron oxides FeO(OH),
    - Geothite Fe₂O₃,
    - Hematite Fe₃O₄,
    - Magnetite FeO(OH),
    - ferrous hydroxide
Oxygen Corrosion Characteristics

- The presence of iron oxides as corrosion by-products is a strong indication that oxygen corrosion is occurring in the system (but not always). If X-Ray Diffraction (XRD) finds magnetite (Fe₃O₄), hematite (Fe₂O₃), and/or akaganeite [Fe³⁺(O,OH,Cl)], which is an iron oxychloride, it is a strong indication that oxygen corrosion is occurring.

- The topography of oxygen corrosion pits includes the following characteristics:
  - round pits
  - shallow pits
  - sloping sidewalls
  - tend to grow into one another
  - bright red rust color

Ref: www.materialsinspectionassociates.com
MIC Pitting

Characteristics of MIC Pitting
MIC Corrosion Characteristics

- **Forms of Attack**
- **Pits**
  - Irregular shaped
  - Sloped edges
  - Satiny bottom
  - Etched sides
  - Terraced sides
- **Corrosion Products**
  - Iron sulfides,
  - Sulfate reducing bacteria (SRB)
  - Slime
  - Growths of bacteria
  - Ref: Nalco Corrosion in Petroleum Industry
MIC Corrosion Characteristics

- The topography of microorganism influenced corrosion pits includes the following characteristics:
  - volcano-shaped craters
  - bulls-eye patterns
  - terraced sidewalls
  - sloping edges
  - etched edges

Ref: www.materialsinspectionassociates.com
MIC Corrosion Characteristics

- MIC has the same basic pit shape characteristics of H2S, often with multiple cracks in the pit bases tunneling around the pit edge and/or unusual anomalies (i.e. shiny splotches) on the surface.

- Ref: norrisrods.com
Getting to Root Cause

- Failure analysis activities that complement laboratory testing

- Or “sometimes pit forensics is not enough”
Getting to Root Cause

- The importance of client communications in a laboratory failure analysis
  - Background information
  - Information needs
  - Technical information
  - Timing needs
  - Establish rapport
Is it CO2?

- **CO₂ Corrosion**
  - CO₂ analysis?
  - Location in the well of the corrosion
  - Fluid flow regime
  - Water cut of production fluid
  - Ratio of CO₂/H₂S
  - Partial pressure of CO₂
    - > 3 psia?
  - Water chemistry
  - Treatment chemicals
  - Corrosion products
    - Magnetite (Fe₃O₄), hematite (Fe₂O₃) corrosion products don’t necessarily point to DO corrosion!
Is it H₂S?

- **H₂S Corrosion**
  - Location in the well of the corrosion
  - Fluid flow regime
  - Ratio of CO₂/H₂S
    - iron sulfide may be the corrosion product scale when the H₂S/CO₂ ratio exceeds about 1/500
    - Other sources suggest H₂S/CO₂ > 0.6
  - Partial pressure of H₂S
  - Water chemistry
  - Treatment chemicals
  - Corrosion Products
  - Sulfate Reducing Bacteria (SRB’s) in formation
Forms of iron sulfide

Iron sulfide exists in several distinct forms, which differ in the ratio of sulfur to iron and properties:

- Pyrrhotite, Fe\(_{1-x}\)S, a mineral, which displays ferrimagnetism and crystallizes in monoclinic system. Iron metal shows ferromagnetism; iron sulfides do not.
- Troilite, FeS, a stoichiometric compound.
- Mackinawite, Fe\(_{1+x}\)S the least stable form of iron sulfide; mackinawite has a layered structure.
- Pyrite and marcasite, which are diamagnetic minerals, have the formula FeS\(_2\).
- Greigite (Fe\(_3\)S\(_4\)) a ferromagnetic species akin to magnetite (Fe\(_3\)O\(_4\)).
The most common forms of iron sulfide as corrosion products are pyrite (FeS$_2$). Other forms could include pyrrhotite (Fe$_7$S$_8$) and mackinwite (Fe$_{1+x}$S).

- FeS$_2$
  - Fe = 22%
  - S = 78%
- Fe$_7$S$_8$
  - Fe = 32%
  - S = 68%
Detection of Iron Sulfide

- Iron sulfide reacts with hydrochloric acid, releasing the pungent and very toxic hydrogen sulfide
  - FeS + 2 HCl → FeCl₂ + H₂S

- Why is this reaction important?

- Other chemical markers
  - Arsenite
Is it DO?

- Water chemistry
- Corrosion Rates
- Treatment chemicals
- Corrosion Products
  - Magnetite ($\text{Fe}_3\text{O}_4$) or hematite ($\text{Fe}_2\text{O}_3$) do not necessarily mean DO corrosion
- Source of DO?
  - DO not normally in produced fluids!
  - Water used to dilute treatment chemicals
  - Reinjected gas for artificial lift
MIC Corrosion

Is it MIC?
Types of MIC

- Sulfate reducing bacteria
- Acid producing bacteria
- Iron or manganese bacteria
- Slime formers
MIC Corrosion Variables

- Location in well
  - In temperature regime for bacteria?
- Treatment chemicals
- Water analysis
- Bacteria culturing
- Previous failures
- Process of elimination?
Identifying MIC

Experts need to use all three of the following confirmation tests to identify MIC.

**Chemical**-Test directly for pH, organic acids and test indirectly (test byproducts) for iron sulfide.

**Biological**-Several methods available. The most common are the MIC Field Kit and/or microbiological culturing.

**Metallurgical**-Visually identify shiny metal underneath corrosion products.
Identifying MIC

- MIC and other corrosion mechanisms operate together. It is often difficult to prove conclusively whether or not the biological role is important in a specific case of corrosion.

- Most common environmental microorganisms have “optimum” temperatures for growth somewhere in the 20° to 50°C (68° to 122°F) range.

- Any given strain of organism generally has a temperature range of only about 10° to 20°C (50° to 68°F) over which that organism grows and functions best. Above or below that range, that particular organism's activities slow down or stop altogether.
Identifying MIC

- With few exceptions, MIC is localized, i.e. pitting or crevice corrosion. However, on bare steel exposed to biologically active water, a general biofouling may occur, under which the MIC “pits” are so close together that they create what is often described as “general, nonuniform corrosion.”

- Certain patterns of corrosion have become associated with MIC. Rounded pits under discrete mounds (tubercles) on carbon steel usually signal MIC. Subsurface cavities along weld seams in SS equipment usually point to iron-oxidizing bacteria.

- Analyze the mound material for elements (i.e. sulfur, phosphorus, iron, manganese, and chlorine) that may be indicative of MIC.
Identifying MIC

- Sulfur, phosphorus, iron, manganese, and chlorine in corrosion products may be indicative of MIC.

- On alloys other than carbon steel and cast iron, the covering deposits associated with SRB usually contain few distinct characteristics other than high levels of iron and common “water particulates,” i.e., silicon and aluminum.

- If iron oxidizers or manganese bacteria are present, high levels of chlorine, with or without manganese, can be expected.

- Mounds associated with subsurface pitting along SS welds offer the best example of this. These mounds typically contain very high levels of iron, chlorine, and manganese.
Identifying MIC

MIC has distinct corrosion products within the corroded areas. This is especially true in the presence of SRB. These organisms produce sulfide which combines with any of several metal ions, including manganese, chromium, iron, and copper.

Sulfate reducing bacteria use phosphorous chemistry to store energy. Therefore, their active regions tend to show significant levels of phosphorous, often in amorphous compounds that defy analysis by x-ray diffraction.

Corrosion products associated with SRB are almost always black. On carbon steel and cast iron, primary elements are iron, phosphorus, and sulfur. On SS, chromium and sulfur are usually prevalent. Iron and phosphorus may be present in the covering biomass but are usually only trace elements in the corrosion product.
Attempts have been made to relate the surface morphology within corroded areas to the presence or absence of biological factors. However, microorganisms cause corrosion by generating a corrosive chemistry at the metal surface, not to the presence or absence of microorganisms.

For example, a faceted corroded surface on properly heat-treated wrought stainless steel or the preferential attack of ferrite phase in SS weld metal indicates that corrosion may have been caused by ferric chloride, but not necessarily that such an environment was biologically produced. Is it likely that such a corrosive chemistry was generated by nonbiological factors? If not, then microorganisms should be suspected.
Identifying MIC

- Microorganisms are required to produce MIC.
- Three requirements to produce microorganisms are:
  - Microorganisms require water to propagate.
  - Microorganisms require a food source to propagate.
  - Microorganisms require specific environments to propagate such as water temperature and stagnant conditions.
CO$_2$ Corrosion Images
CO₂ Corrosion Images
CO$_2$ Corrosion
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CO₂ Corrosion
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MIC Corrosion Images
MIC Corrosion Images
MIC Corrosion Images
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MIC Corrosion
MIC Corrosion
MIC Corrosion
What have we learned?
What have we learned?

- Pitting appearance cannot always be relied on to verify the type of pitting.
- Corrosion product analysis cannot always be used to arbitrate the corrosive species.
- Have to utilize other resources (deduction) to arrive at the most probable pitting agent.
- More than one pitting agent can be currently active!
- A useful tool in analyzing a failure is to go through a process of elimination and see what is left.
What have we learned?

- CO₂ Corrosion
  - CO₂ in well fluid?
  - Carbonates in well fluid?
  - What is the CO₂ partial pressure?
  - What is the CO₂/H₂S ratio
  - Is the corrosion location specific? (along tubing or in well)
  - Most erosion-corrosion wall loss will be CO₂ based
  - Previous failures?
  - Corrosion rates?
  - Dislodged pearlite in corrosion product in metallurgical mount?

- Where do we get this information?
What have we learned?

- **DO Corrosion**
  - Most down hole pitting failures not due to DO
  - Is there a source of DO?
  - Corrosion rates
  - Corrosion products?
  - Temperature, pressure?
  - Density of pitting
What have we learned?

- H$_2$S Corrosion
  - Rare compared with CO2, MIC corrosion
  - CO2/H$_2$S ratios?
  - Black deposit in pit bottom?
  - Shape of pit?
What have we learned?

- MIC Corrosion
  - Temperature at corroded area of tubing?
  - Corrosion on OD or ID?
  - Light density, broad pitting?
  - Shiny pit bottoms?
  - Bacteria counts in produced water?
  - Corrosion products include MIC markers?
    - High phosphorus
    - High sulfur
    - High manganese
  - Are there nutrients for bacteria growth?
  - Get photos and proper samples!
Rented Tubing Failure

- L80 tubing
- Rented for a fracing operation
- In the hole for two weeks
- Exposed to fresh water with 2% KCL
  - No DO scavengers or corrosion inhibitors
  - Down hole temperatures ranged from ambient to 200F
- Rental company wanted compensation for wall loss from corrosion while rented.
Rental Tubing Corrosion

- Laboratory work included:
  - Metallographic examination
  - Pit depth measurements

- Other forensic analysis
  - Review workover reports
  - Discuss background with client
  - Research KCL corrosion
Assumptions

- Exposure time to 2% for the rental tubing was ~288 hours
- The KCL solution was not circulated; therefore any DO in the water used to make up the KCL solution would be used up during exposure to the tubing string and initial corrosion rates would therefore decrease as the DO was used up.
- The KCL solution was not contaminated with corrosive formation gases, including CO2 and H2S.
- The pH of the 2% KCL solution was probably neutral to slightly basic.
Rental Tubing Failure

- Pit depths of 0.042”-0.050” measured
- Pit depths vs. exposure time meant that corrosion rates approximated ~1300-1500 mpy.
- Pitting in the KCl solution would be based on DO.
- Literature suggested that corrosion rates of KCL saturated with DO would be ~13-25 mpy.
- Therefore, the two-week rental period could not have caused the corrosion observed.
- Could not have arrived at that conclusion without input from client.
Cap String Failures

Horton Dickson #529 Well
Willow Springs Field
Greg County, TX.
Horton Dickson Well Cap String Tubing

- **Background**
  - 1/4” Inconel 625 (ASTM/ASME B/SB 704-03 UNS N06625) welded nickel alloy tubing received for analysis.
  - Submitted tubing sample from spool #1792 and shipped on July 7, 2008.
  - Material Test Report showed the tube passing the bend test, reverse bend test, flange test, flare test, flattening test, reverse flattening test, hydro test (glycol mix, 1 hour at 15,000 psi) and NST Electric (ASTM A 450 or A 1016, E309, or E426).
## Horton Dickson Well Cap String Tubing

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<thead>
<tr>
<th>COMPONENT</th>
<th>MOL%</th>
<th>GPM</th>
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<tbody>
<tr>
<td>Oxygen</td>
<td>0.010</td>
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<tr>
<td>Nitrogen</td>
<td>0.637</td>
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<tr>
<td>Carbon Dioxide</td>
<td>1.740</td>
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<tr>
<td>Methane</td>
<td>90.992</td>
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<td>Ethane</td>
<td>4.210</td>
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<tr>
<td>Propane</td>
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<td>Isobutane</td>
<td>0.316</td>
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<td>n-Butane</td>
<td>0.369</td>
<td>0.116</td>
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<tr>
<td>Isopentane</td>
<td>0.182</td>
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<tr>
<td>n-Pentane</td>
<td>0.139</td>
<td>0.050</td>
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<tr>
<td>Hexanes</td>
<td>0.142</td>
<td>0.058</td>
</tr>
<tr>
<td>Heptanes Plus</td>
<td>0.168</td>
<td>0.081</td>
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<tr>
<td><strong>Totals:</strong></td>
<td><strong>100.000</strong></td>
<td><strong>1.894</strong></td>
</tr>
</tbody>
</table>

*The Hendrix Group*
Background cont.

- Tubing run in the Horton Dickson #529 Well in Greg County, TX. on July 28, 2008 to 10,000 feet and raised one month later to 8500 feet.
- BHP and BHT 1855 psi and 275°F.
- The temperature at 8500 feet ~240°F.
- The chloride concentration ~130,000 ppm.
Background cont.

- August 5, 2009, the string pulled for well maintenance.
- Tubing parted at 6500 feet, leaving 2000 feet of tubing in the hole.
- Pitted the entire 6500 feet length.
- It had been pulled one time prior, on March 1, 2009, to pressure test and flush the tubing.
- Produced gas 1.91 mol% carbon dioxide, with remainder being various hydrocarbons.
- Water samples from similar wells in the Willow Springs field analyzed. Analysis for incubated bacteria revealed small amounts in two wells and no detectable population in two more wells.
Horton Dickson Well Cap String Tubing

As-received Tube Sample

Overload fracture
Horton Dickson Well Cap String Tubing

OD Pit
Horton Dickson Well Cap String Tubing

OD Deposits

[Image of OD Deposits]
<table>
<thead>
<tr>
<th>Element</th>
<th>Tube Composition</th>
<th>Requirements</th>
<th>MTR</th>
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</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.031</td>
<td>0.10 max</td>
<td>0.020</td>
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<tr>
<td>Manganese</td>
<td>0.24</td>
<td>0.50 max</td>
<td>0.110</td>
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<tr>
<td>Phosphorus</td>
<td>0.007</td>
<td>0.015 max</td>
<td>0.011</td>
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<tr>
<td>Sulfur</td>
<td>0.001</td>
<td>0.015 max</td>
<td>0.001</td>
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<tr>
<td>Silicon</td>
<td>0.21</td>
<td>0.50 max</td>
<td>0.070</td>
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<tr>
<td>Chromium</td>
<td>20.79</td>
<td>20.0-23.0</td>
<td>21.370</td>
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<tr>
<td>Nickel</td>
<td>62.2</td>
<td>58.0 min</td>
<td>61.110</td>
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<tr>
<td>Molybdenum</td>
<td>8.78</td>
<td>8.00-10.00</td>
<td>9.080</td>
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<td>Aluminum</td>
<td>0.067</td>
<td>0.40 max</td>
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<td>Cobalt</td>
<td>0.11</td>
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<td>Niobium+</td>
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<tr>
<td>Tantalum</td>
<td>3.81</td>
<td>3.15-4.15</td>
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<tr>
<td>Titanium</td>
<td>0.89</td>
<td>0.40 max</td>
<td>0.240</td>
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<tr>
<td>Iron</td>
<td>4.02</td>
<td>5.0 max</td>
<td>4.250</td>
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## Horton Dickson Well Cap String Tubing

### Table 2: EDS Analysis (wt%)

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<tr>
<th>Element</th>
<th>Coating</th>
<th>Yellow Deposit</th>
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<tbody>
<tr>
<td>Carbon</td>
<td>39.85</td>
<td>34.14</td>
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<tr>
<td>Oxygen</td>
<td>24.23</td>
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<tr>
<td>Sodium</td>
<td>3.12</td>
<td>1.88</td>
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<tr>
<td>Aluminum</td>
<td>0.63</td>
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<tr>
<td>Silicon</td>
<td>1.36</td>
<td>1.64</td>
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<tr>
<td>Phosphorus</td>
<td>0.87</td>
<td>0.87</td>
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<tr>
<td>Chlorides</td>
<td>4.50</td>
<td>3.03</td>
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<tr>
<td>Potassium</td>
<td>0.27</td>
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<tr>
<td>Calcium</td>
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<td>1.98</td>
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<tr>
<td>Titanium</td>
<td>--</td>
<td>0.67</td>
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<tr>
<td>Chromium</td>
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<td>Iron</td>
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<td>Niobium</td>
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<td>7.78</td>
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<tr>
<td>Molybdenum</td>
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<td>4.24</td>
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Horton Dickson Well Cap String Tubing

Conclusions

- Tube sample failed due to tensile overload at an area of reduced wall loss from external corrosion.
- External corrosion caused by exposure to an aqueous, *acidic?* phase high in chlorides. Deposits at the areas of corrosion probably participated in the corrosion process by concentrating chlorides.
- Several clues that bacteria might have been involved in the corrosion. However, deposition of chloride salts without a bacteria contribution could have also caused the corrosion. *Temp too high for bacteria?*
- The tube met the composition requirements for Inconel 625 and was otherwise of a good and acceptable quality.
Kirsch #17 Well

Teague Field
**Kirsch #17 Well**

- **Background**
  - Tubing inserted in the production tubing through a packer to deliver treatment chemicals for the producing well.
  - Treatment chemicals included corrosion Inhibitor, foamer, scale remover and scale inhibitor.
  - When cap string was pulled from the well, severe corrosion including perforations, had occurred along the bottom 526 feet of tubing. The tubing broke in several places during attempts to retrieve from the well leaving ~170 feet of tubing in the well, including the bottom hole assembly (BHA).
  - The well had been in operation since April 2007.
Kirsch #17 Well

♦ Well Production

− The well produces primarily gas (methane) with no associated oil.
− Water cut is 40 bbls./mmcf.
− The produced fluids also included 800 ppm hydrogen sulfide (H\textsubscript{2}S) and 2.5 mole % carbon dioxide (CO\textsubscript{2}).
− BHT 295F with a maximum shut in pressure of ~1000 psi.
Kirsch #17 Well

- **Produced Water Analysis**
  - Produced water includes 139,000 mg/l TDS with 84,500 mg/l of that being chlorides.
  - Remainder comprised of sodium, calcium magnesium strontium, barium and iron.
  - Calcite (CaCO$_3$), Anhydrite (CaSO$_4$), Celestite (SrSO$_4$), and Barite (BaSO$_4$) would have been scaling at BHTs.
Kirsch #17 Well

- Treatment chemicals
  - Corrosion inhibitor
    - MeOH
    - Quat ammonium compounds
    - Alkylpydirine salts
    - Ammonium bisulfite
    - pH = 4-5
  - Foamer
    - Alkyl quarternary ammonium salt
    - Sodium chloride (salt)
    - pH = 7.9
Kirsch #17 Well

- Treatment chemicals (cont.)
  - Scale inhibitor
    - MeOH
    - Organo phosphorus salt
    - Sodium chloride (salt)
    - pH = 4.7
  - Scale Remover
    - Citric acid
    - Amino alkyl phosphonic acid
    - Glycolic acid
    - pH < 1
Kirsch #17 Well

- Cut end
- Tensile failure end
Kirsch #17 Well

OD corrosion
# Kirsch #17 Well

## Chemical analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Tubing Sample</th>
<th>ASTM 444 NO6625</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.07</td>
<td>0.10max</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.15</td>
<td>0.50max</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.24</td>
<td>0.50max</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.007</td>
<td>0.015max</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.001</td>
<td>0.015max</td>
</tr>
<tr>
<td>Chromium</td>
<td>20.54</td>
<td>20.0-23.0</td>
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<tr>
<td>Molybdenum</td>
<td>9.11</td>
<td>8.0-10.0</td>
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<tr>
<td>Nickel</td>
<td>61.4</td>
<td>58.0min</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.13</td>
<td>0.40max</td>
</tr>
<tr>
<td>Copper</td>
<td>0.31</td>
<td>-</td>
</tr>
<tr>
<td>Columbium</td>
<td>3.48</td>
<td>Co + Ta 3.15min</td>
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<tr>
<td>Titanium</td>
<td>0.21</td>
<td>0.40max</td>
</tr>
<tr>
<td>Tantalum</td>
<td>0.012</td>
<td>5.0max</td>
</tr>
<tr>
<td>Iron</td>
<td>4.09</td>
<td>1.0max</td>
</tr>
<tr>
<td>Cobalt</td>
<td>0.13</td>
<td></td>
</tr>
</tbody>
</table>
### Kirsch #17 Well

#### Deposit analysis

**Table 1 - EDS (wt%)**

<table>
<thead>
<tr>
<th>Element</th>
<th>Black OD Scale</th>
<th>OD Pit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>44.58</td>
<td>45.42</td>
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<tr>
<td>Oxygen</td>
<td>19.56</td>
<td>6.41</td>
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<tr>
<td>Sodium</td>
<td>0.88</td>
<td>0.84</td>
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<tr>
<td>Magnesium</td>
<td>0.56</td>
<td>0.62</td>
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<tr>
<td>Aluminum</td>
<td>0.48</td>
<td>0.70</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>2.05</td>
<td>-</td>
</tr>
<tr>
<td>Silicon</td>
<td>-</td>
<td>0.64</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2.37</td>
<td>0.00</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.88</td>
<td>0.42</td>
</tr>
<tr>
<td>Calcium</td>
<td>2.12</td>
<td>0.49</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.61</td>
<td>0.43</td>
</tr>
<tr>
<td>Chromium</td>
<td>8.82</td>
<td>10.17</td>
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<tr>
<td>Iron</td>
<td>1.56</td>
<td>2.15</td>
</tr>
<tr>
<td>Nickel</td>
<td>7.23</td>
<td>24.07</td>
</tr>
<tr>
<td>Zirconium</td>
<td>2.19</td>
<td>-</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>6.11</td>
<td>7.64</td>
</tr>
</tbody>
</table>

*The Hendrix Group*
Kirsch #17 Well

**Conclusions**

- The sample suffered several metal wastage of the OD.
- The sample was manufactured from alloy 625 as specified; therefore an inadvertent use of a lesser resistant material does not account for the observed corrosion.
- The specified use of alloy 625 suggests that someone was expecting aggressive well fluid conditions.
- This author believes that alloy 625 should be resistant to the reported downhole environment. Other referenced literature also confirms that alloy 625 should be resistant to the reported Kirsch #17 well conditions.
- Alloy 625, in its solution annealed condition, should be completely resistant to corrosion and environmental cracking at the analyzed levels of dissolved CO$_2$ and H$_2$S in the well.
Conclusions (cont.)

- References 2 and 5 contain data points that also suggest alloy 625 should resist up to 20% NaCl at temperatures up to 200°C.
- Alloy 625 while being extremely corrosion resistant, is susceptible to corrosion in some environments in O&G production, including high levels of chlorides at high temperatures, especially if acidic, possibly elemental sulfur and some completion brines.
- Based on the low H₂S levels in the well, elemental sulfur is likely not present. This would tend to eliminate all but chlorides and completion brines.
- Downhole temperature is considered too high for bacteria (MIC).
Kirsch #17 Well

- Hypothesis to explain the corrosion
  - Corrosion in bottom portion of well
  - Location of wet gas lift valves
  - Gas lift valves used to re-start well flow after water flooding
  - Corroded portion of the 625 cap string subject to alternating wet-dry conditions.
  - Wet-dry conditions acted to concentrate chloride salts and formed salt deposits.
  - Deposits developed an acidic condition under the deposits (underdeposit corrosion).
  - Deposits removed during retrieval of string through wiper so deposit evidence lost.
Alloy 625 Properties

- Alloy 625 (UNS N06625) is a low-carbon nickel-chromium molybdenum-niobium alloy which shows excellent resistance to a variety of corrosive media.

- Due to its low carbon content and stabilizing heat treatment, Alloy 625 shows little tendency to sensitization even after 50 hours at temperatures in the range 650–900°C (1200–1650°F).

- The alloy is supplied in the soft-annealed condition for applications involving wet corrosion.
Alloy 625 Properties

- The alloy is characterized by:
  - outstanding resistance to pitting, crevice corrosion, impingement
  - corrosion and intergranular attack
  - almost complete freedom from chloride-induced stress-corrosion cracking
  - good resistance to mineral acids, such as nitric, phosphoric, sulfuric and hydrochloric acids
  - good resistance to alkalis and organic acids
  - good mechanical properties
Alloy 625 Properties

- Alloy 625 shows excellent corrosion resistance in a wide range of media:
  - outstanding resistance to pitting and crevice corrosion in chloride bearing media and to impingement corrosion or intergranular attack.
  - high resistance to corrosive attack by mineral acids, such as nitric phosphoric, sulfuric and hydrochloric acids, as well as to alkalis and organic acids in both oxidizing and reducing conditions.
  - virtual immunity to chloride-induced stress-corrosion cracking.
  - practically no corrosive attack in marine and industrial atmospheres.
  - High resistance to seawater and brackish water, even at high temperatures.
Corrosion of Alloy 625 in O&G Environments

- Reference 2
  - $\rho H_2S_{\text{bar}} = 60$
  - $T_{\text{oC}} = 200$
  - $\% \text{NaCl} = 25$ (250,000 ppm)
  - From Cabval data, NKK data, and Ref. 26 (Ref. 3 in slide 56)
  - Severe corrosion or cracking can arise during acidizing, when the environment may be temporarily highly aggressive to the metal, so correct selection of inhibitor by testing compatibility at the acidizing temperature is advised.
  - Compatibility with completion fluids is another key issue since some of these (particularly the heavier brines) can be severely corrosive to CRAs at high temperature.
Corrosion of Alloy 625 in O&G Environments

- Reference 3

“Generally immune to all concentrations of CO₂ and, therefore, are limited only by H₂S and temperature. They are also not very sensitive to chloride concentration except at quite high chloride levels.”

Sulfur has been found to cause severe pitting and catastrophic cracking of these alloys under certain conditions, although Alloy C 276 is by far the most resistant, but not immune, alloy to this type of corrosion and cracking.

“Resistance of 625 in H₂S/CO₂ environments in absence of elemental sulfur. Corrosion rates of ≤0.05 mm/yr (2 mpy) and no SSC or SCC.”
Corrosion of Alloy 625 in O&G Environments

- Reference 5
  - Gas wells present corrosion problems due to condensation of water when the temperature of the gas falls below the dew point. This occurs at a specific point in the tubing string based on the temperature profile of the well.
  - When multiphase (gas-liquid) conditions exist, the wetting of the steel surface is greatly dependent on the flow regime.
Corrosion of Alloy 625 in O&G Environments

- Reference 5 (cont.)
  - Field Experience with UNS NO8625 alloy

<table>
<thead>
<tr>
<th>Temp 0°C</th>
<th>H₂S - psi</th>
<th>CO₂ - psi</th>
<th>NaCl - g/L</th>
<th>NOTE</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 to 100</td>
<td>&lt;.05</td>
<td>&lt;1000</td>
<td>&lt;100</td>
<td></td>
</tr>
<tr>
<td>80 to 140</td>
<td>.05 to .50</td>
<td>&lt;1000</td>
<td>&lt;100</td>
<td></td>
</tr>
<tr>
<td>60 to 120</td>
<td>.50 to 5.0</td>
<td>&lt;1000</td>
<td>&lt;100</td>
<td></td>
</tr>
<tr>
<td>0 to 80</td>
<td>50 to 50</td>
<td>&lt;1000</td>
<td>&lt;100</td>
<td></td>
</tr>
<tr>
<td>140 to 160</td>
<td>.50 to 5.0</td>
<td>&lt;1000</td>
<td>&gt; 100</td>
<td></td>
</tr>
<tr>
<td>80 to 100</td>
<td>5.0 to 50</td>
<td>&lt;1000</td>
<td>&gt; 100</td>
<td></td>
</tr>
<tr>
<td>120 to 180+</td>
<td>&gt;50</td>
<td>&lt;1000</td>
<td>&gt; 100</td>
<td></td>
</tr>
<tr>
<td>100 to 120</td>
<td>.05 to .50</td>
<td>&lt;1000</td>
<td>&lt;100</td>
<td>Free Sulphur</td>
</tr>
</tbody>
</table>
Corrosion of Alloy 625 in O&G Environments

Resistance of 625 vs. 276
Corrosion of Alloy 625 in O&G Environments

- Pitting resistance of various CRA’s
Corrosion of Alloy 625 in O&G Environments

- Cap string services company website info
  - Corrosion resistant in the most severe environments
    - Chlorides + 200,000 ppm
    - Temperature + 400º
    - High H2S resistant
    - Oxygen resistant
Kirsch and HD Well Cap String Corrosion

Talking points

- For alloy 625 to have corroded to the extent that it did, it seems reasonable to hypothesize that it was exposed to extremely harsh, downhole conditions.
- HD tubing failed along entire length. Kirsch tubing failed at bottom?
- Having eliminated elemental sulfur as a candidate?, an environment including high chlorides at high temperatures at possibly acidic conditions is a probable scenario.
- A review of the injected chemicals against the NACE CorSur Metals Corrosion Database does not show any of the chemicals listed in the MSDS sheets as being particularly corrosive to alloy 625, even at high concentrations. Also, no uniform or pitting corrosion of the tubing ID.
Talking points (cont.)

- Based on the patchy appearance of the corroded tubing sample, it is likely that the observed corrosion occurred under deposits.
- One corrosion scenario is based on corrosion of the tubing under deposited and/or precipitated salts.
- Kirsch tubing string might have been plugged at some time.
- Plugging of the tubing would have had two effects:
  - prevent corrosion and scaling chemicals from contacting the OD of the tubing
  - increase tubing metal temperatures
  - plugging and high metal temperatures could have facilitated the formation of corrosive salts on the tubing OD. The local environment under the deposits would have turned acidic.
Kirsch and HD Well Cap String Corrosion

- Talking points (cont.)
  - Condition of the production tubing/casing in the two wells?
  - Similarities and differences in the produced fluids?
  - Differences in the field formations?
  - Differences in how the two wells were completed and fractured?
  - Differences in the well bore design?
  - Any monitoring methods available?
  - Differences in chemical treatment?