Chemical Usage in Hydraulic Fracturing and Corrosion Characteristics of Produced Water

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1. Introduction

Hydraulic fracturing ("fracking") is a technique used to enhance the recovery of oil and gas from tight formations by injecting high-pressure fluids to create and propagate fractures in the reservoir rock. The fluid mixture typically contains water, proppants (such as sand), and a variety of chemical additives tailored to the specific geology of the well.

This white paper outlines the primary chemical constituents used in hydraulic fracturing, the expected composition of produced waters, and the associated equipment integrity issues, including corrosion from acid and solvent exposure. It concludes with a discussion of field-recognized visual indicators of such degradation and includes an addendum of visual references.

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2. Chemical Constituents Used in Hydraulic Fracturing

Fracturing fluids contain a complex formulation of components, which can be grouped as follows:

- **Base Fluid:** Typically water (90–97%)
- **Proppant:** Sand or ceramic particles (3–10%)
- **Chemical Additives (0.5–2%)**

Key Chemical Additives:

Function	Chemical Example(s)	Purpose
Acid	Hydrochloric acid (HCl)	Dissolves minerals, initiates fractures
Biocide	Glutaraldehyde, DBNPA	Prevents bacterial growth
Corrosion Inhibitor	Quaternary ammonium compounds	Protects pipe and equipment
Friction Reducer	Polyacrylamide	Reduces surface friction
Gelling Agent	Guar gum, Hydroxyethyl cellulose	Increases fluid viscosity
Crosslinker	Borate salts	Enhances viscosity by linking gel molecules
Breaker	Ammonium persulfate	Reduces viscosity post-fracture
Surfactant	Isopropanol, Nonylphenol ethoxylate	Improves fluid recovery
Solvent	2-Butoxyethanol	Carrier for other chemicals; penetrant

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3. Composition of Produced Water

Produced water is the fluid that returns to the surface after hydraulic fracturing. It is a mixture of injected fluids and formation water, containing a complex blend of organic and inorganic constituents.

Typical Components in Produced Water:

- **Total Dissolved Solids (TDS):** 10,000 – 300,000 mg/L
- **Chloride (Cl^-):** 1,000 – 200,000 mg/L
- **Sodium (Na^+):** 1,000 – 80,000 mg/L
- **Calcium (Ca^{2+}):** 500 – 40,000 mg/L
- **Magnesium (Mg^{2+}):** 100 – 5,000 mg/L
- **Barium (Ba^{2+}):** 10 – 10,000 mg/L
- **Iron (Fe^{2+}/Fe^{3+}):** 1 – 1,000 mg/L
- **Hydrocarbons:** Oil, condensate, BTEX compounds (Benzene, Toluene, Ethylbenzene, Xylene)
- **Residual Fracturing Additives:** Acid, surfactants, biocides, solvents

References: Veil, J. (2015). *U.S. Produced Water Volumes and Management Practices in 2012*. GWPC.
Stringfellow, W.T. et al. (2014). *Chemical Composition of Fracturing Fluids and Produced Waters*, J. Hazard. Mater.

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4. Corrosion Challenges in Produced Water Systems

Produced water can be corrosive to infrastructure, particularly due to residual acid gases, chloride content, organic solvents, and microbial activity.

4.1 Hydrochloric Acid (HCl) Impacts on Carbon Steel

Hydrochloric acid, even in vapor form, is highly corrosive to carbon steel. The reaction of HCl with steel produces soluble ferrous chloride:

$$\mathbf{Fe + 2HCl \rightarrow FeCl_2 + H_2\uparrow}$$

Ferrous chloride can oxidize to ferric chloride ($FeCl_3$), which is hygroscopic and self-propagates corrosion by absorbing moisture. The absence of passivating oxide layers leads to rapid pitting and underfilm attack.

Visual Signature of HCl Corrosion on Steel:

- Bright orange or yellow rust (ferric chloride)
- Sticky, glossy residue under humid conditions

- Pitting and delamination of coatings
- Blistering of protective films
- Laminated, flaking delamination resembling **baklava pastry**, caused by interlayer acid migration

Reference: Schweitzer, P. A. *Corrosion of Linings and Coatings*, CRC Press, 2006.
Winnik, S., Vander Wielen, J. "Failure Analysis of Epoxy Coated Steel in Acidic Environments," *JPCL*, 2009.

4.2 2-Butoxyethanol and Epoxy Coating Degradation

2-Butoxyethanol is a glycol ether used as a solvent and carrier for fracturing chemicals, including gels and surfactants. It is also a common ingredient in industrial paint removers.

Effects on Epoxy Coatings:

- Acts as a plasticizer, lowering the glass transition temperature (Tg)
- Promotes swelling and underfilm separation
- Leads to discoloration, chalking, and adhesion loss
- Facilitates water and chemical permeation into substrate
- Residual solvent can inhibit proper curing of repair coatings

References: ATSDR, *Toxicological Profile for 2-Butoxyethanol*, 1998.
Wicks, Z. W. et al. *Organic Coatings: Science and Technology*, Wiley-Interscience, 2007.

4.3 Corrosion from Other Additives

- **Biocides (e.g., glutaraldehyde)** can create localized acidification, increasing the risk of microbiologically influenced corrosion (MIC), particularly under biofilms.
- **Surfactants and solvents** can destabilize protective oxide layers and facilitate ingress of aggressive species.
- **Friction reducers and gelling agents** may carry trace impurities (like formates or chlorides) that catalyze localized pitting.
- **Breakers (oxidizers like ammonium persulfate)** can generate oxidative stress on coatings and metallic surfaces, promoting under-deposit corrosion.

4.4 Chloride Corrosion and Scaling from Cations

- **Chloride ions (Cl^-)** aggressively penetrate protective oxide films on carbon steel and stainless steel, leading to pitting and crevice corrosion.
- **Scaling:** High concentrations of cations such as **calcium, barium, and magnesium** form insoluble salts (e.g., $BaSO_4$, $CaCO_3$), which:
    - Impede flow
    - Increase pressure drop
    - Provide nucleation sites for under-deposit corrosion

Reference: ASM International, *Corrosion: Fundamentals, Testing, and Protection*, Vol. 13A, 2003.

4.5 Galvanic Corrosion and Sacrificial Anode Protection

- In systems where dissimilar metals are present (e.g., carbon steel with stainless steel valves or fittings), **galvanic corrosion** occurs due to electrochemical potential differences.
- Corrosion concentrates on the more anodic (less noble) metal in the galvanic series.

Use of Sacrificial Anodes:

- **Magnesium and aluminum anodes** are commonly employed in tanks and separators to protect steel components.
- They corrode preferentially, thus **sacrificing themselves** to protect adjacent steel.
- Benefits:
    - Cost-effective mitigation strategy
    - Easy visual confirmation of consumption
    - Compatible with a wide range of systems

Reference: Jones, D.A., *Principles and Prevention of Corrosion*, 2nd ed., Prentice Hall, 1996.

4.6 Blistering

There are several ways in which blistering can affect the corrosion of the substrate. While blisters formed by cathodic polarization can weaken adhesion of a coating, they will typically have little effect on the underlying substrate. The cathodic reactions produce hydroxide at the substrate, which can contribute to the delamination and growth of the blister.[3,7] Yet, the pH of water found in these blisters is usually alkaline at values around 10–11.[4] At this pH, steel is normally passive and does not corrode. Typically, if a cathodic blister is opened, bright, uncorroded steel will be found underneath. Therefore, these blisters are not considered a risk to the substrate.

On the other hand, anodic blistering will certainly have corrosion products forming below the coating. Anodic blistering usually begins below a pore or microdefect in the coating or next to a macrodefect like a scribe or crack in the coating.[3,4] In the case of blistering at small defects or pores, corrosion will begin where oxygen and ionic species, often salts like NaCl, are able to pass through the coating to the substrate and initiate corrosion. As corrosion product builds up, the pore or defect will become blocked, once again making the coating film semipermeable to the surroundings.[3,4,8] The corrosion products then react with incoming oxygen, making the area under the pore oxygen-deficient. The whole area below the pore becomes anodic, and cathodic reactions at the surrounding perimeter begin to disbond the coating. This process supports continued osmosis and electroosmosis to bring water and ionic species into the blister, and the blister growth continues. If an anodic blister is opened, a ring of black-red rust will be found on the underside of the dome and surrounding the central anodic area.

5. Conclusions

Hydraulic fracturing relies on a range of chemical inputs, some of which pose significant risks to the longevity and integrity of oilfield infrastructure. Produced water contains high levels of corrosive ions, residual chemicals, and hydrocarbons that can degrade coatings and corrode steel. Understanding these interactions—particularly those involving HCl and glycol ether solvents like 2-butoxyethanol—is critical to designing protective strategies and selecting compatible materials.

Addendum: Visual Indicators of Corrosion Damage

To be supplemented with photographs and schematic illustrations showing:

- Ferric chloride (bright orange) corrosion products on carbon steel
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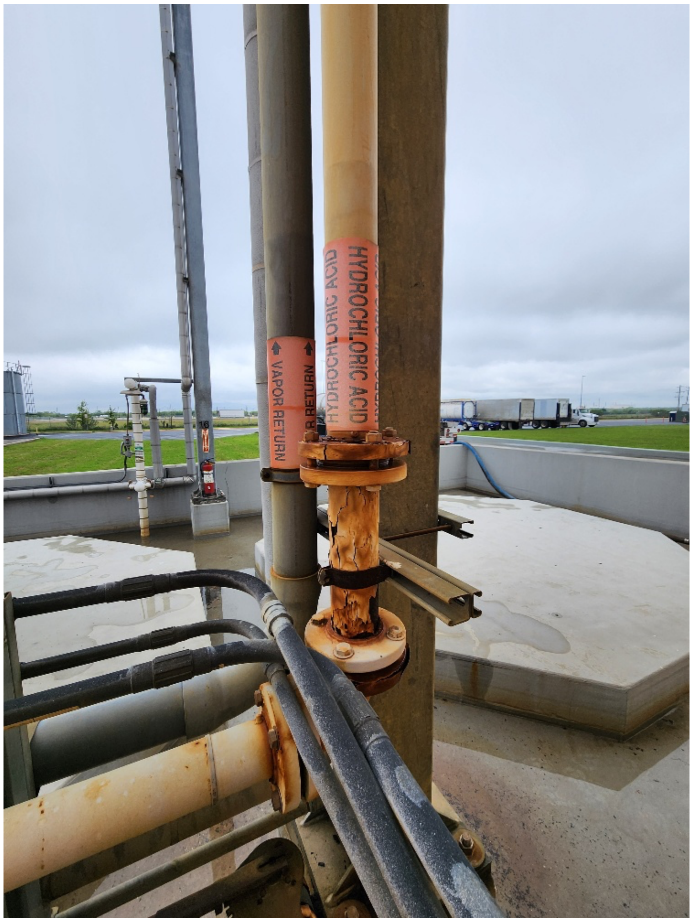
- Baklava-style delamination of carbon steel.

- 
VAPOR RETURN
VAPOR RETURN
HYDROCHLORIC ACID
HYDROCHLORIC ACID

- Osmotic blistering from underfilm acid exposure

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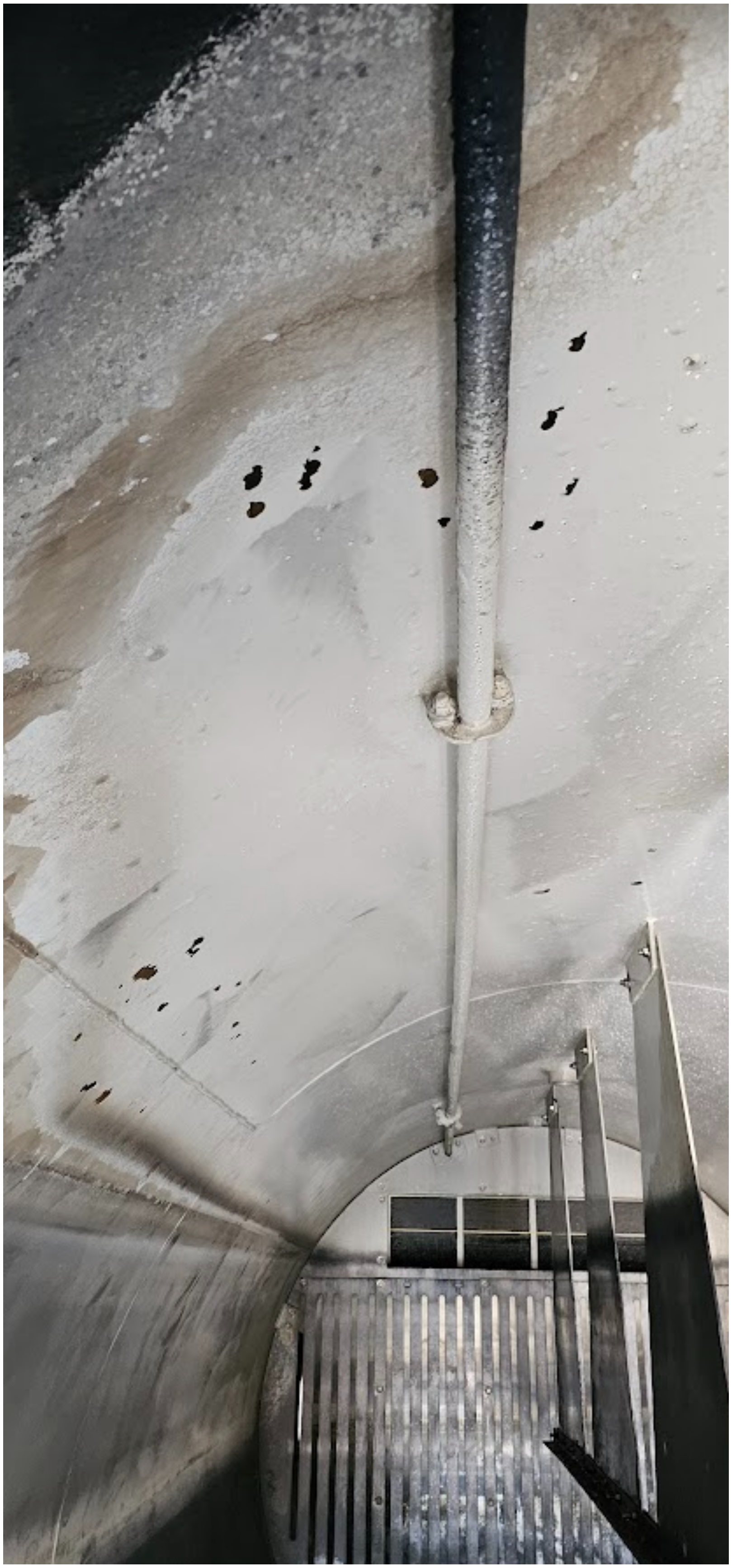

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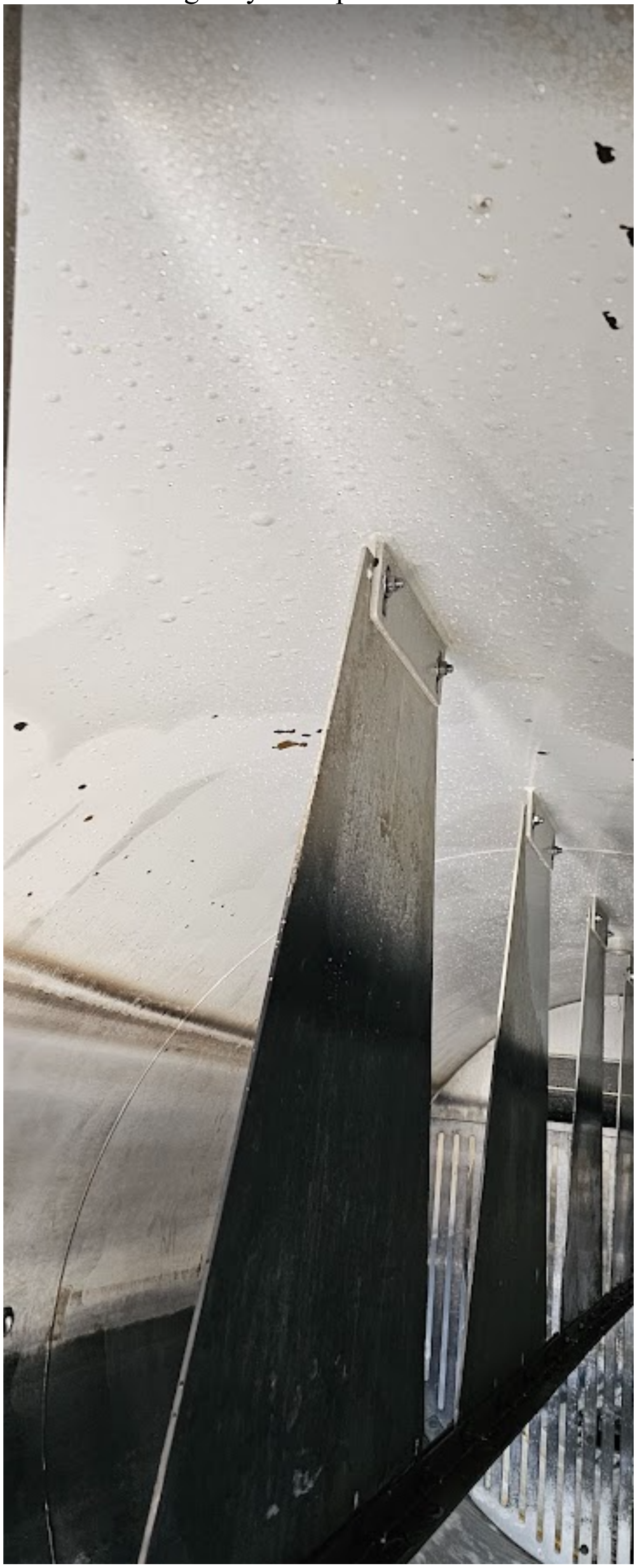
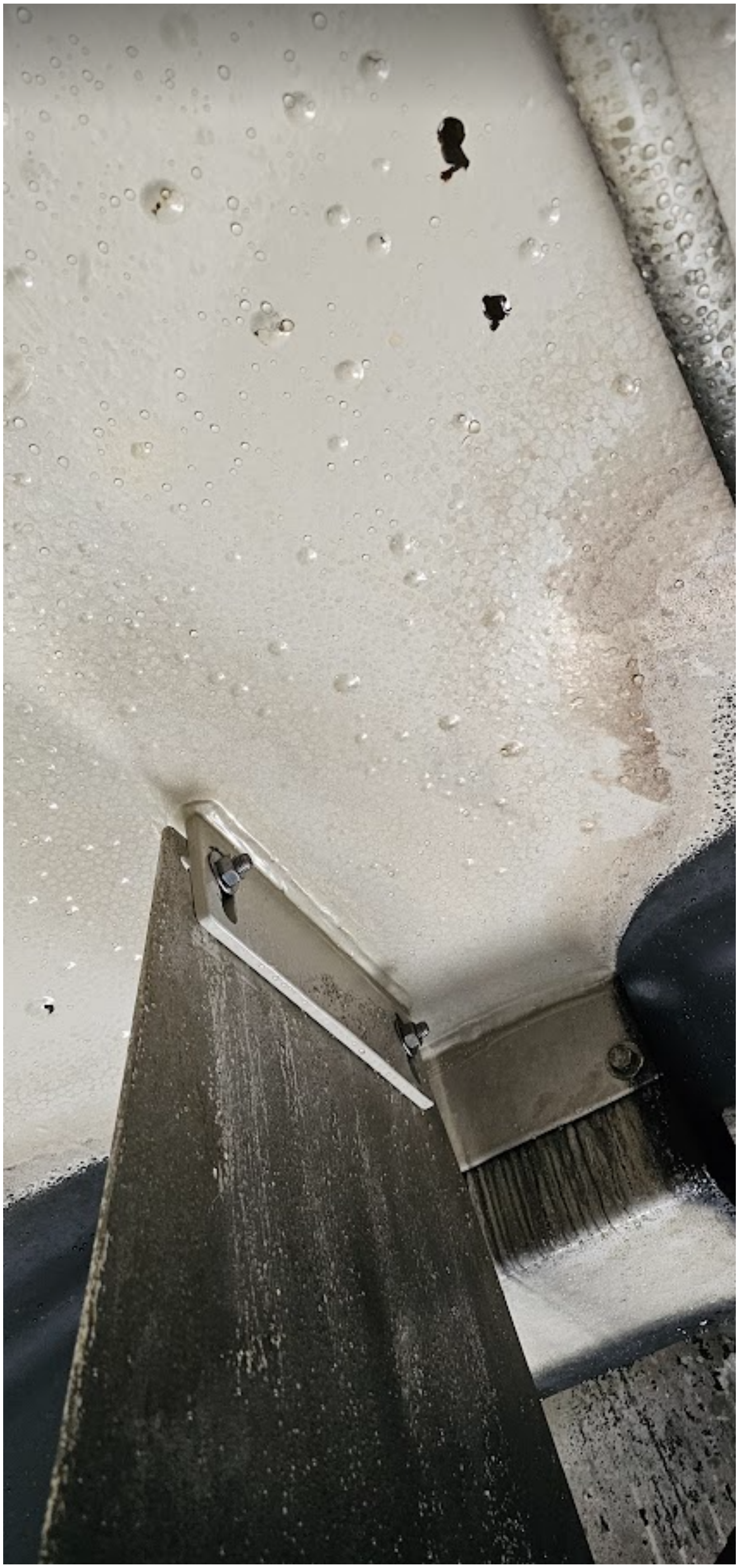
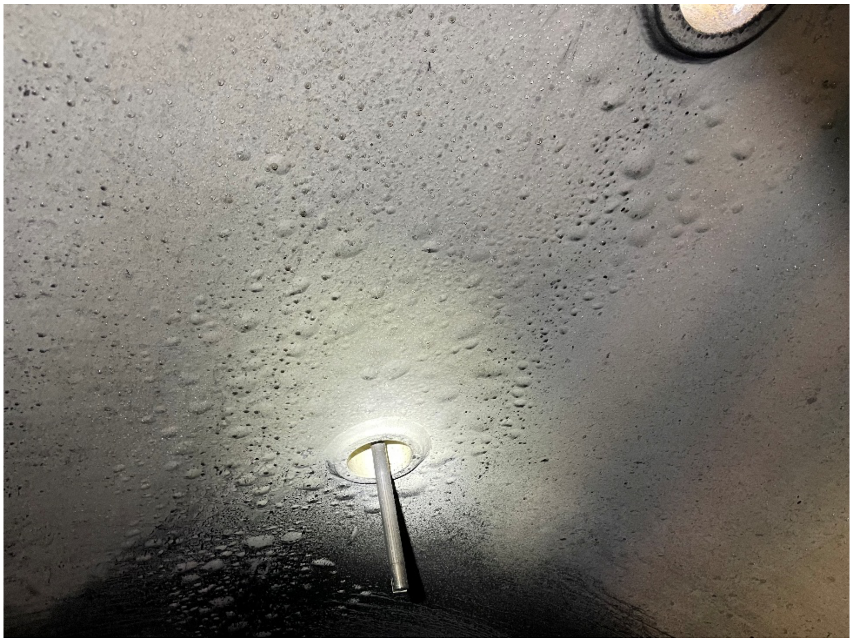
- Note: Blistering only in Vapor Phase.
- 

- 

    - 
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- Epoxy softening and discoloration after solvent contact
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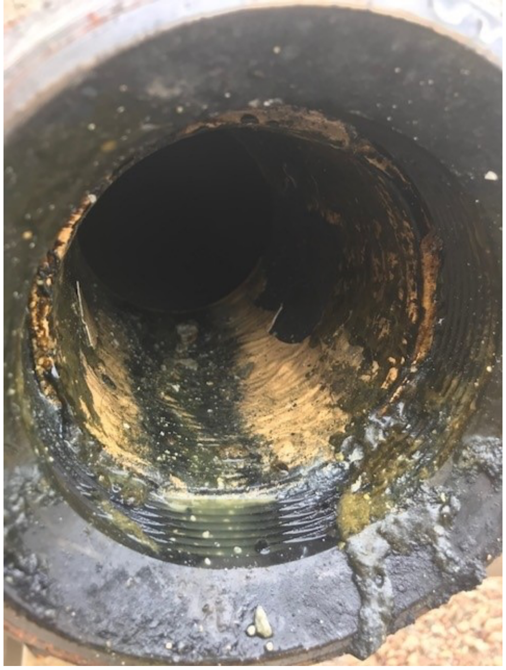
- Failed coatings with interlayer separation
    - 

- Pitting corrosion from High Chloride High Temperature environment adjacent to scale deposits
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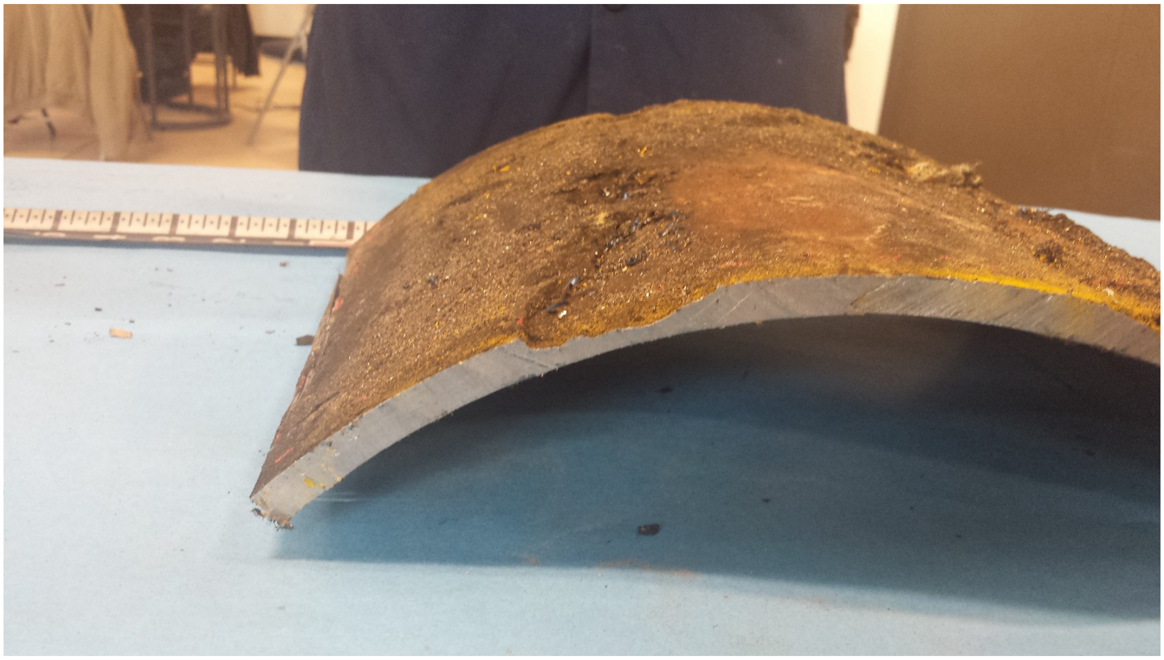

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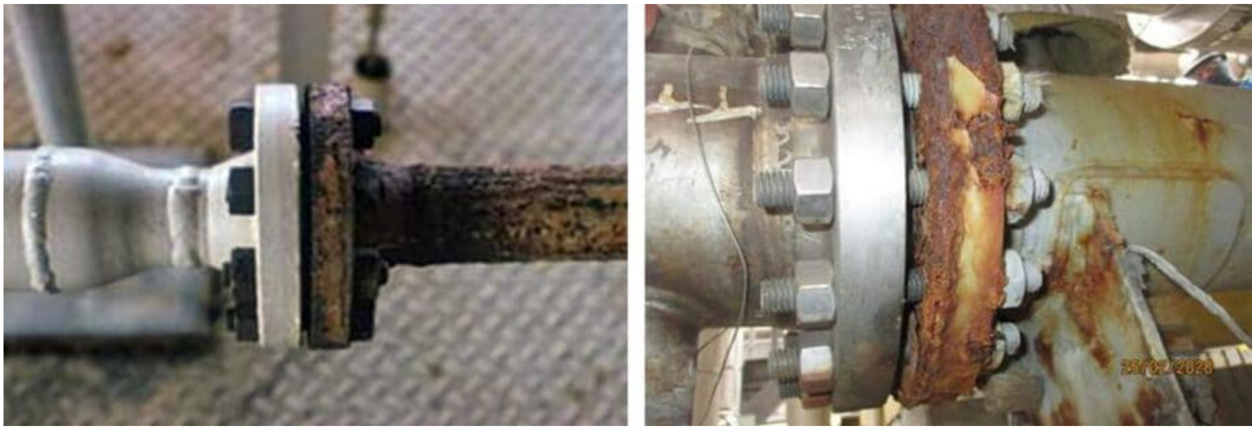
- Galvanic corrosion at dissimilar metal interfaces
  - 

- Sacrificial anode depletion profiles
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(Additional Images to be appended or embedded based on field inspection photos.)