Corrosion

- Corrosion Basics
  - General corrosion theory
  - Corrosion examples
- Specialty Problems
  - CO_2 and H_2S
  - O_2 in sea water injection
  - Acid Treatment
  - Packer Fluids

Major Causes of Corrosion

- Salt water (excellent electrolyte, chloride source)
- H_2S (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_2S more soluble in H_20)
- Velocity - important in stripping films, even for sweet systems
- Wear/Abrasion (accelerates corrosion)
- Solids – strips film and erodes metal

Chemical Corrosion

- H_2S
  - **weak acid, source of H^+**
  - **very corrosive, especially at low pressure**
  - **different regions of corrosion w/temp.**
- CO_2
  - **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

REMOVAL OF "PROTECTIVE" FILM

- 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.

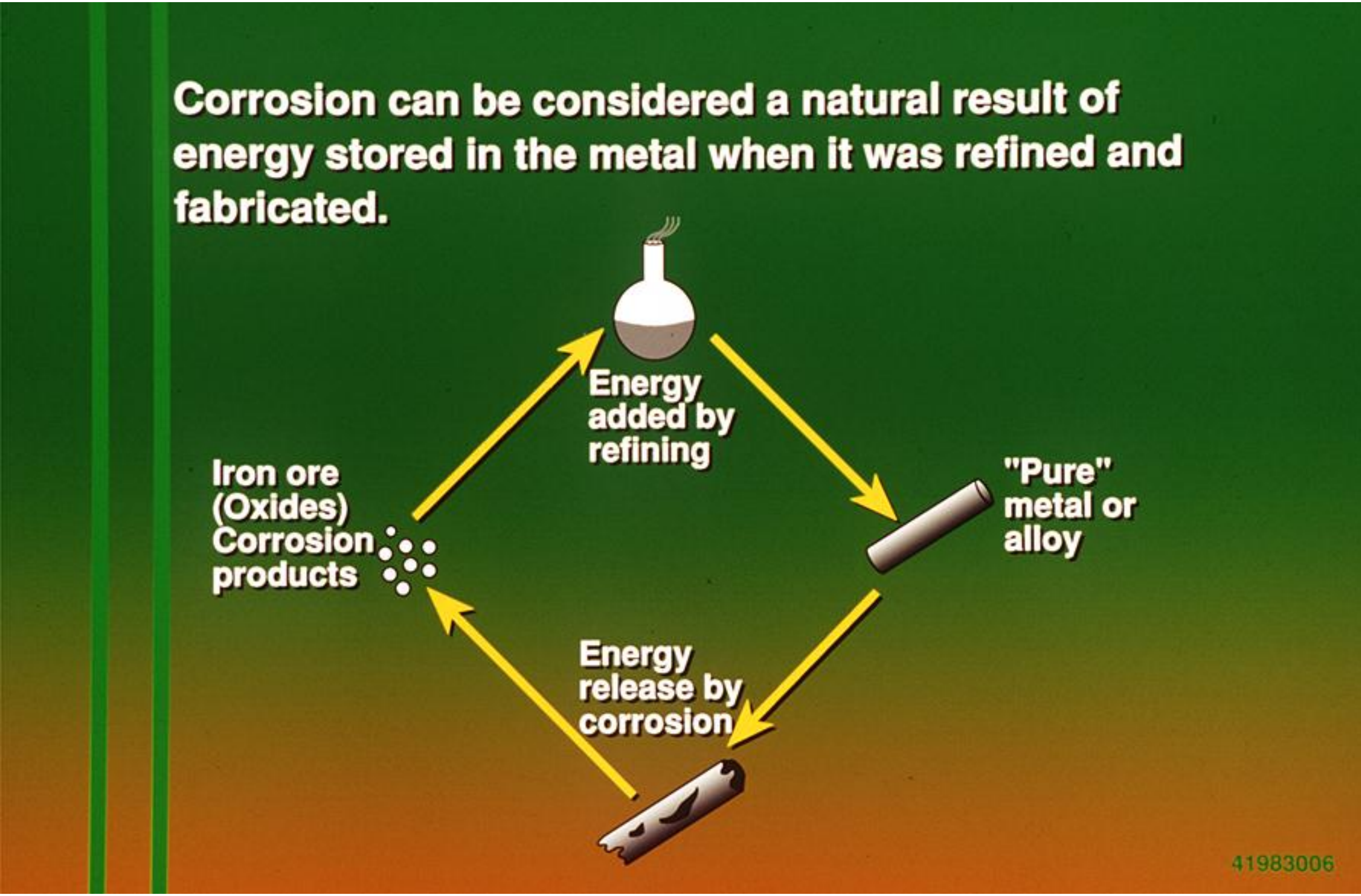
corrosion in tubing exacerbated by abrasion from wireline operators.

1970’s Industry Study of Failures

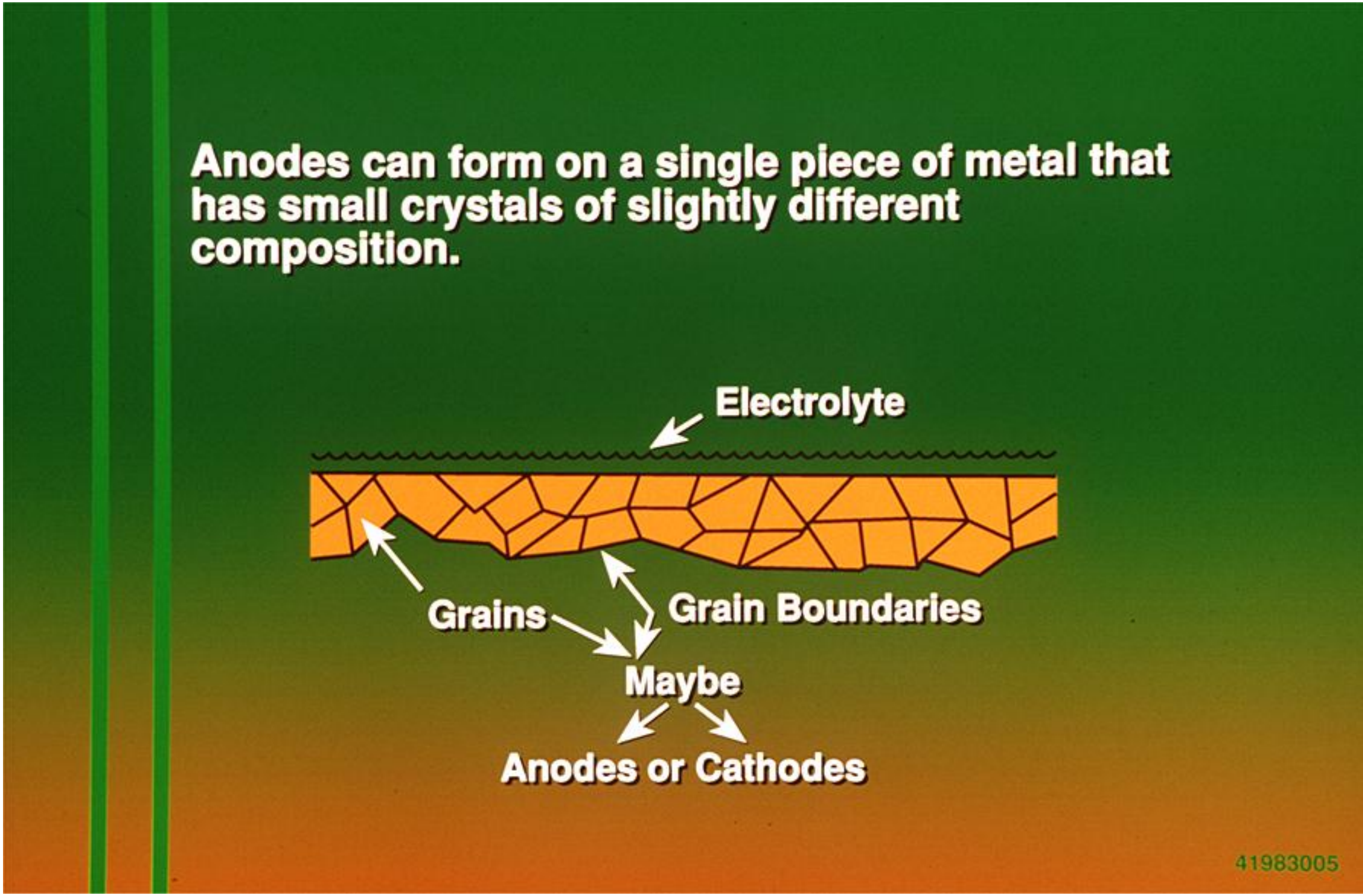
Method	**% of Failures**
Corrosion (all types)	33%
Fatigue	18%
Brittle Fracture	9%
Mechanical Damage	14%
Fab./Welding Defects	16%
Other	10%

Causes of Petroleum Related Failures (1970's study)

Cause	**% of Failures**
CO_2 Corrosion	28%
H_2S Corrosion	18%
Corrosion at the weld	18%
Pitting	12%
Erosion Corrosion	9%
Galvanic	6%
Crevice	3%
Impingement	3%
Stress Corrosion	3%



Schlumberger O.F.R.



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** – H_2S gas a water creates an acid gas environment resulting in 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..

CO_2 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.

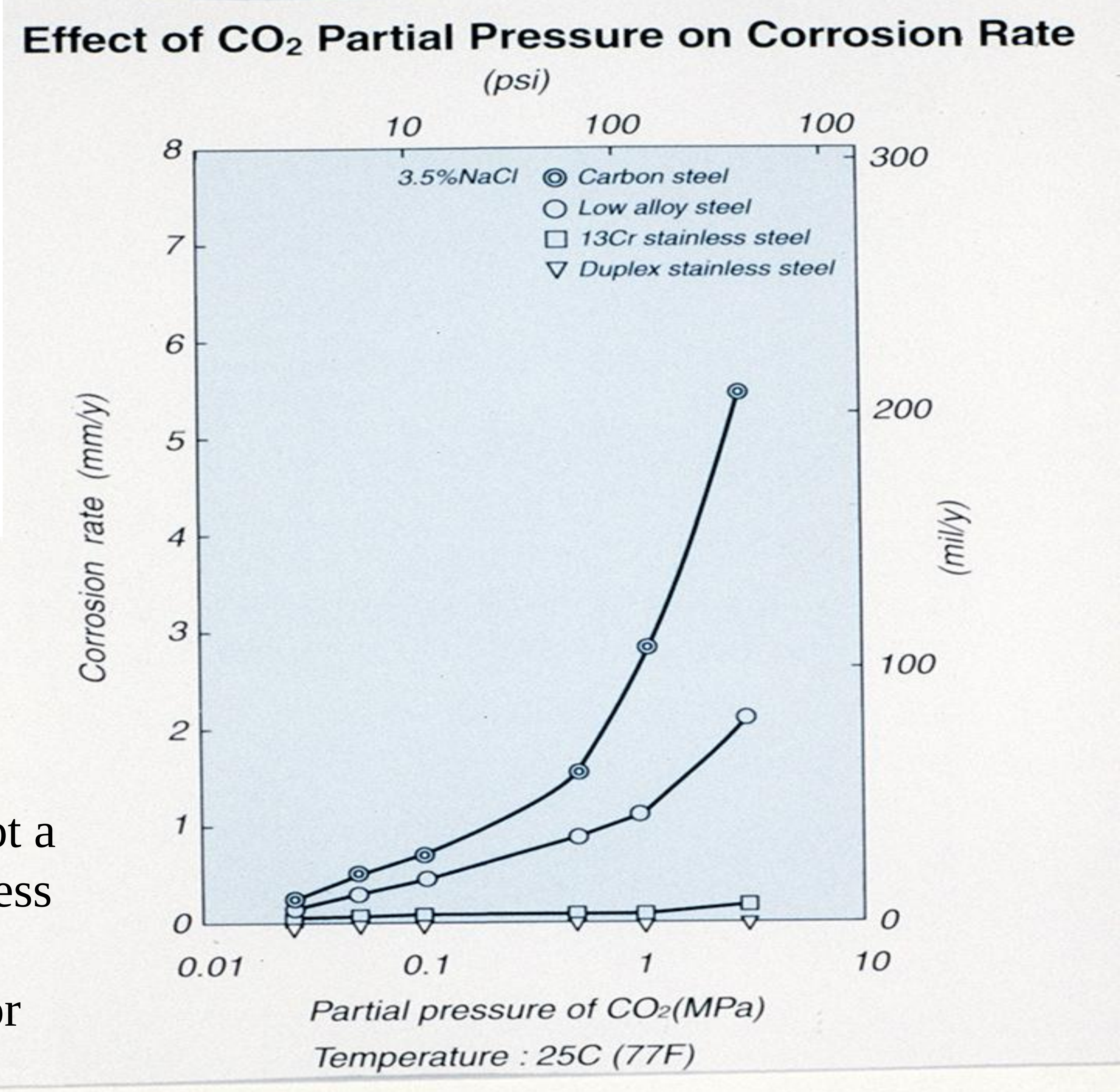
Partial pressure is the mole fraction of the specific gas times the total pressure. If the CO_2 mole concentration is 1% and the pressure is 200 psi, the partial pressure is $0.01 \times 200 = 2$ psi.

CO_2 corrosion

CO_2 localised attack in 7" production tubing

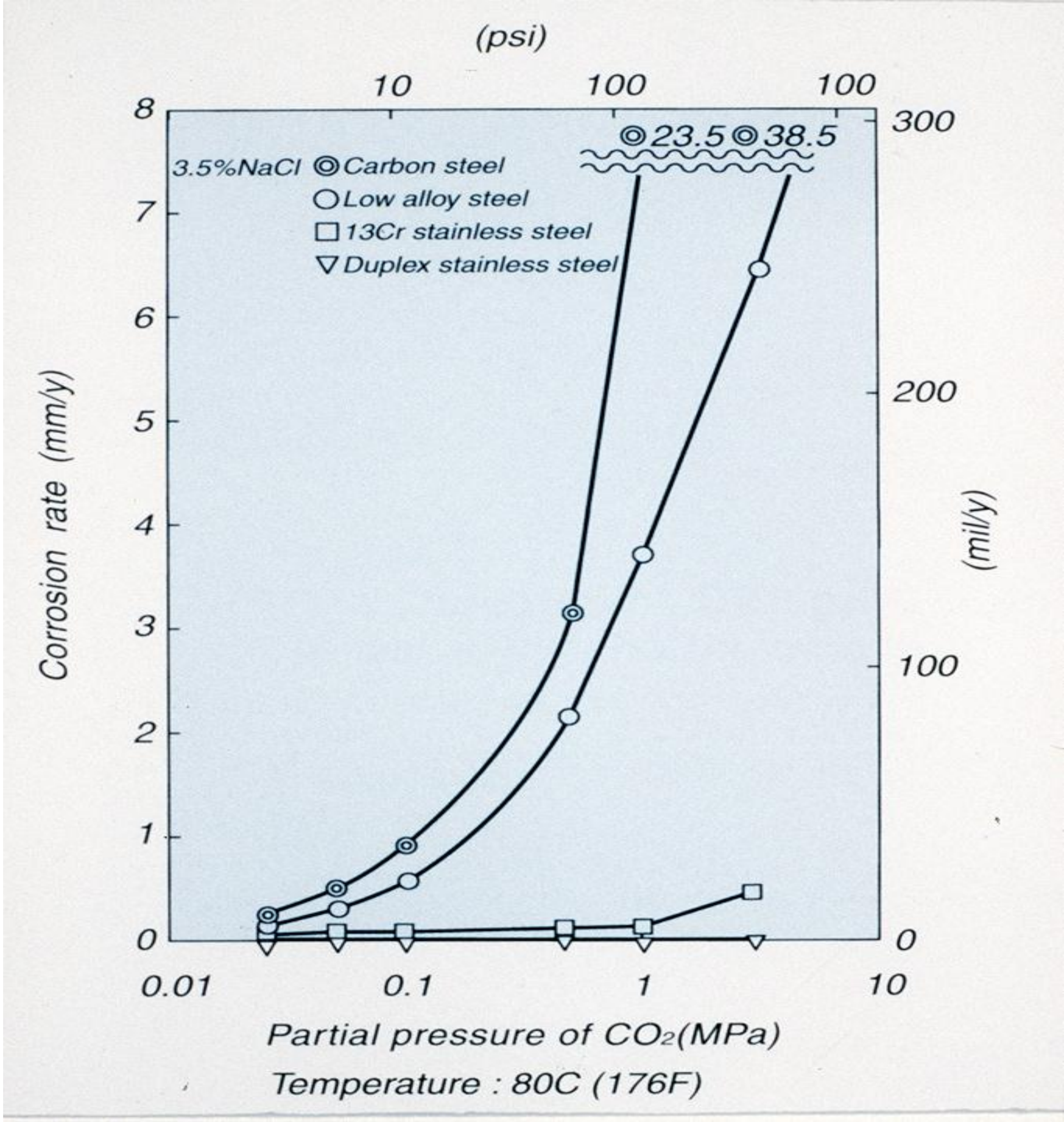
The corrosion rate of CO2 is a function of partial pressure, temperature, chloride presence of water and the type of material.

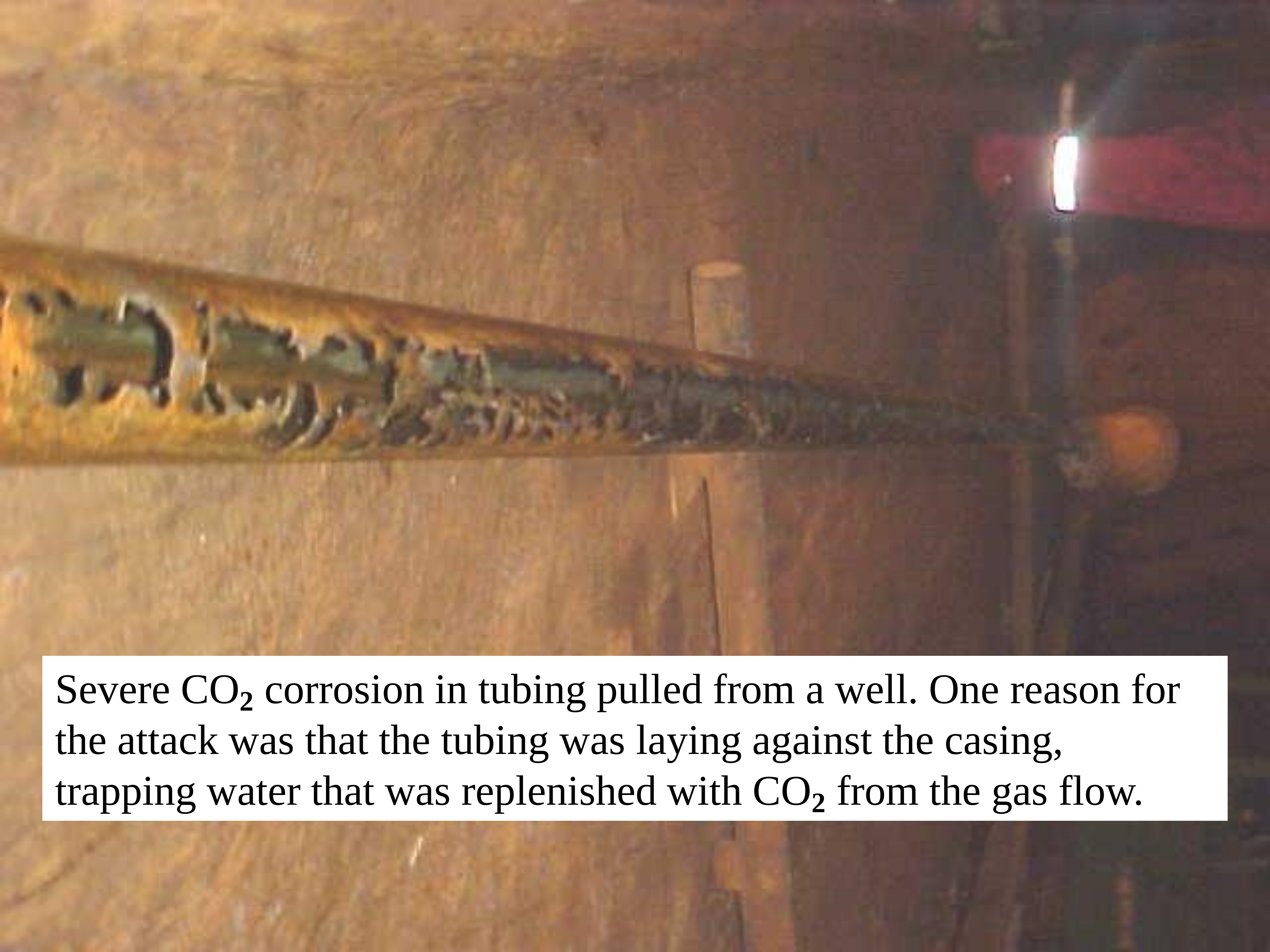
Corrosion rate in MPY – mills per year is a standard method of expression, but not a good way to express corrosion where pitting is the major failure.



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).

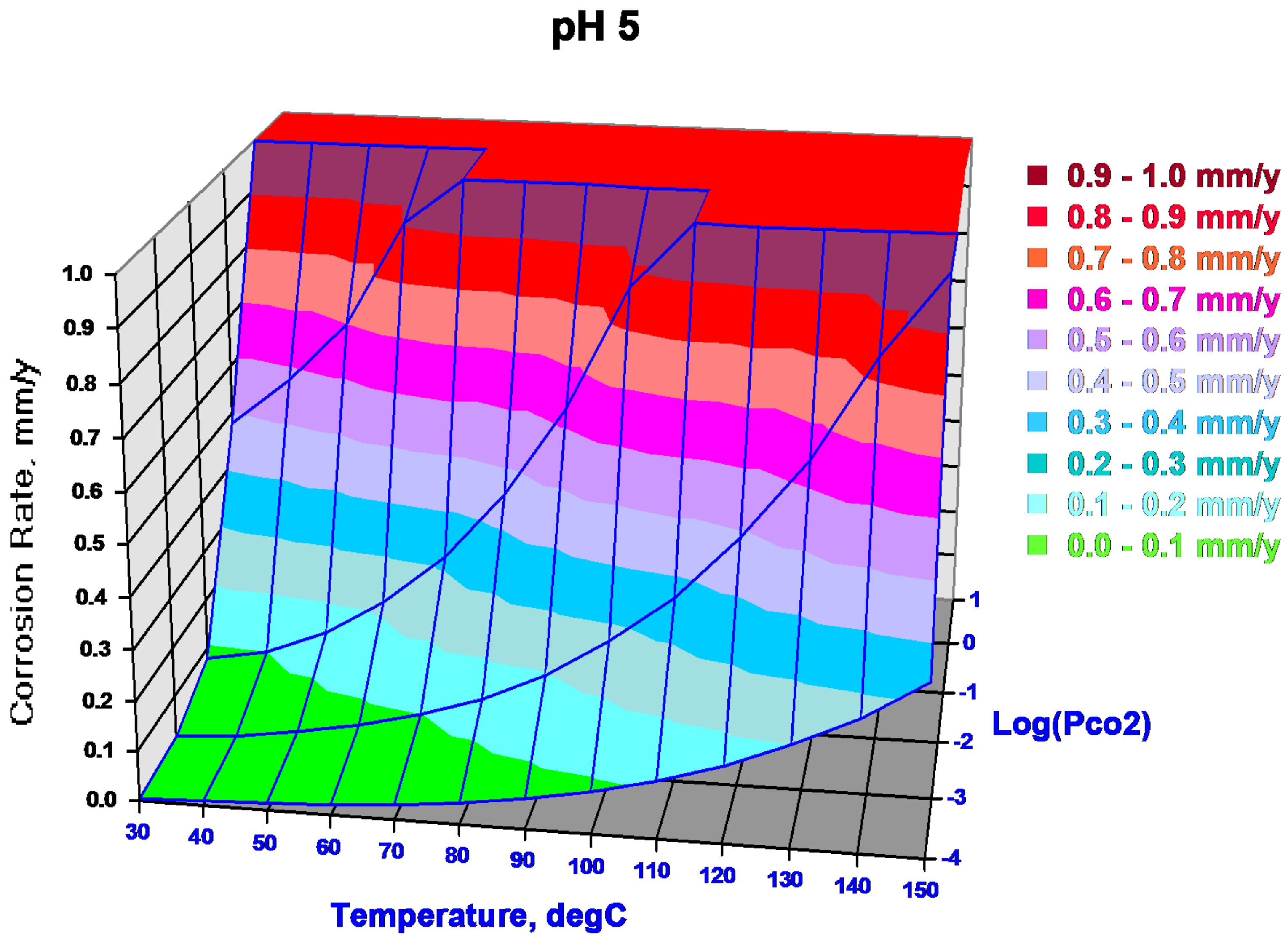




Severe CO_2 corrosion in tubing pulled from a well. One reason for the attack was that the tubing was laying against the casing, trapping water that was replenished with CO_2 from the gas flow.

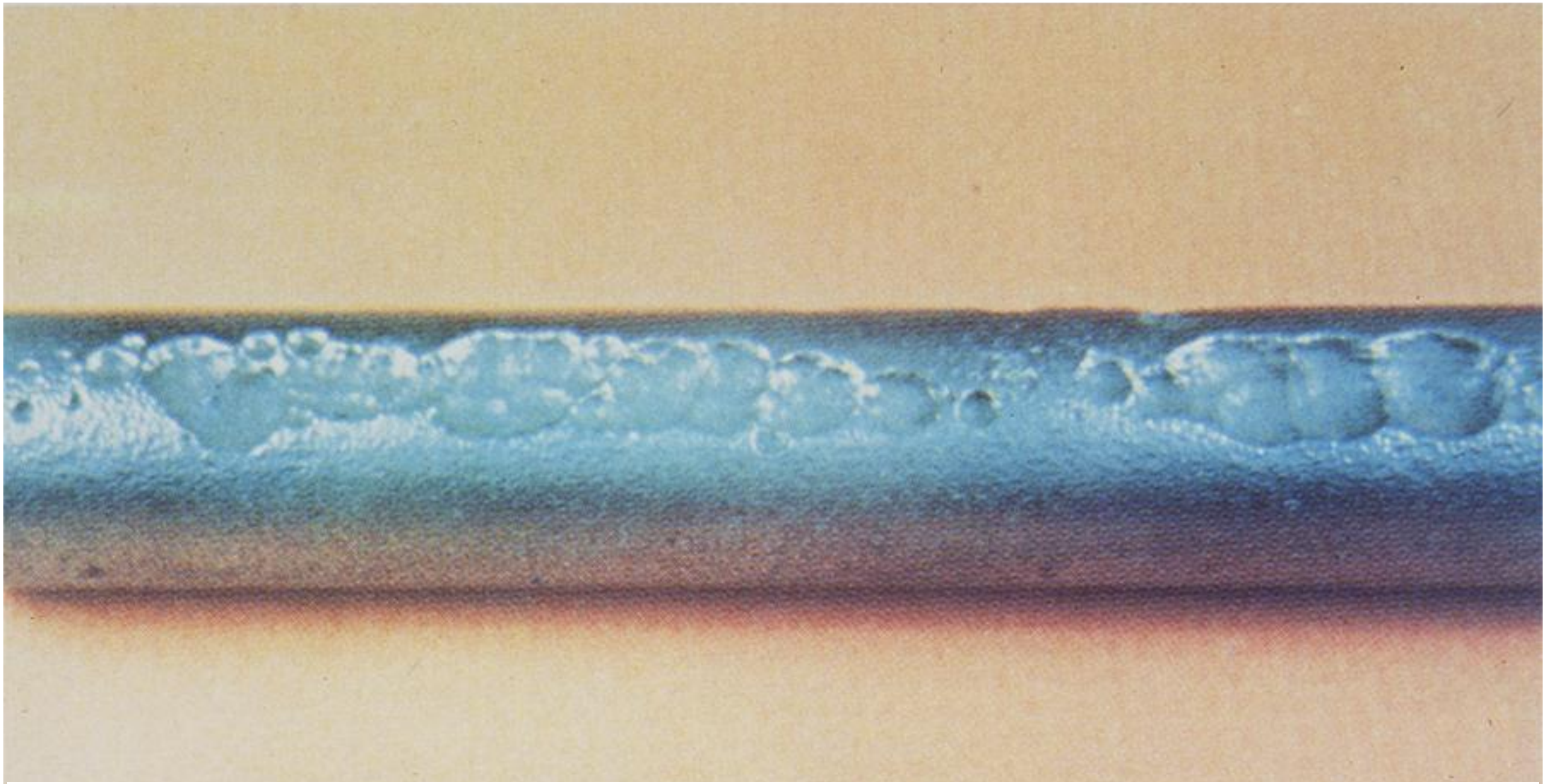
Thinned and embrittled tubing twisted apart when trying to break connection during a tubing pull.

CO_2 CORROSION ISOPLOT



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 H_2S and water.
- Generates atomic hydrogen. Hydrogen moves between grains of the metal. Reduces metal ductility.

API/SPEC 5A, 5AC, 5AX Tubing and Casing

	Strength				
	Yield		Tensile		
Grade	Min.	Max.	Min.	H_2S	Spec.
H-40	40,000	--	60,000	Yes	5A
J-55	55,000	80,000	75,000	Yes	5A
K-55	55,000	80,000	95,000	Yes	5A
N-80	80,000	110,000	100,000	?	5A
C-75	75,000	90,000	95,000	Yes	5AC
L-80	80,000	95,000	95,000	Yes	5AC
C-95	95,000	110,000	105,000	?	5AC
P-105	105,000	135,000	120,000	No	5AX
P-110	110,000	140,000	125,000	No	5AX

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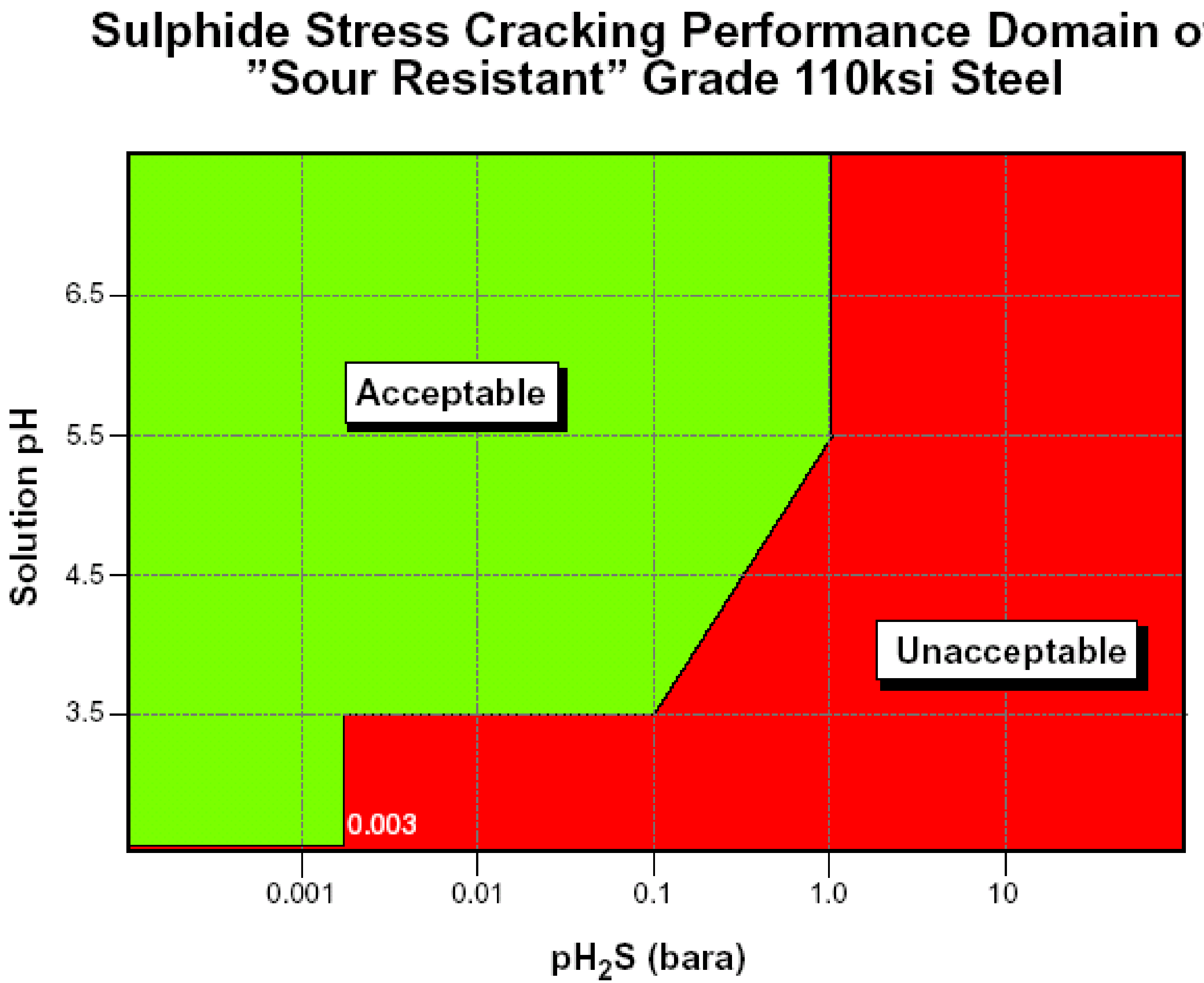
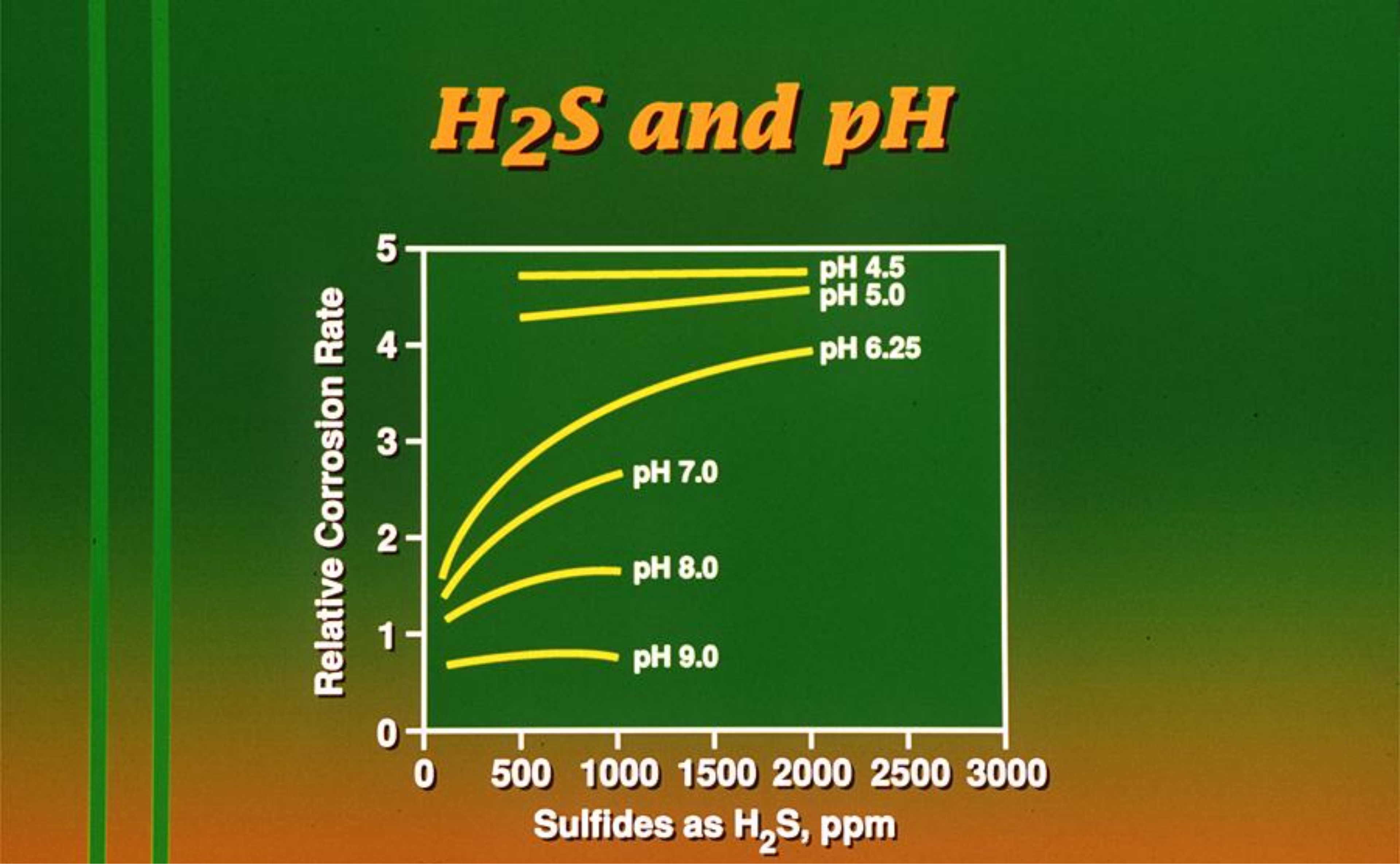
Domain Diagram for C110



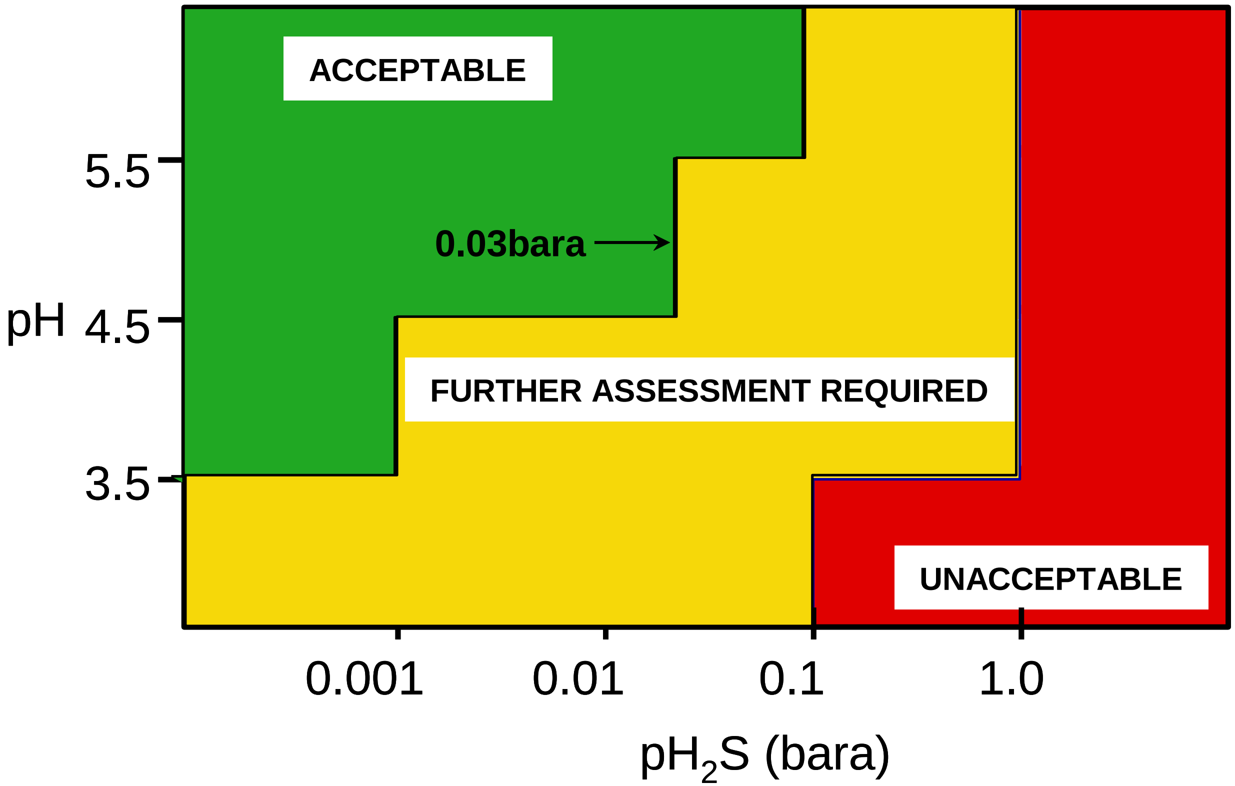
Hydrogen Sulfide Corrosion

- $Fe + H_2S + H_20 \leftarrow\rightarrow FeS_x + H_2 + H_2O$
- FeS - cathode to steel: accelerates corrosion
- FeS is a plugging solid
- Damage Results
  - Sulfide Stress Cracking
  - Blistering
  - Hydrogen induced cracking
  - Hydrogen embrittlement



H_2S corrosion is minimized by sweetening the gas (knocking the H_2S out or raising pH.

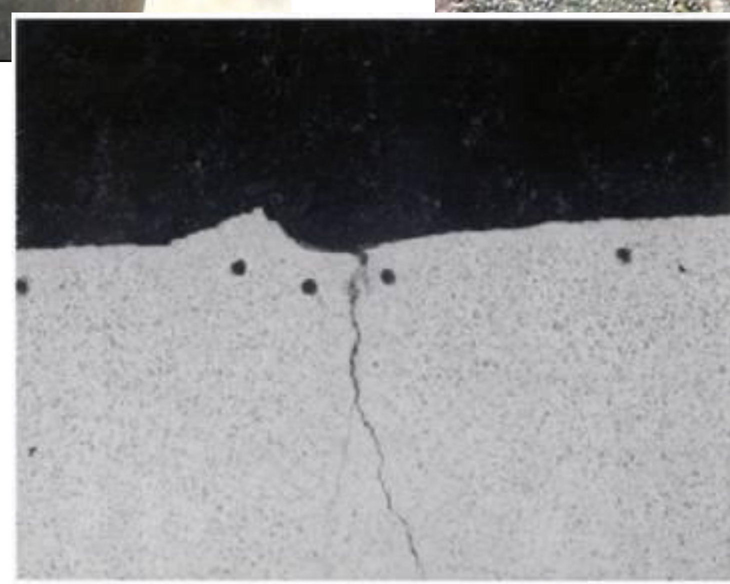
Domain Diagram for Super 13Cr



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

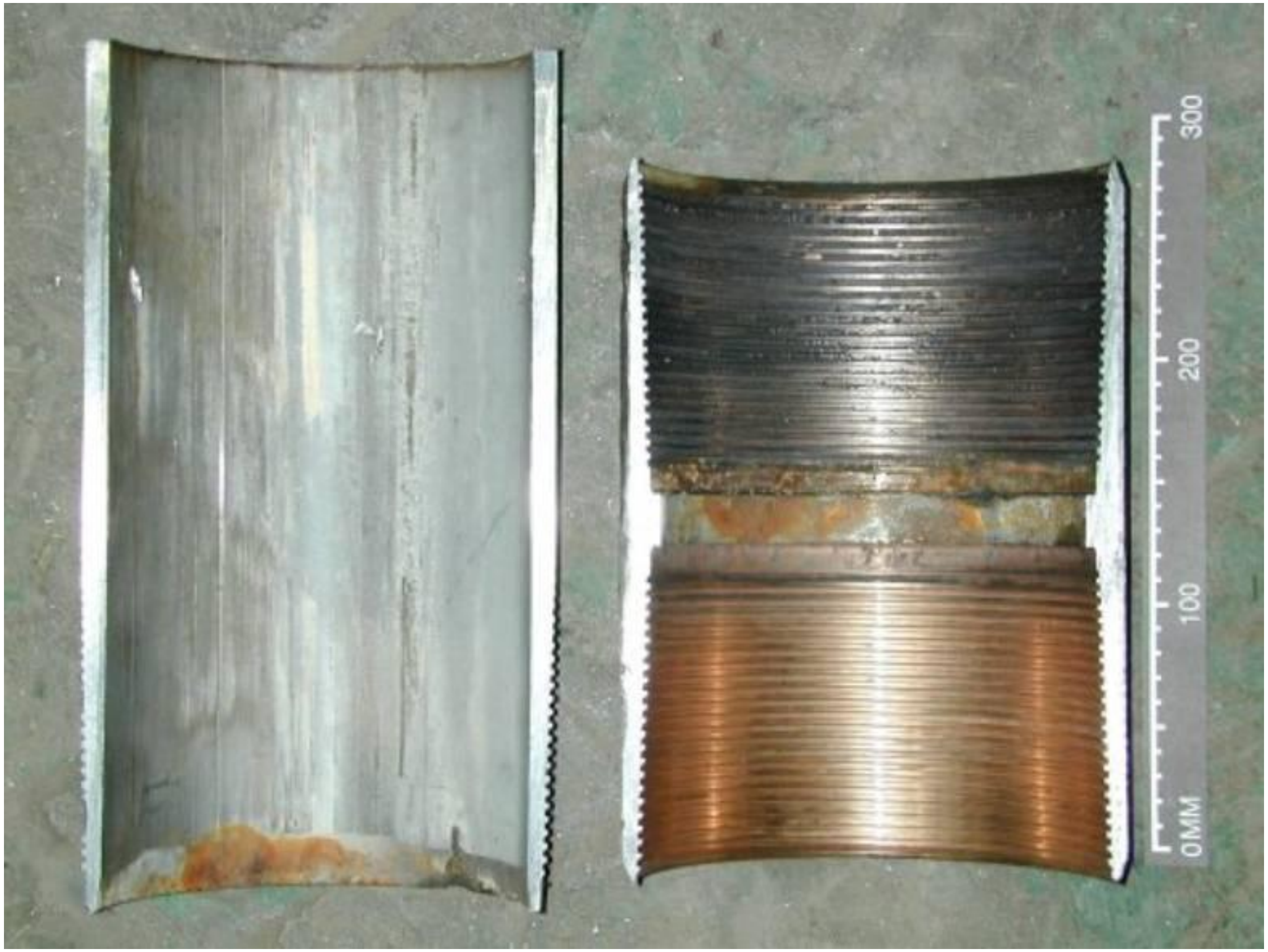
Crevice Corrosion

- **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.

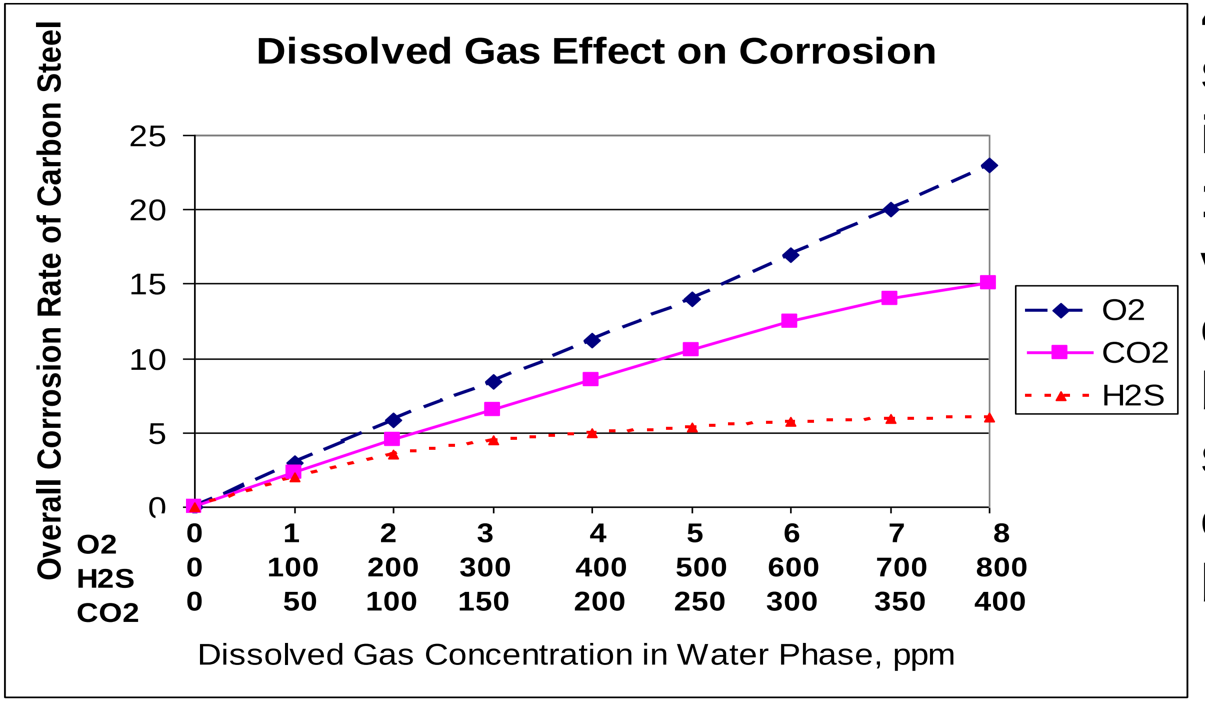


Crevice Corrosion

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

O_2 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 O_2 limit for seawater in carbon steel injection tubulars.
13Cr is CO_2 resistant but very susceptible to pitting corrosion in aerated brines. 5 ppb O_2 is suggested as a limit, but even these levels have not been confirmed.

Oxygen in Surface Waters

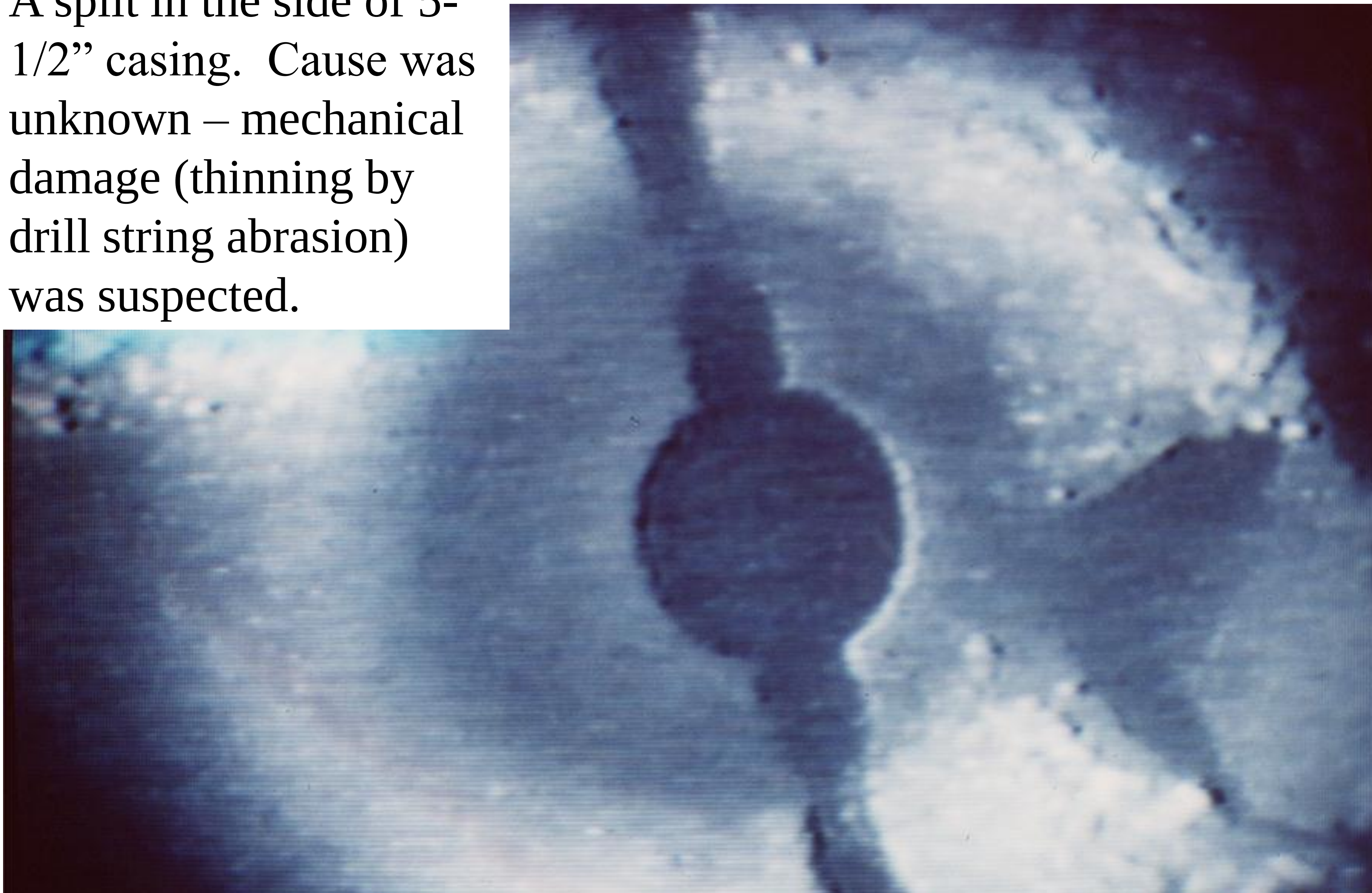
- 32ºF - 10 ppm (saturation)
- 212ºF - 0 ppm

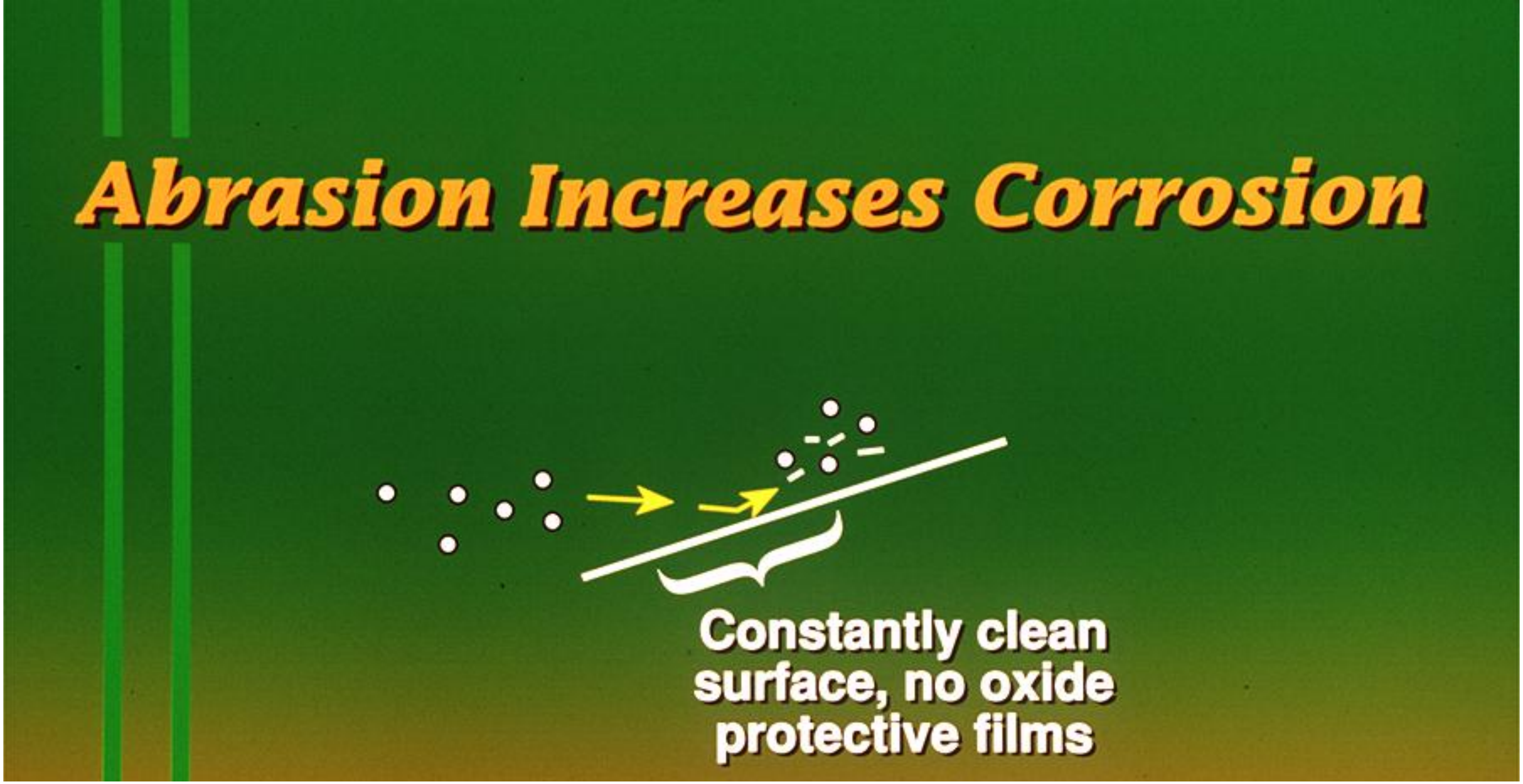
$$\text{ppm } O_2 = 10 - 0.055\,(T - 30^{\circ})$$

T = water system temperature, ºF

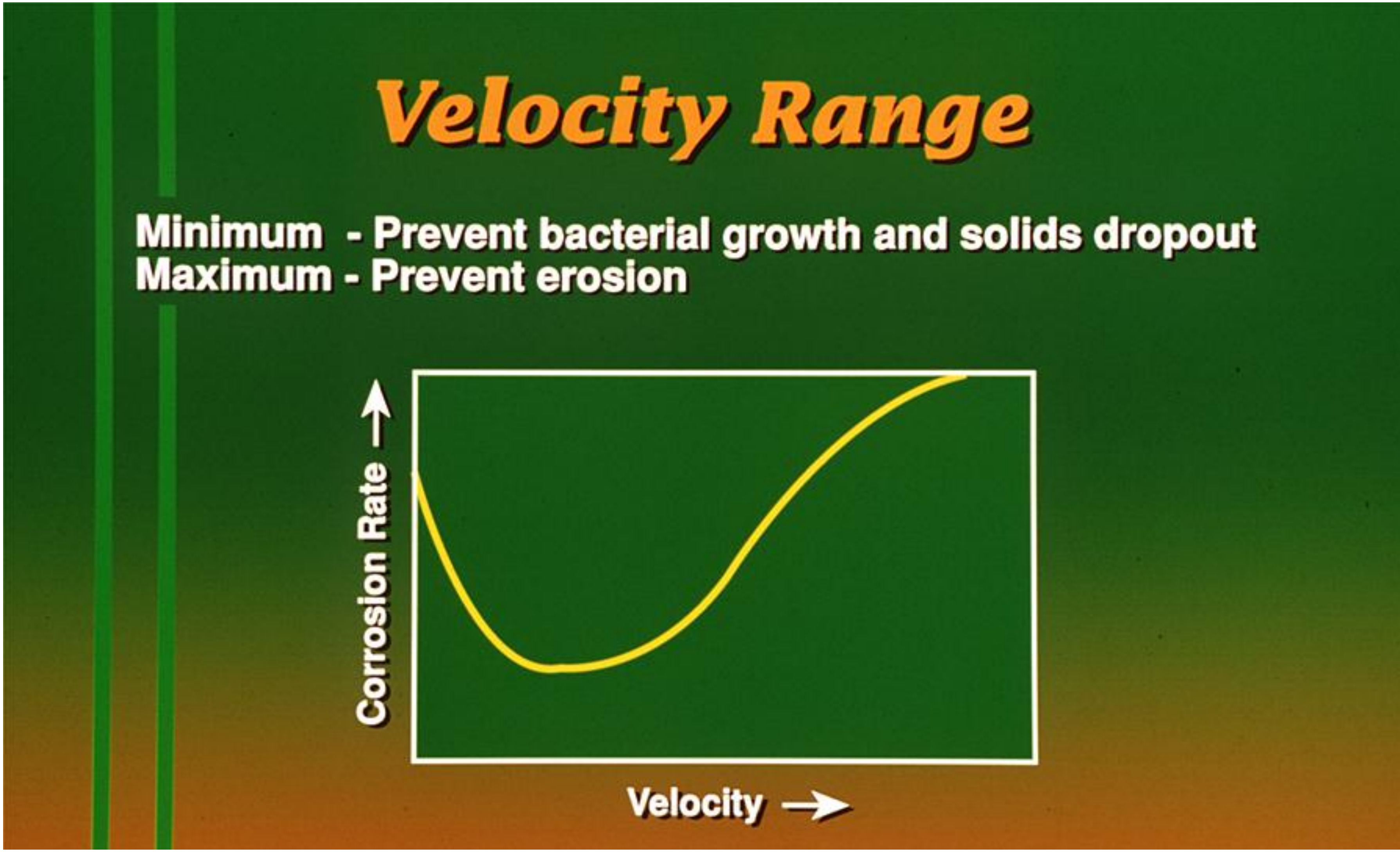
Wear Damage

A split in the side of 5-1/2” casing. Cause was unknown – mechanical damage (thinning by drill string abrasion) was suspected.



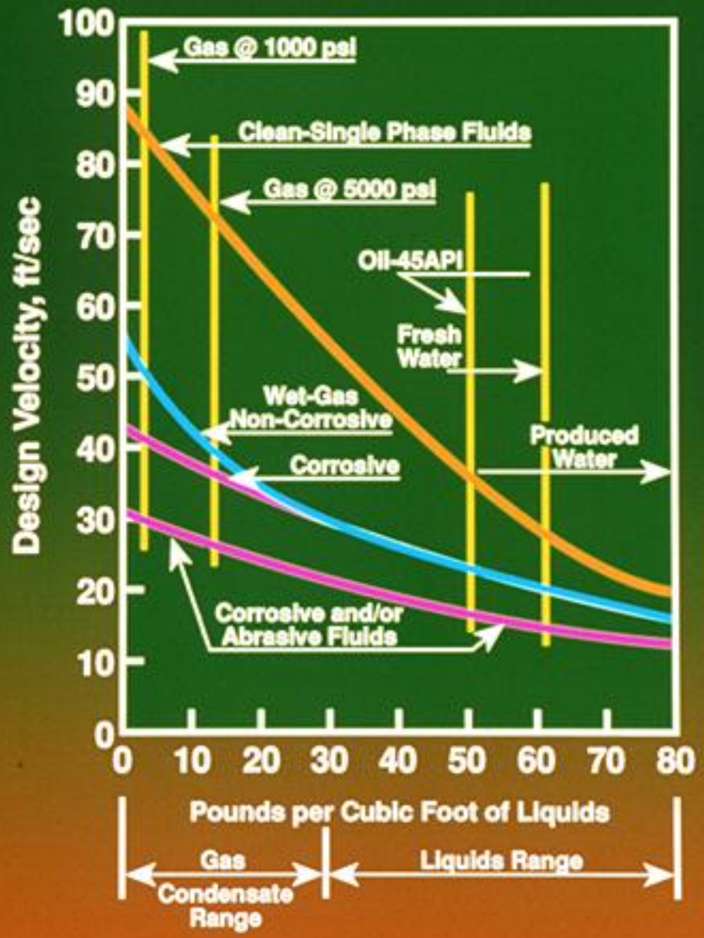


Abrasion by solids, gas bubbles or liquid droplets may significantly increase corrosion by continuously removing the protective oxide or other films that cover the surface following the initial chemical reaction.



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 CO_2 or other gas, increasing corrosion. Minimum rates are about 3.5 ft/sec for clean fluids.

Tubing Design Velocities



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 (density)$^{1/2}$

where: V_c = critical flow velocity, ft/sec

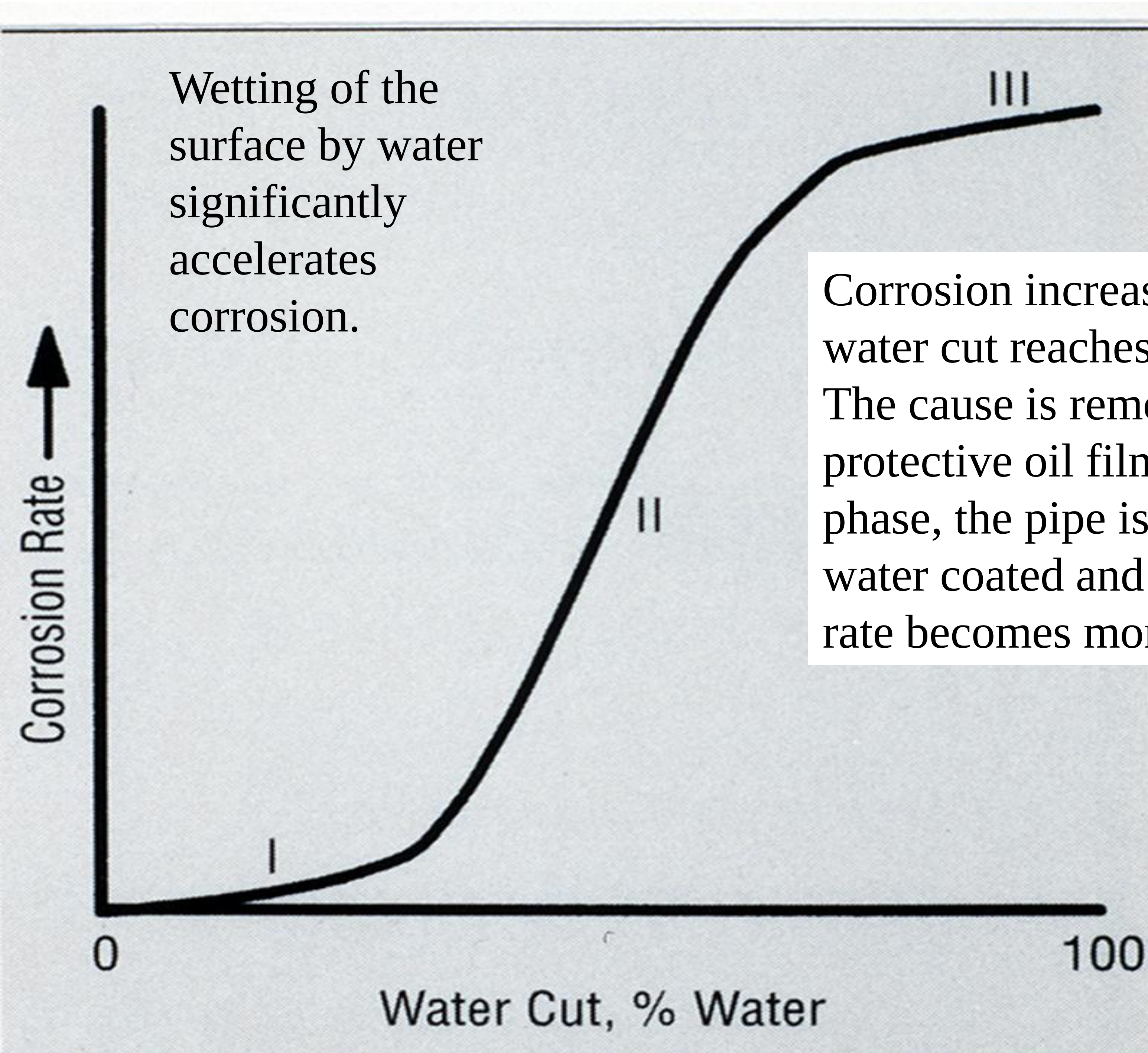
density = fluid density in g/cc

C = 100 for long life projects

C = 150 for short life project

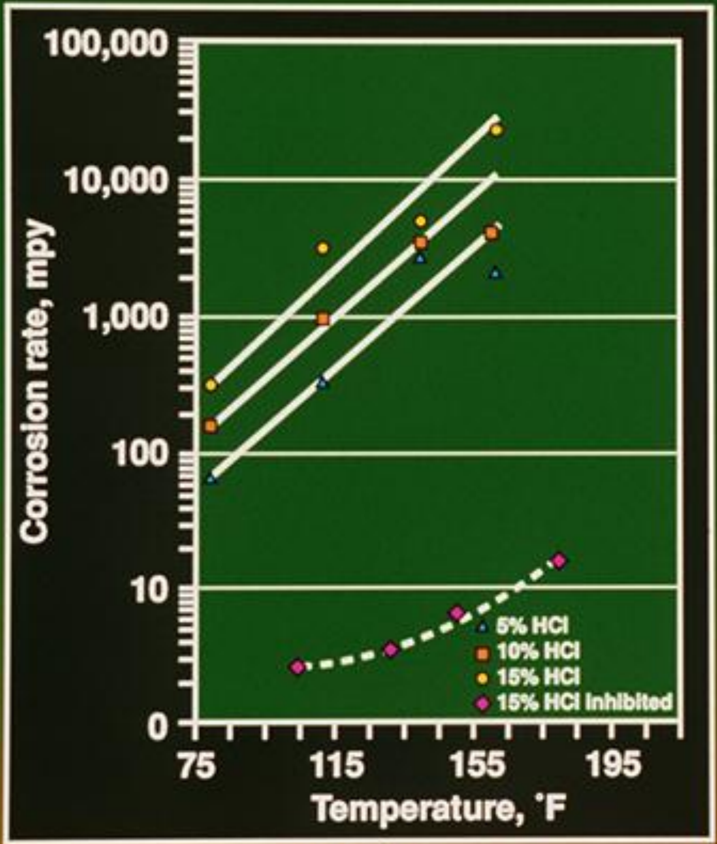
C = >200 for peak flows

Wetting of the surface by water significantly accelerates corrosion.

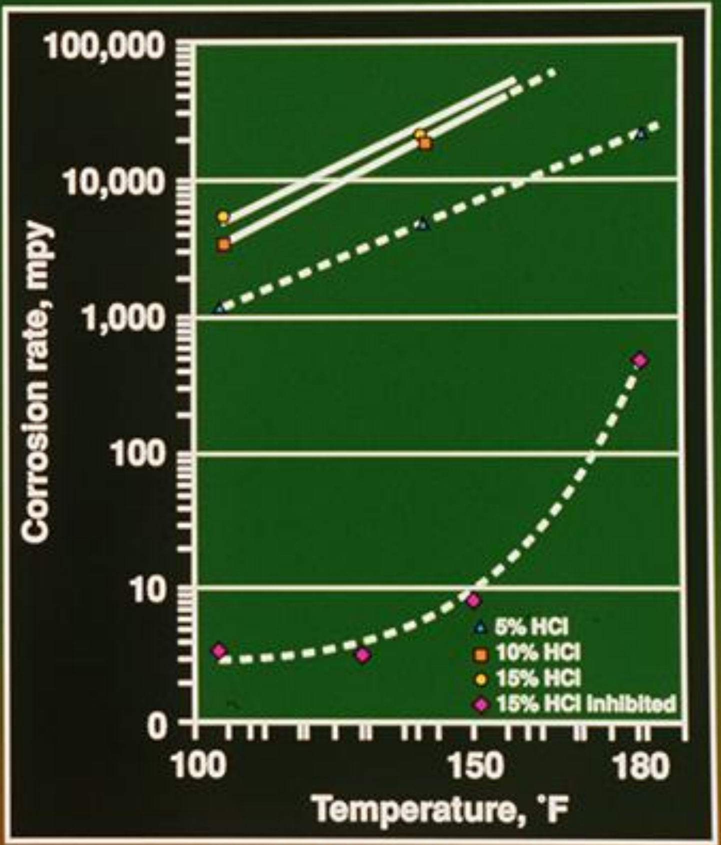


Corrosion increases after water cut reaches 10 to 20%. The cause is removal of the protective oil film. In the third phase, the pipe is completely water coated and corrosion rate becomes more constant.

Acid Corrosion Rates on Alloys



N-80



410-Stainless

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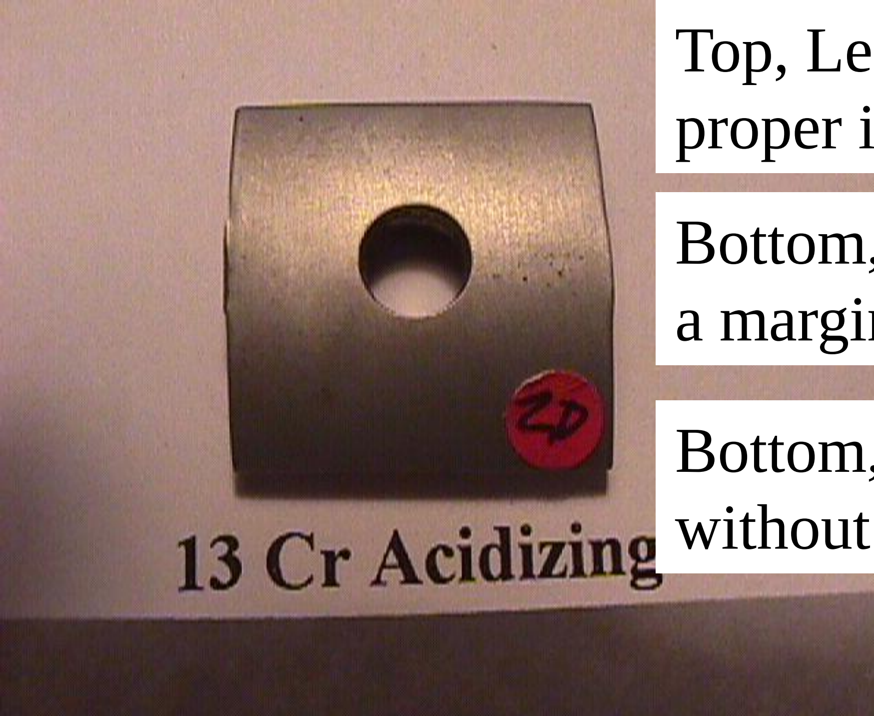
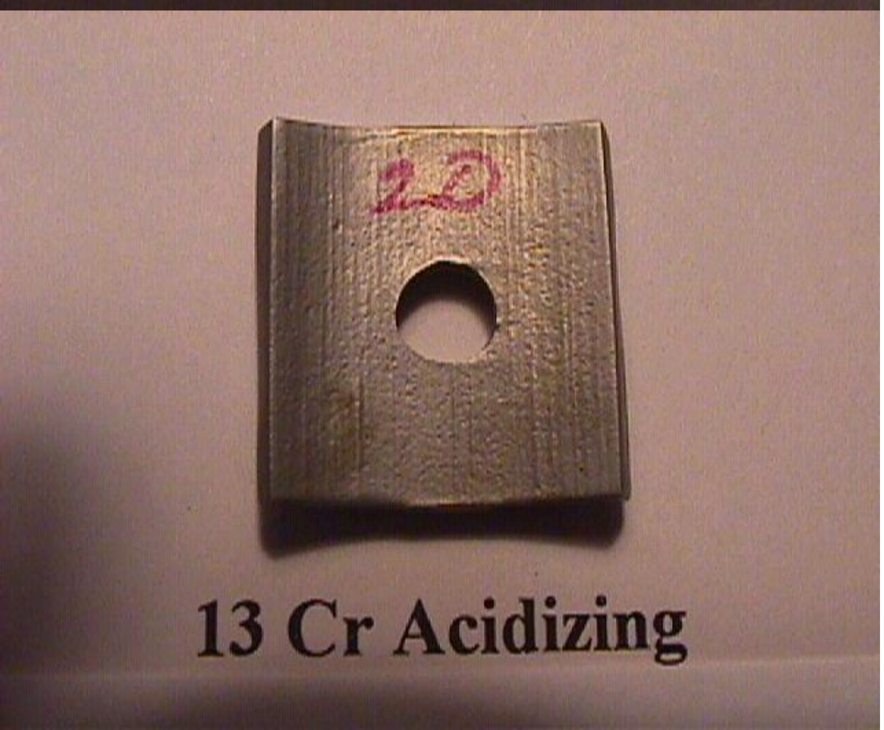


Top, Left: Chrome pipe after acidizing with the proper inhibitor and inhibitor intensifier.

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.

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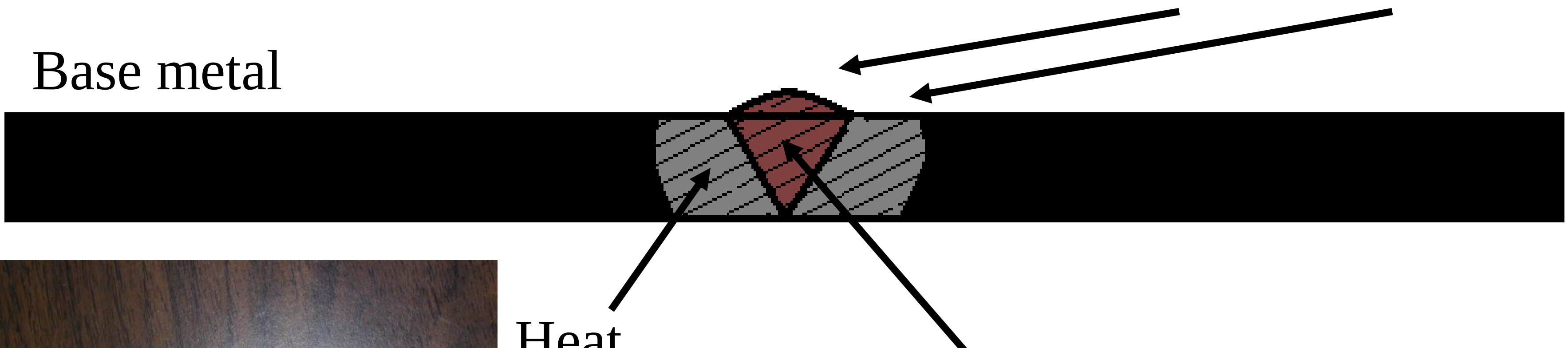
Welds

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



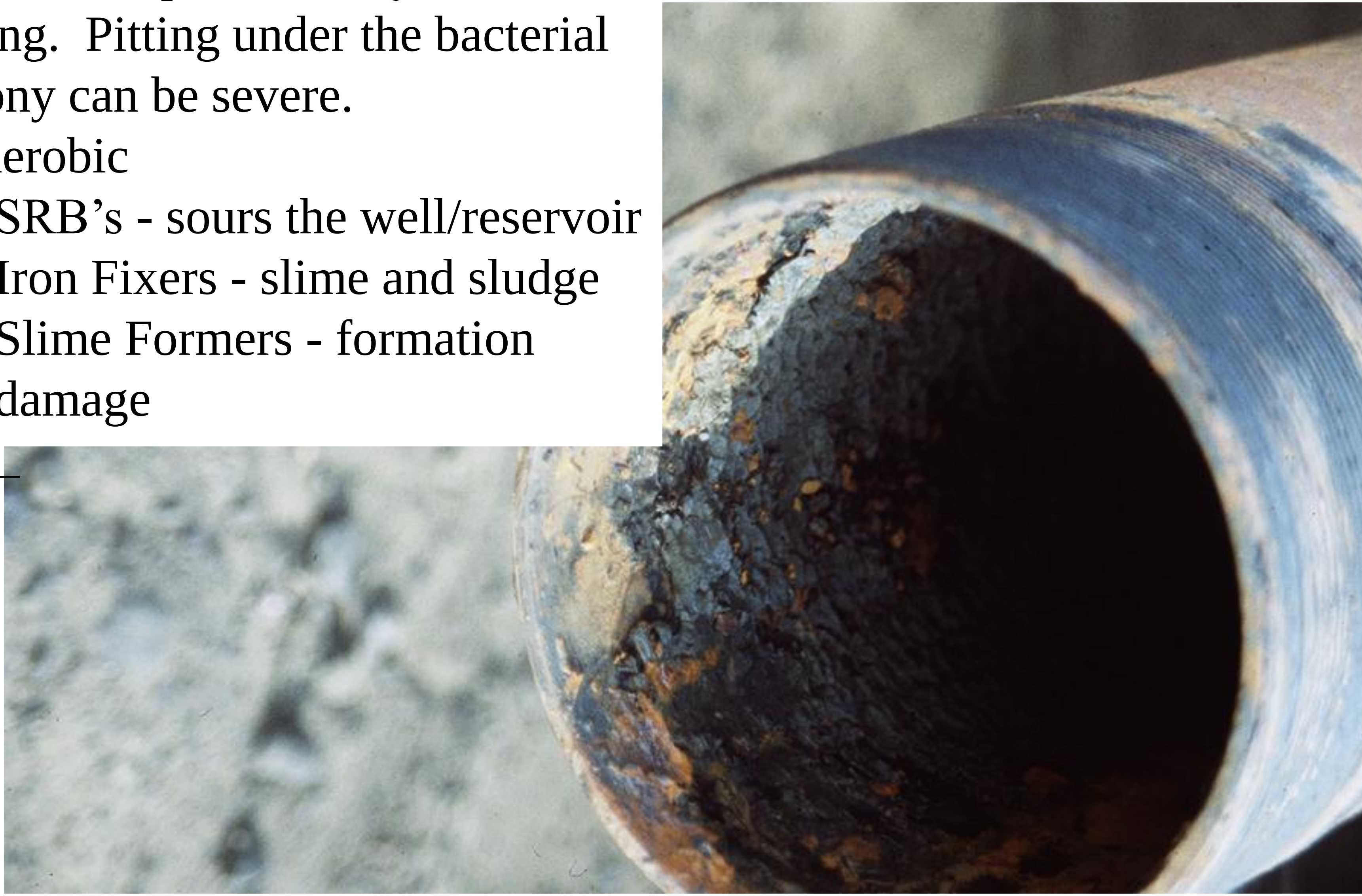
Heat affected zone

Weld metal (added and different from original base metal)

Bacterial deposits on injection tubing. Pitting under the bacterial colony can be severe.

Anaerobic

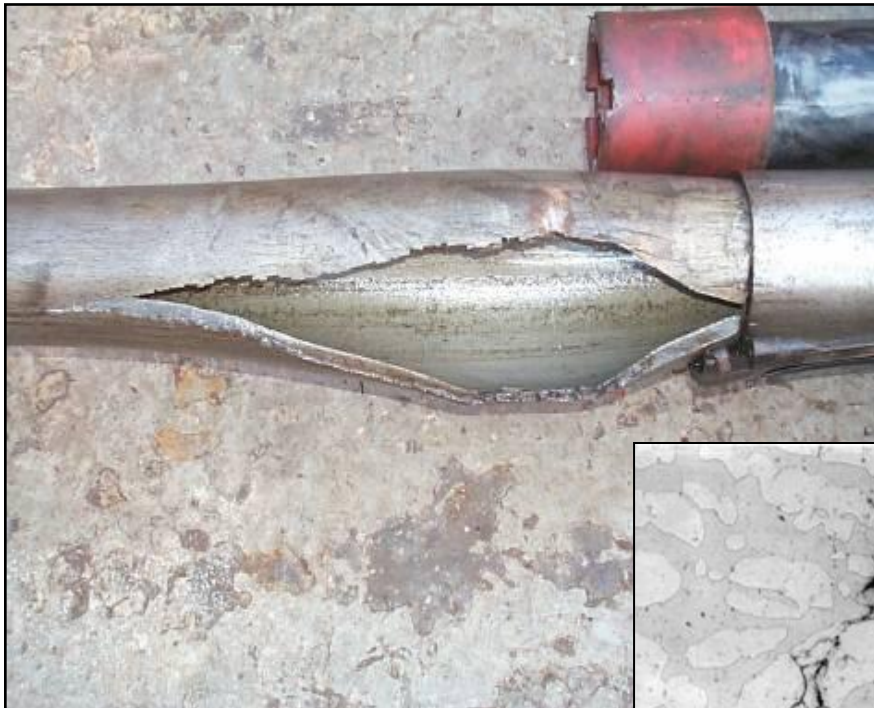
- SRB’s - sours the well/reservoir
- Iron Fixers - slime and sludge
- Slime Formers - formation damage
-

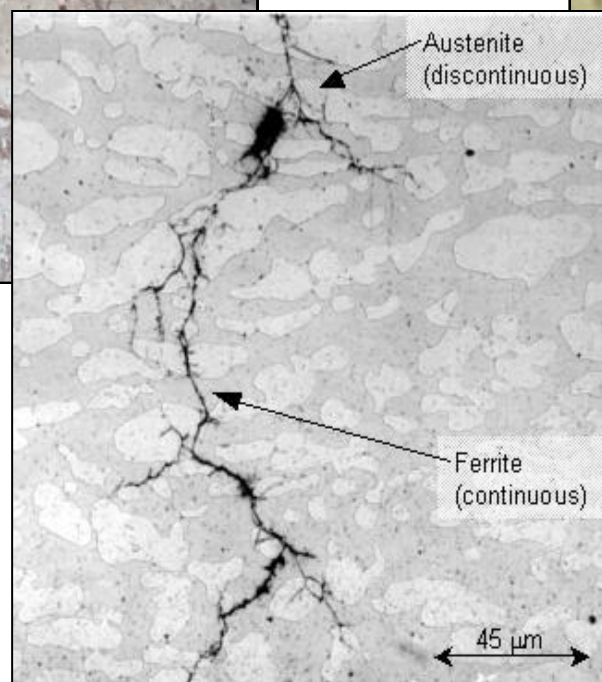


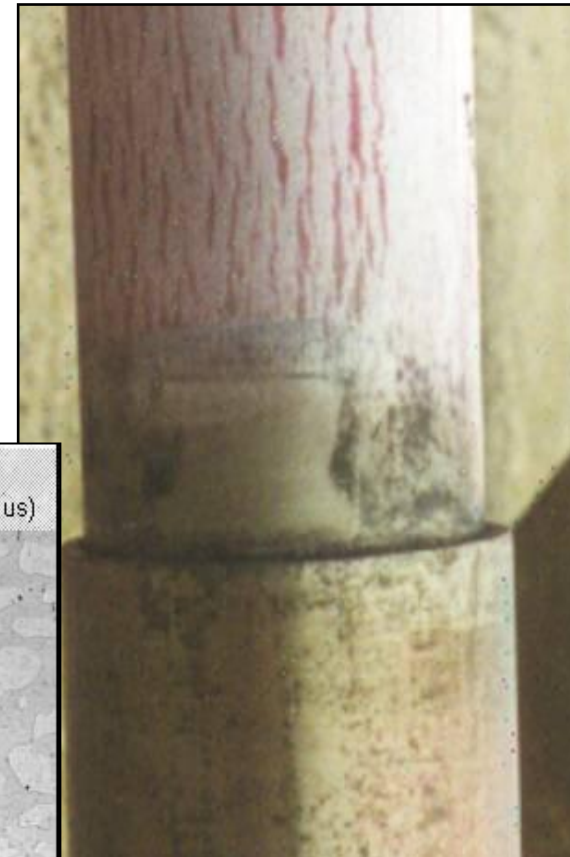
Sulfate Reducing Bacteria

- SRB’s anaerobic bacteria
  - colony growth most numerous
  - low pH below colony
- Generates high H_2S concentration in small area
- worst where velocity < 3-1/2 fps

Erskine – Failure of 25Cr Duplex SS





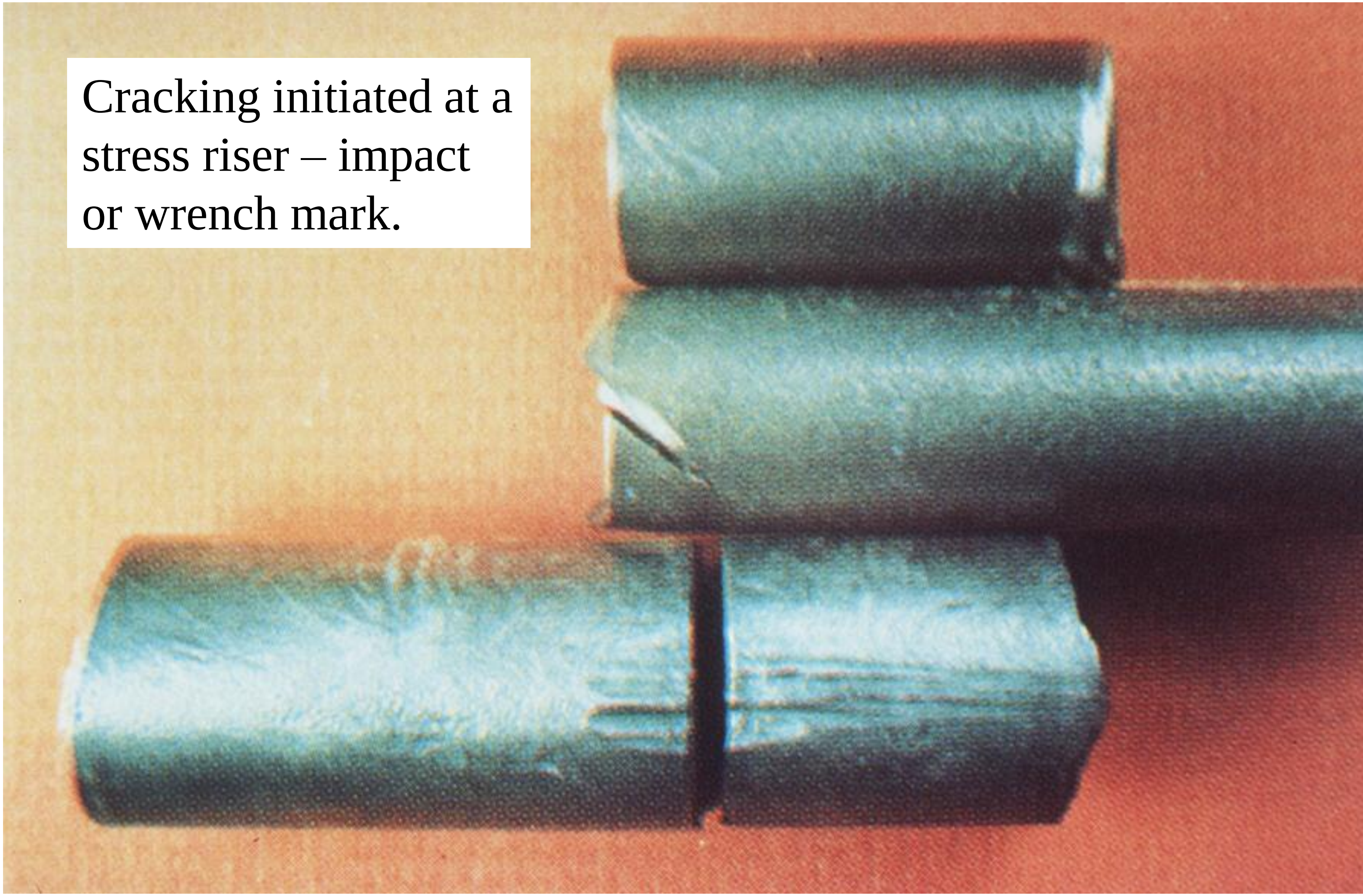


Many of the super alloy failures have been linked backed to the brines used for completions.

Source – BP Corrosion – John Alkire and John JW Martin

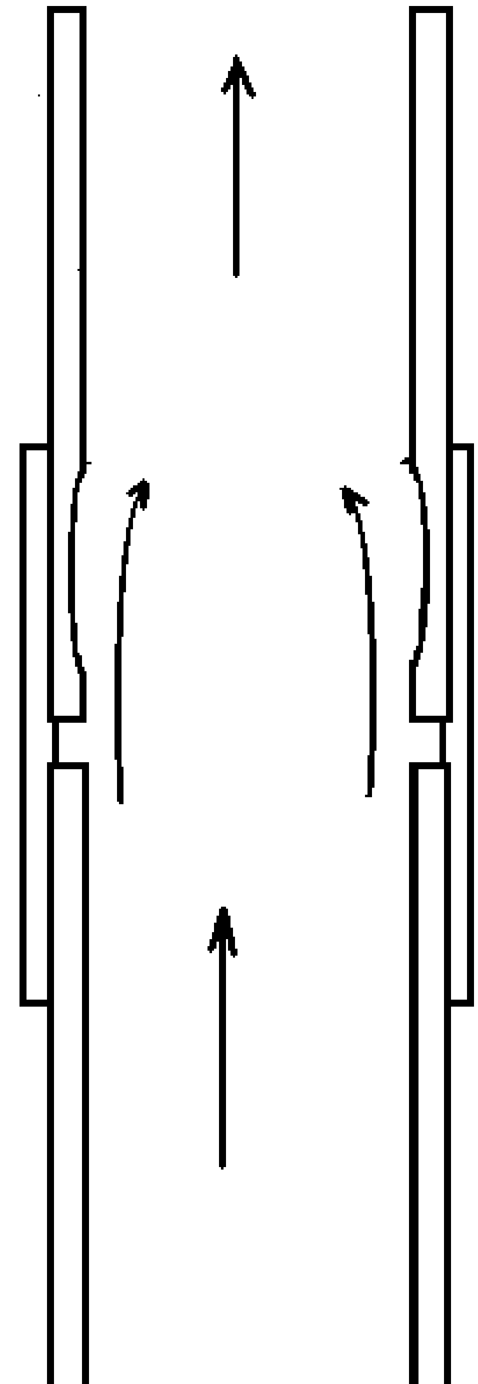
High Island – Failure of 13Cr Alloy



Cracking initiated at a stress riser – impact or wrench mark.

CO_2 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)


1742.4 '
211 F
11:41:36
7.0 Casing Collar


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

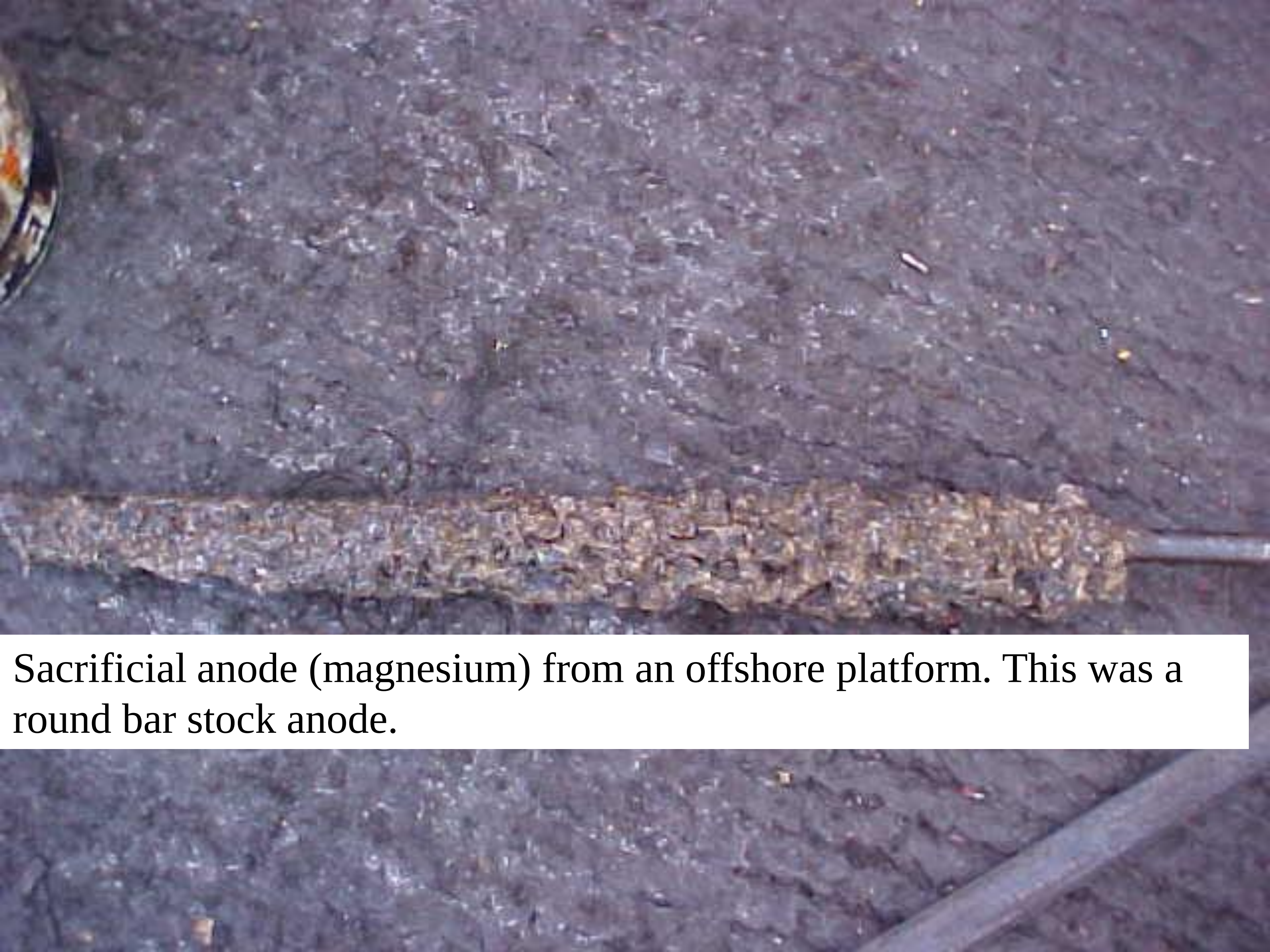
7. stainless steel (300 series)

8. lead

9. brass and bronze

10. Inconel

11. Hasteloy C 276

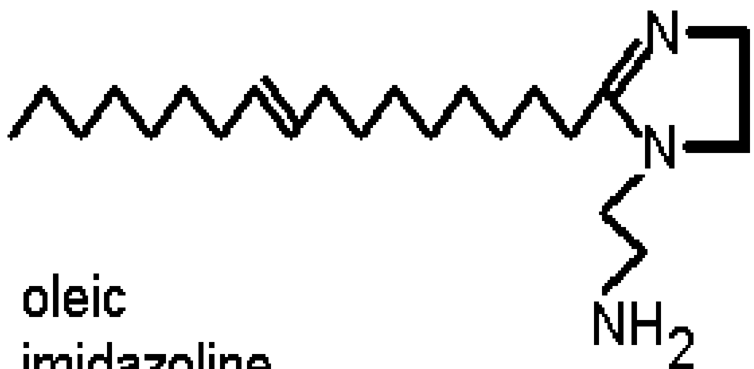


Sacrificial anode (magnesium) from an offshore platform. This was a round bar stock anode.

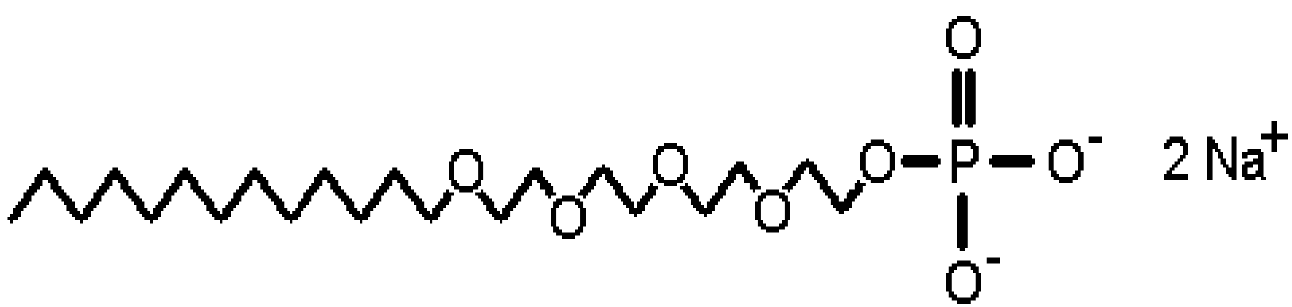
Controlling Corrosion

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

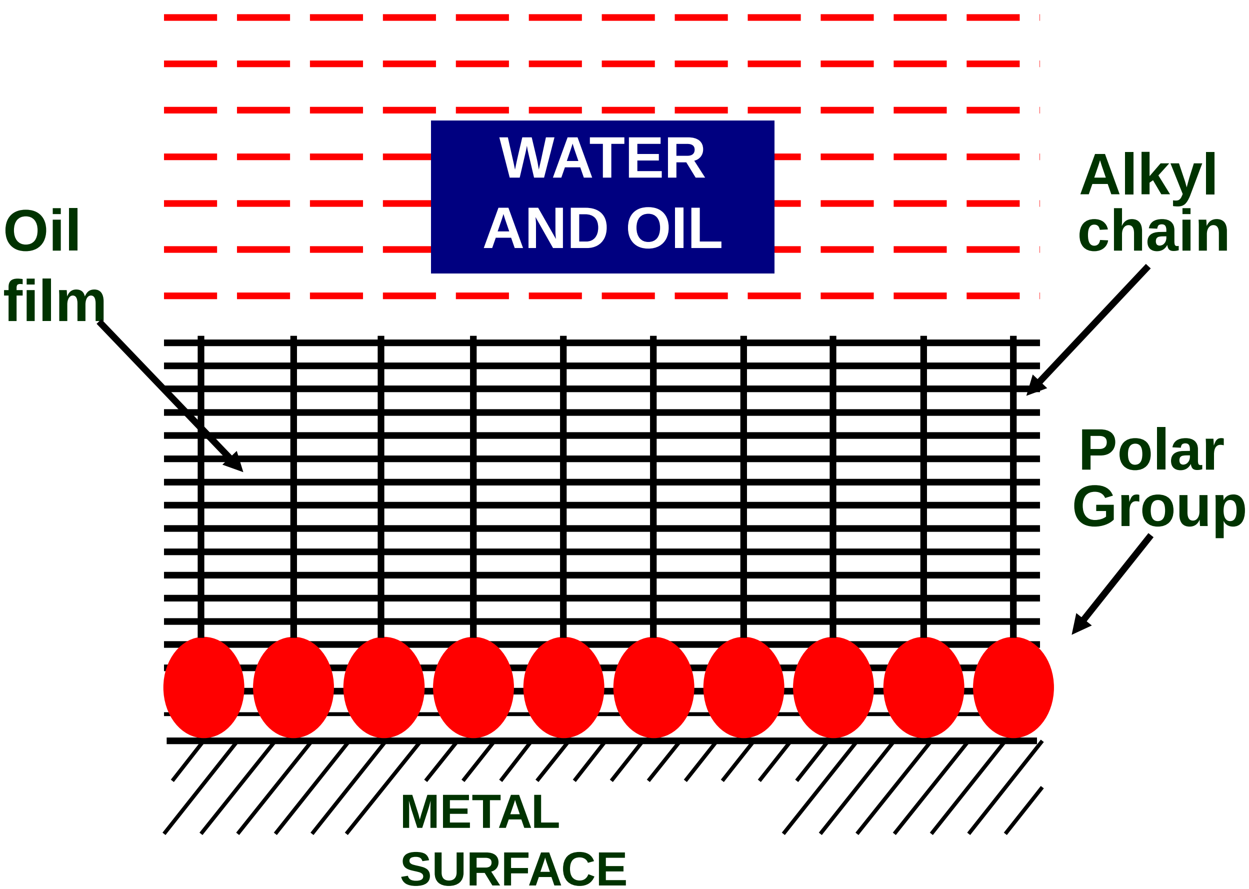


oleic
imidazoline



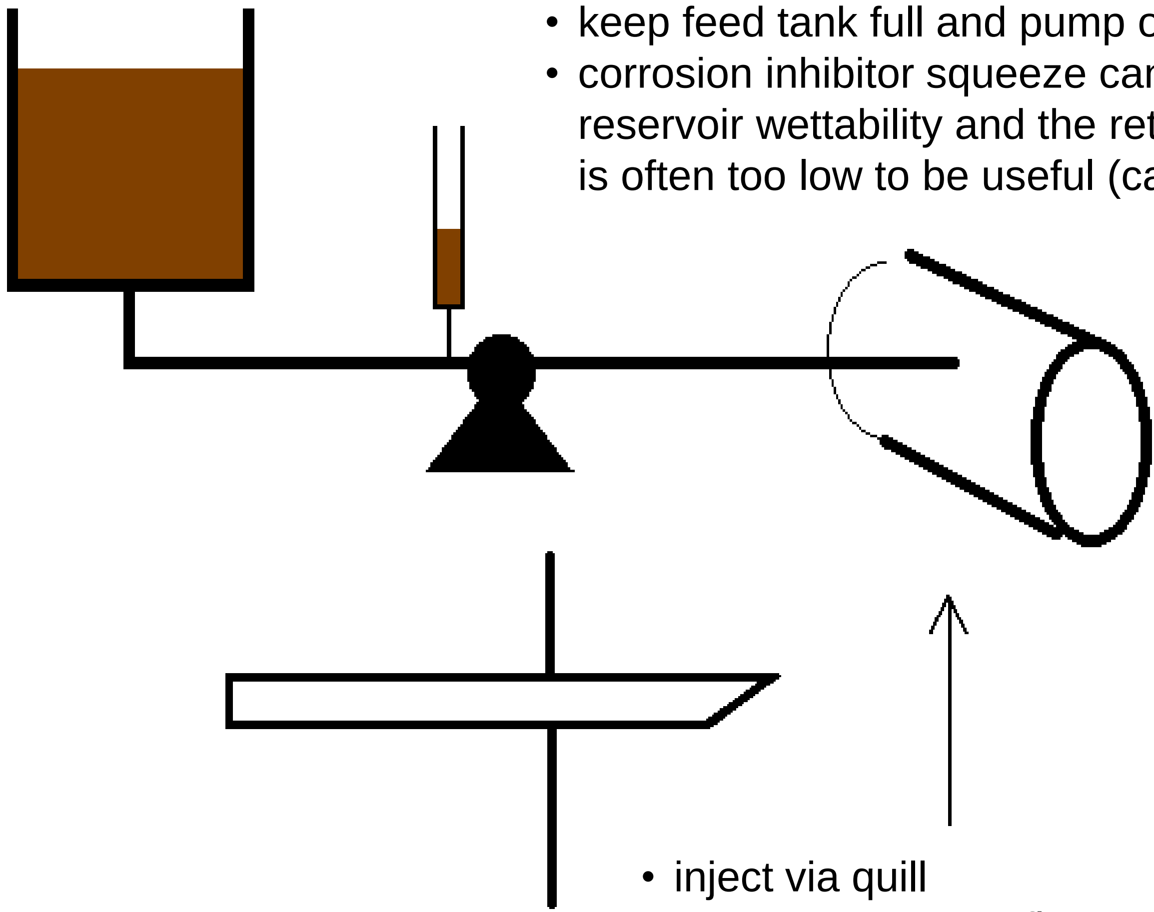
alkyl ethoxy phosphate

How do Corrosion Inhibitors Work?



Inhibitor Deployment

- 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)



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