Galvanic Corrosion
Dealloying Corrosion
Velocity Phenomena

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Galvanic, Dealloying and Fluid Velocity Corrosion Learning Objectives

- Understand the mechanism of galvanic corrosion
  - ♦ Does “galvanic corrosion” always involve different metals?
  - ♦ Is corrosion essentially always galvanic corrosion?
  - ♦ Cathodic protection
- Identify dealloying corrosion
- Understand the mechanism of the effects of fluid flow on corrosion
  - ♦ Flow-accelerated corrosion (FAC)

Specific Forms of Corrosion

1. General or uniform corrosion
2. Galvanic corrosion
3. De-alloying corrosion
4. Velocity phenomena - erosion corrosion, cavitation, impingement, fretting and FAC
5. Crevice corrosion

(Items 2–5: Macro Localized Corrosion)

6. Pitting corrosion
7. Intergranular corrosion
8. Corrosion fatigue
9. Stress corrosion cracking

(Items 6–9: Micro Localized Corrosion)

Microbiological activity can affect all of the above

Galvanic Corrosion

Galvanic Corrosion

- History
- Mechanism
- LWR Case Study Examples
  - Condensers
  - Sensitization of stainless steel

Galvanic Corrosion

- If you could fabricate a component from only one alloy, galvanic corrosion would not be a problem. Or would it?
  - Different temperatures
  - Cold work
  - Welding
  - Flow
  - Anything that can locally change E can produce a galvanic cell!
- Galvanic corrosion is caused by the diversity of materials and environments!

Galvanic Corrosion

- Associated with the current of a galvanic cell consisting of:
  - ♦ Two or more dissimilar metals in contact in a single electrolyte

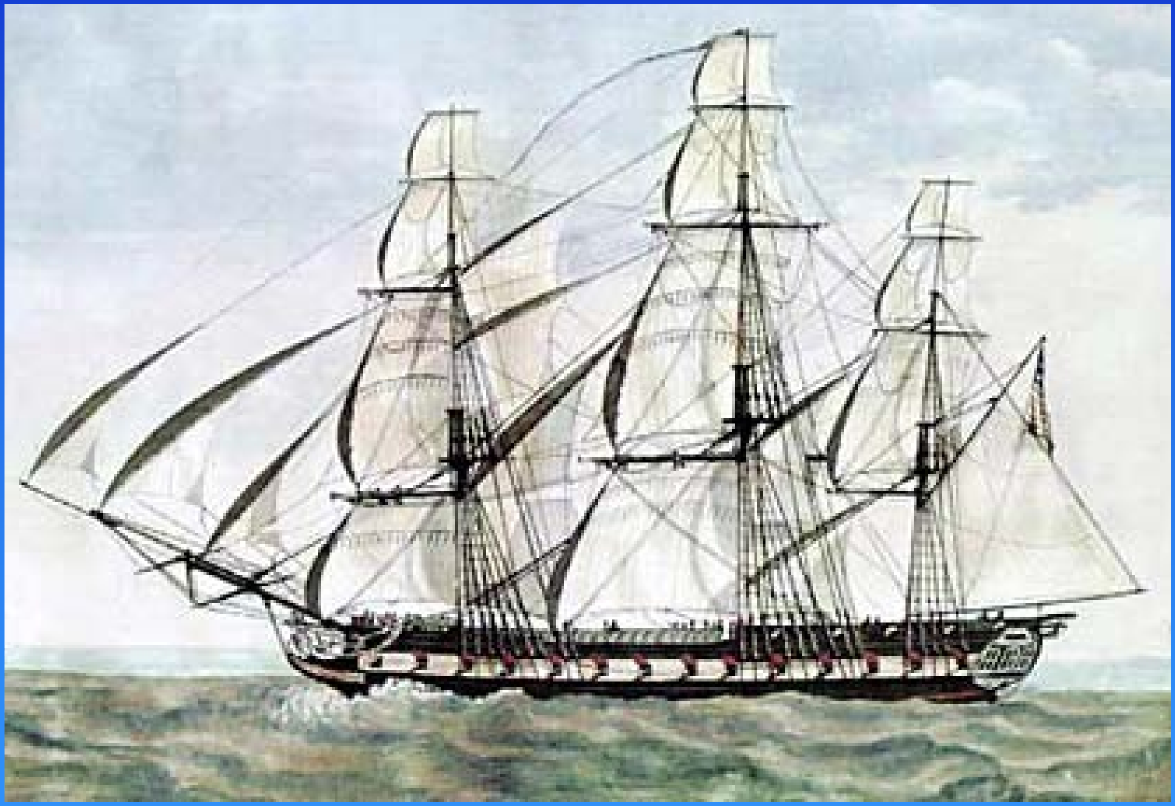
Or

  - ♦ One metal in two or more dissimilar electrolytes (concentration cells, temperature)

Galvanic Corrosion in 1761 HSM Alarm

- Deterioration of the hull of a wooden ships due to wood-boring bivalves, i.e., shipworms
- 1708 - Charles Perry suggests Cu sheathing
  - First rejected by Navy Board due to high cost and perceived maintenance difficulties
- Late 1750s - 1st experiments with Cu sheathing
  - Bottoms and sides of several ships' keels and false keels were sheathed with Cu plates
- 1761 - 32-gun frigate HMS Alarm operating in the Caribbean was ordered to have her entire bottom coppered (using iron nails) to eliminate shipworms

HMS Alarm




HMS ALARM
COPPER UNFAIR TO BARNACLES!
DOWN WITH Cu!
COPPER MADE US HOMELESS!
Cu

Shipworms and Their Art

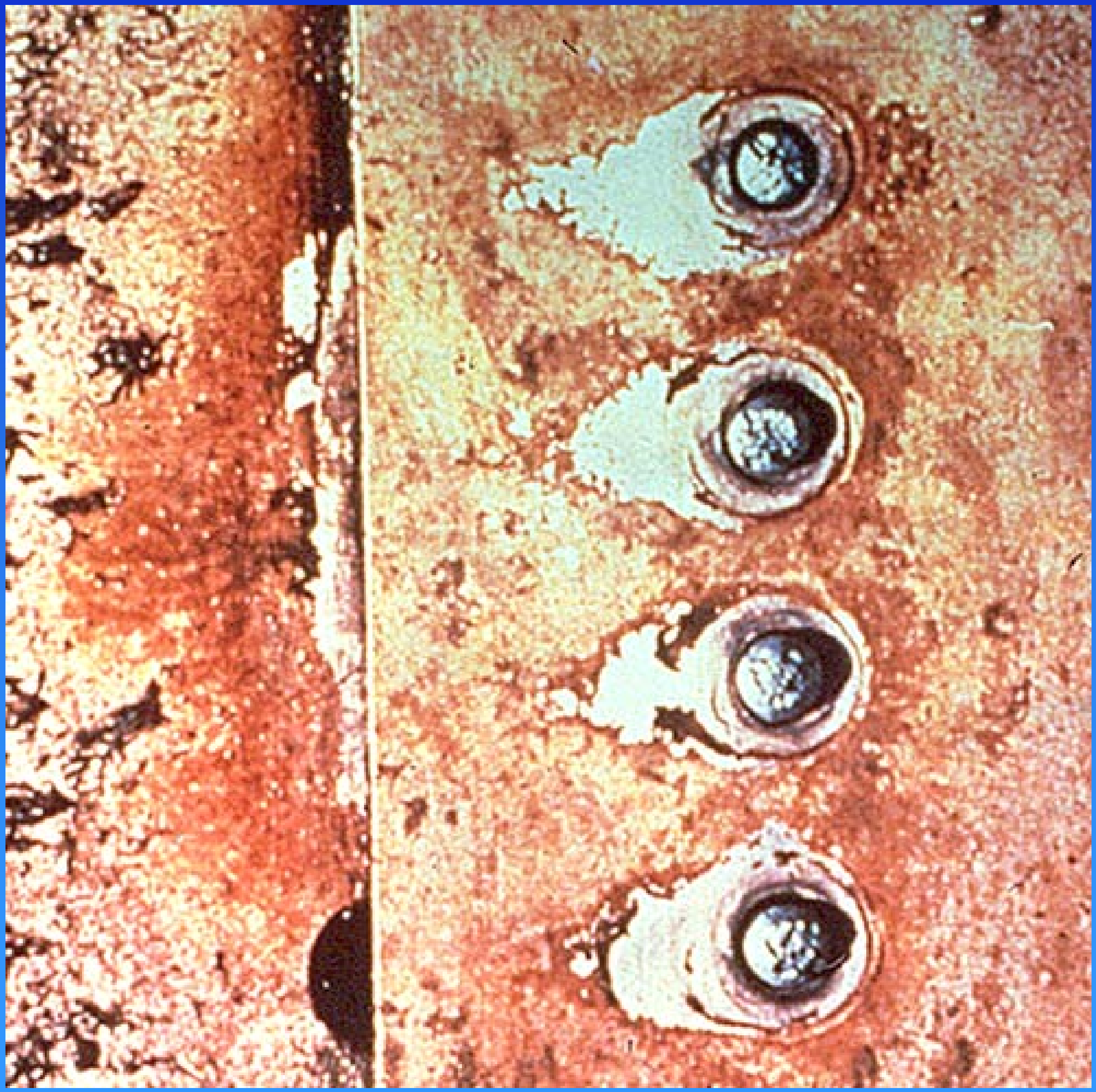
Teredos Navalis

Wood riddled with holes

British Admiralty Report - 1763

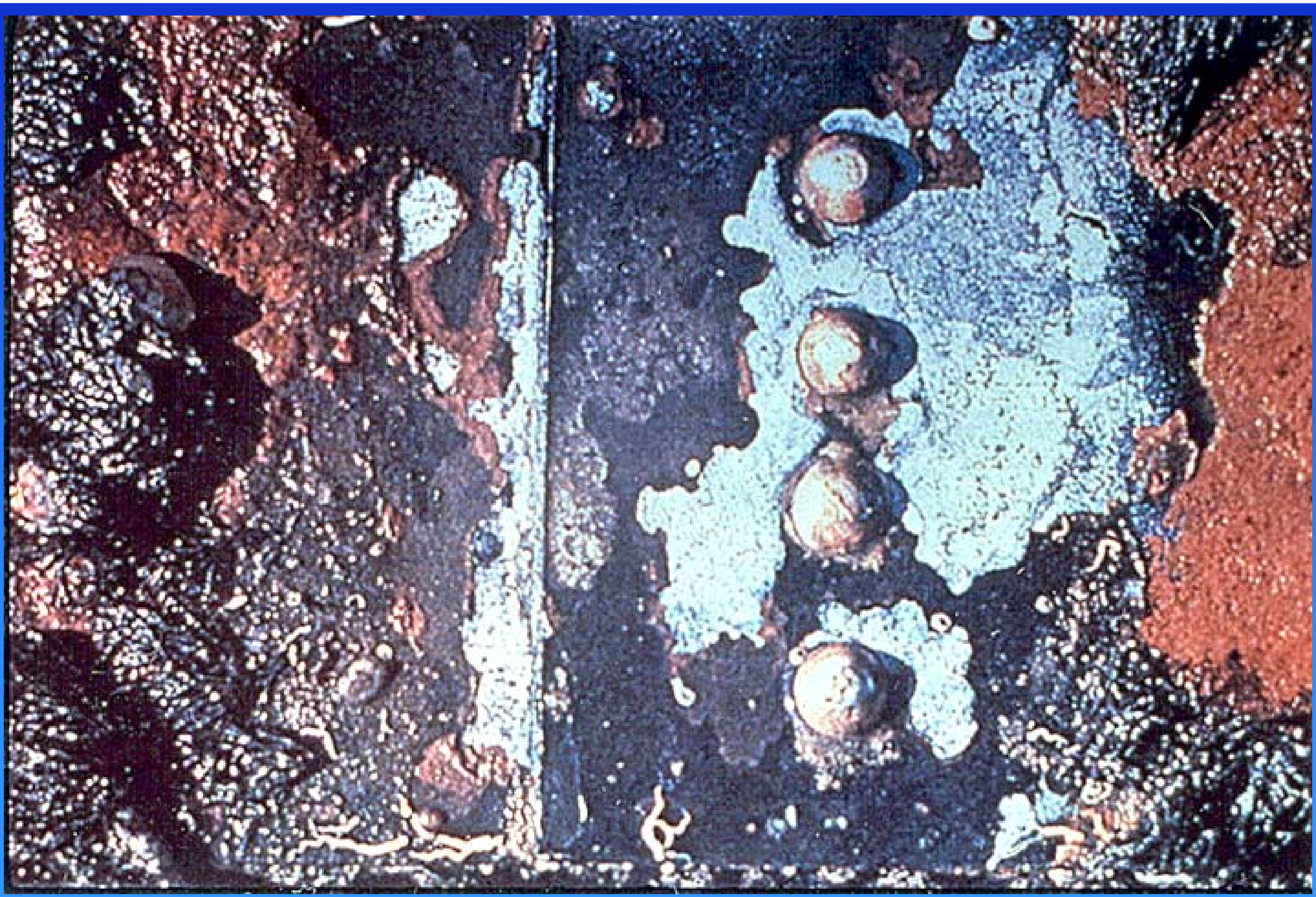
- First documented case of galvanic corrosion
  - ♦ Crew was “greatly surprised to perceive the effect copper had had upon the iron where the two metals touched.”
  - ♦ “Upon examination … nails and staples … were found to dissolved into a kind of rusty paste.”
  - ♦ “Except where brown paper … separated the two metals, the iron was preserved from injury.”
- HMS Alarm's copper was removed and was not replaced

Fe Rivets on Cu Plate



Large cathode to anode area ratio

Cu Rivets on Fe Plate



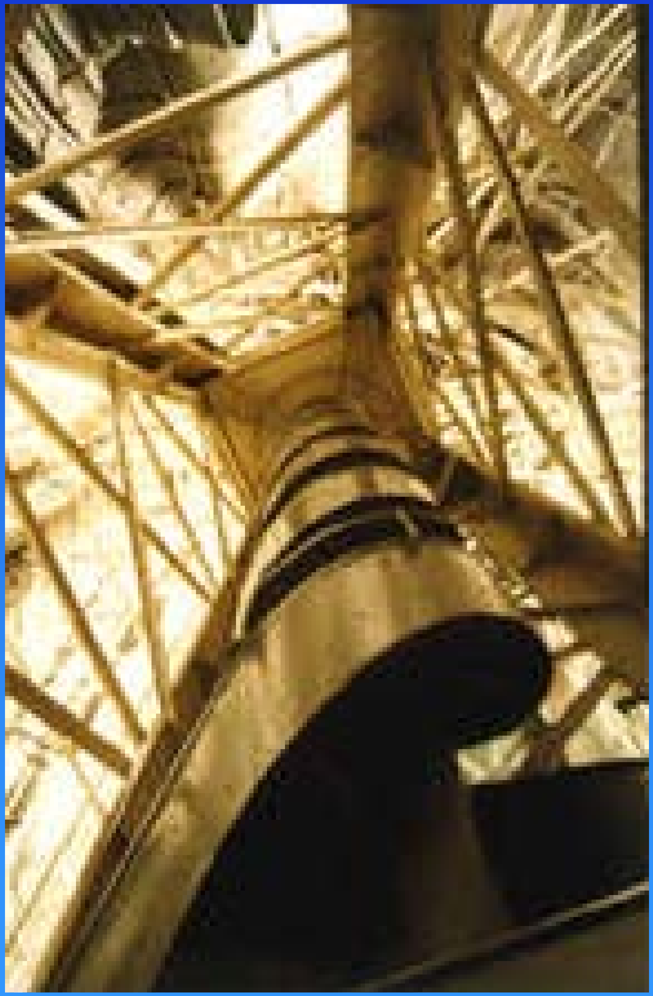
Small cathode to anode area ratio

Coppering of Entire British Fleet

- American War of Independence - Royal Navy coppers bottoms of the entire fleet
  - Mandated by declarations of war by France (1778), Spain (1779) and the Netherlands (1780)
  - Cu allowed the British navy to keep at sea for longer periods without the need for cleaning and repairs to the underwater hulls
- By 1781 – 393 navy ships are coppered
- 1783 – Hull bolt corrosion problems appear
  - Solved by "suitable alloy" (Cu – Zn) bolts
- 1786 – Re-bolted every ship in the Royal Navy

Galvanic Corrosion in 1886
Statue of Liberty

- **November 20, 1886 *Scientific American* article on the new Statue of Liberty:**
  - **"There are five dangers to be feared, namely, earthquake, wind, lightning, galvanic action and man."**
  - **To mitigate galvanic corrosion it was reported that "an ingenious insulation of the copper from the (iron) framework has been employed, the insulating material used being asbestos cloth soaked with shellac."**
  - **"In no place do the two metals come in contact with each other."**



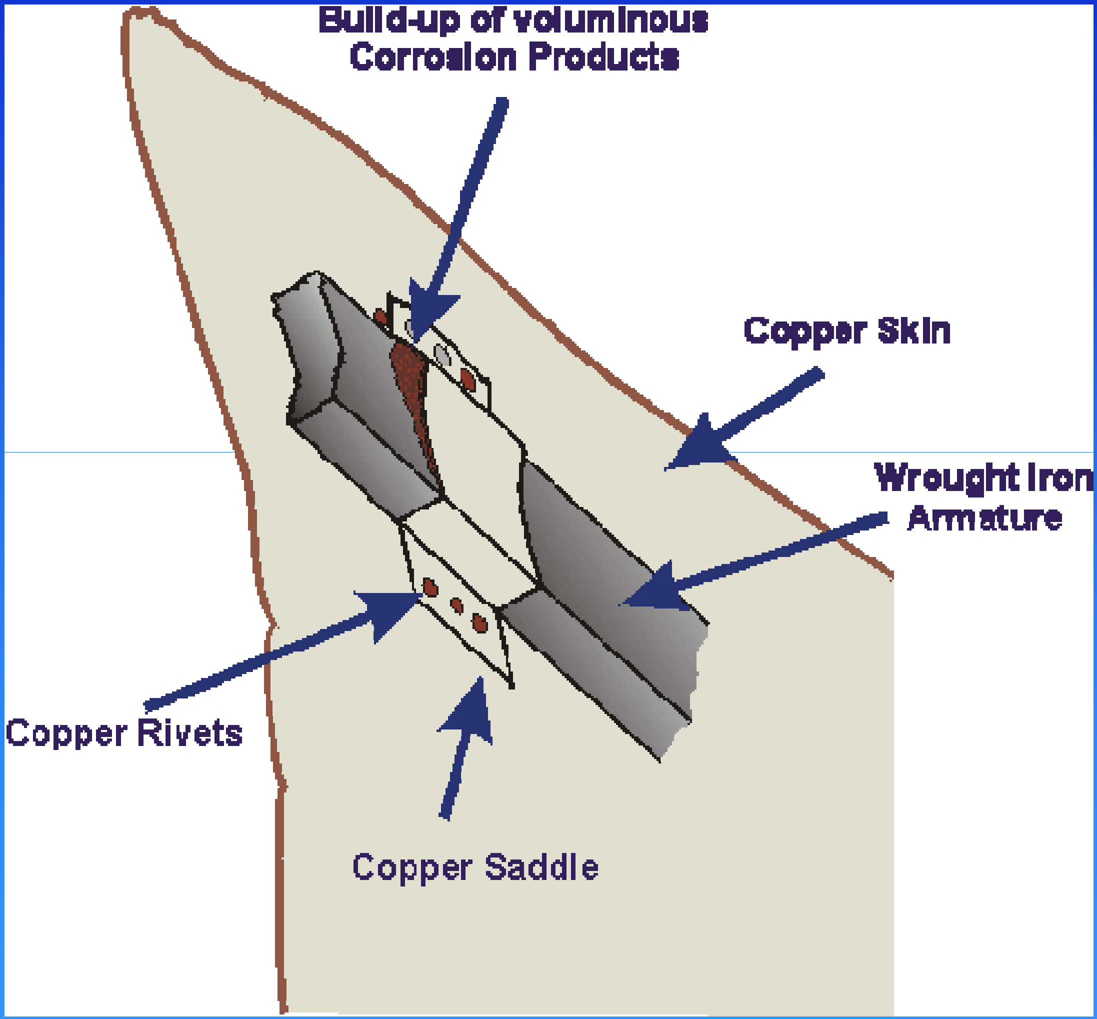
Not so "ingenious." It promoted galvanic corrosion!

Galvanic Corrosion in 1981 Statue of Liberty

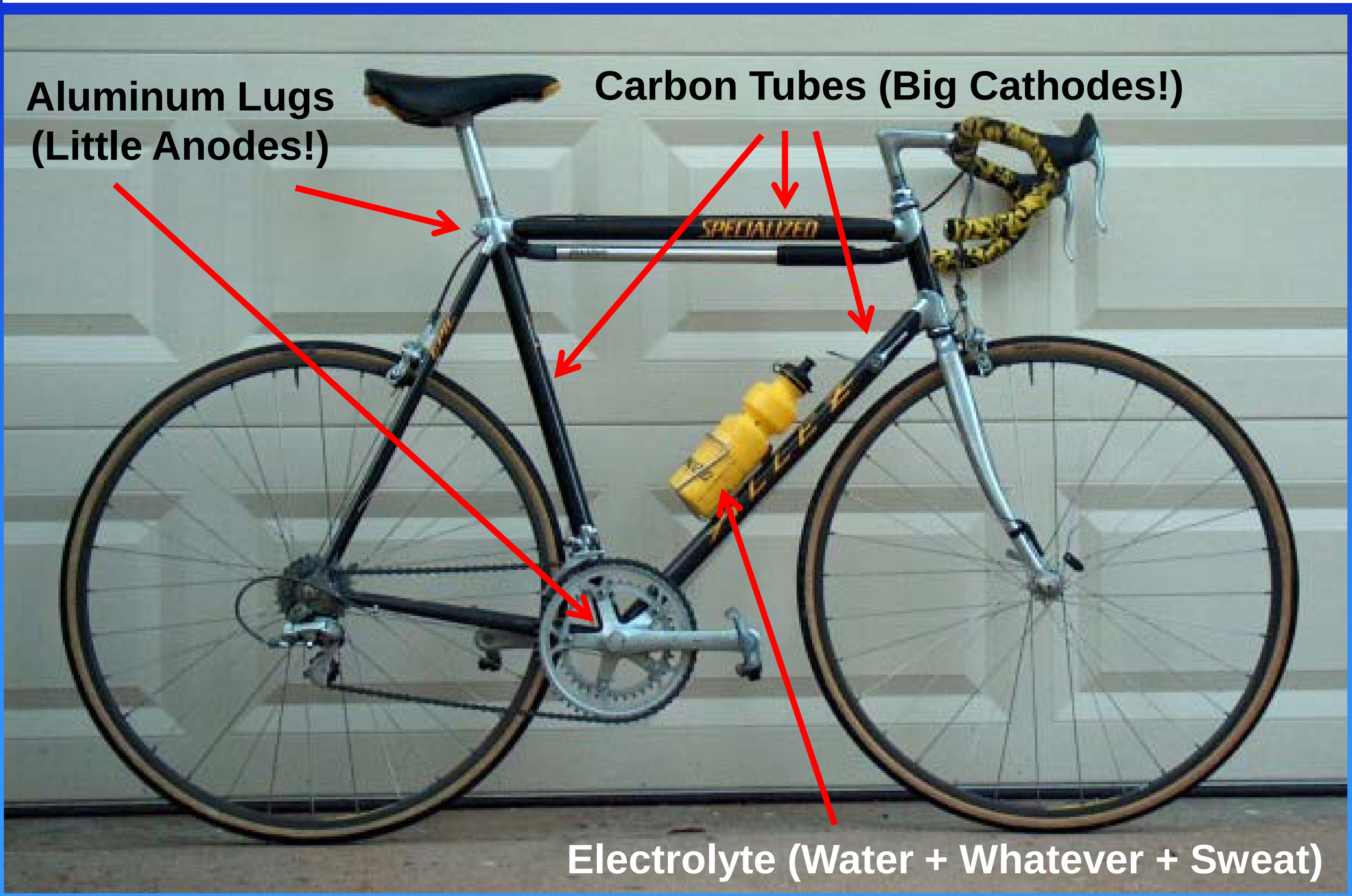
Statue's restoration in 1981 was required due to galvanic corrosion of the iron armature in contact with the copper skin

Insulating with asbestos cloths was only a temporary barrier that became porous with age and allowed the creation of a metallic and ionic circuit by wicking and capillary action

Mitigation: Fe structure was replaced with Type 316L stainless steel



Galvanic Corrosion in 1992
Specialized Allez Carbon Fiber Frame



Mitigation of Bottom Bracket Galvanic Corrosion

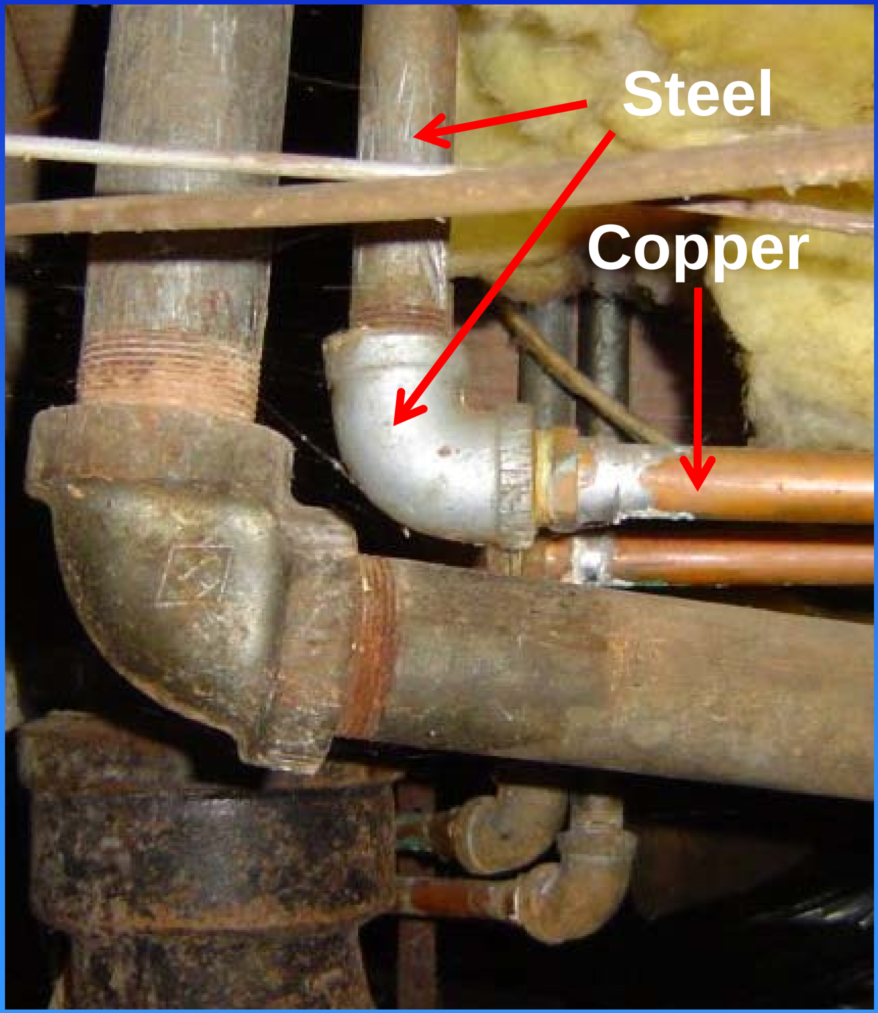
Galvanic Corrosion in 2003
Space Shuttle Columbia

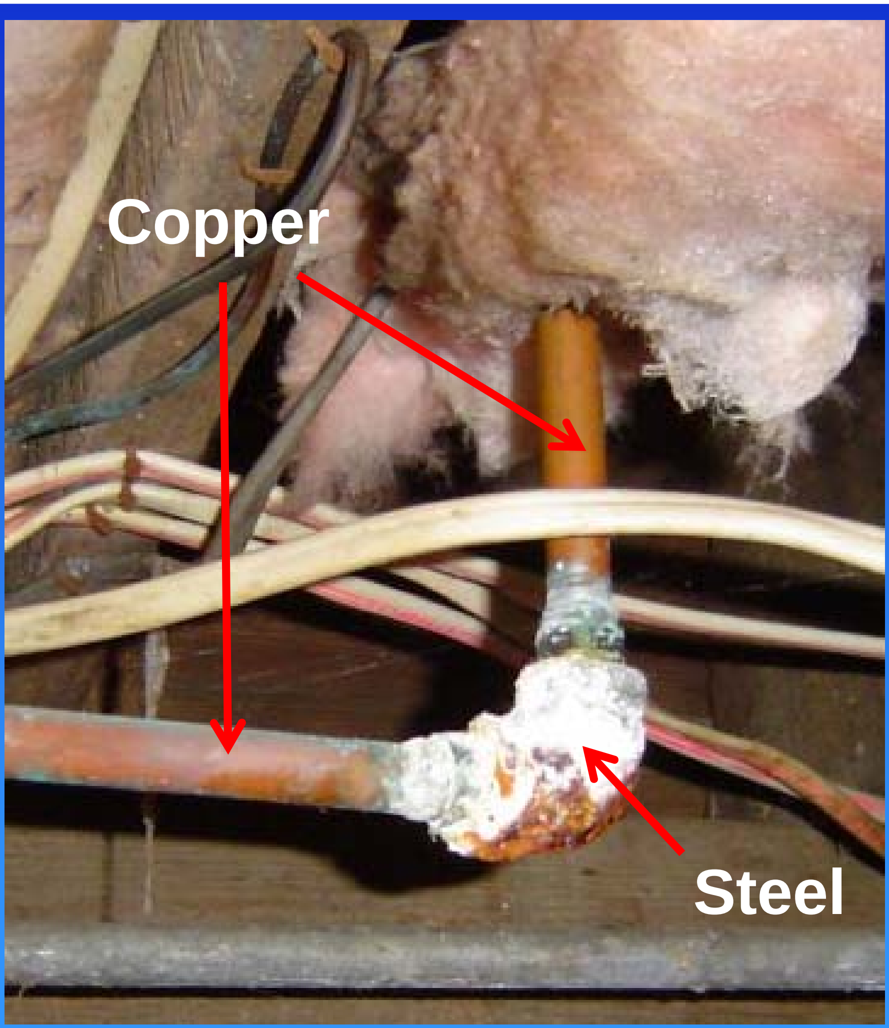
"Veteran space shuttle engineer Ray Erikson offers 'one possible explanation': 'corrosion of the leading edge spars' on the left wing had already so weakened that structure that the small additional damage from the debris was then enough to cause the later failure."

Galvanic couple: Alloy 718 and A286 bolts coupled to 2024 Al honeycomb

Al preferentially corrodes when salt spray from the nearby ocean was dissolved in rainwater and seeped into the structure while Columbia was on the launch pad

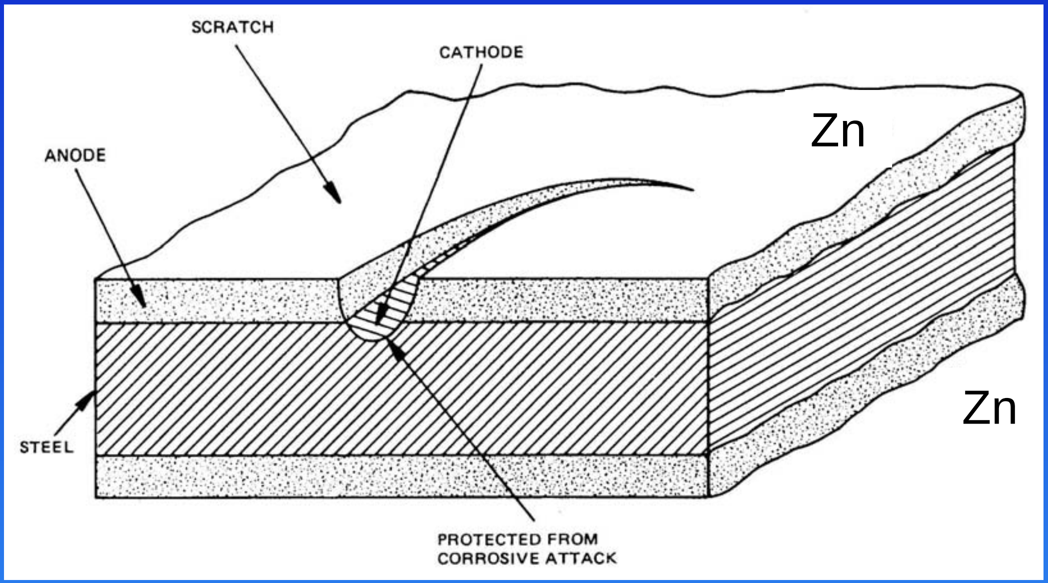
Galvanic Corrosion in 2011

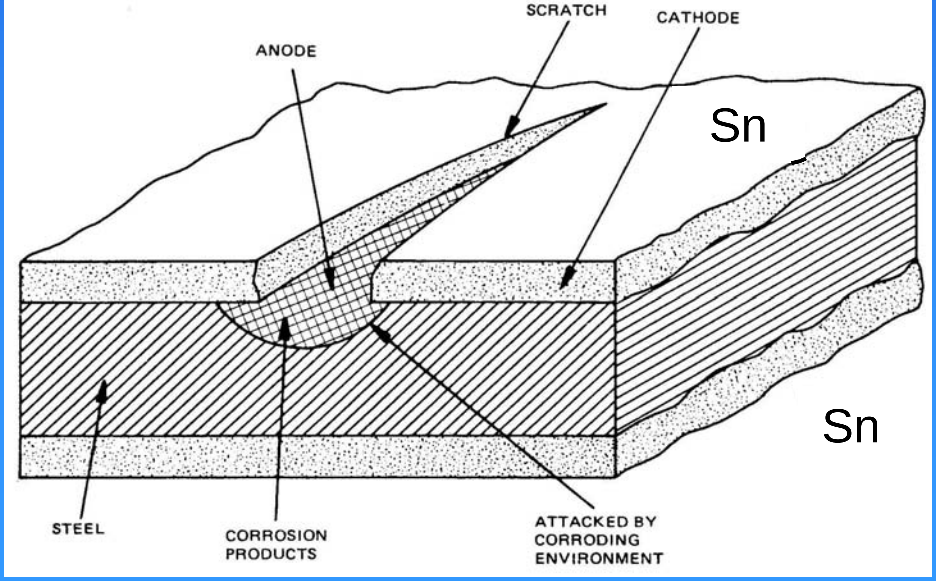




Bad **Worse**

Differences Between Galvanized (Zn) and Tinplated (Sn) Steel





Exposed Fe sacrifices itself for the Sn

Galvanic Corrosion Cell

Anode

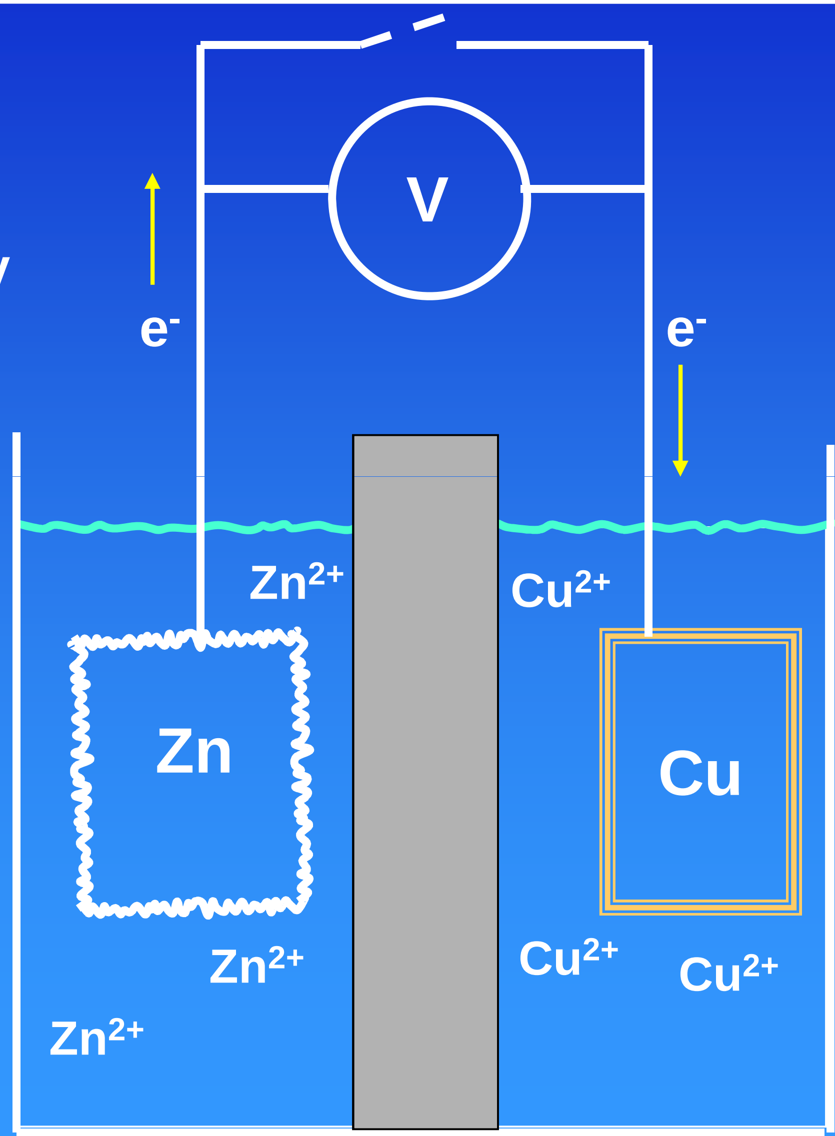
$Zn \rightarrow Zn^{2+} + 2e^-$

$E^0_{Zn/Zn^{2+}} = -0.76\ V$

Cathode

$Cu \rightarrow Cu^{2+} + 2e^-$

$E^0_{Cu/Cu^{2+}} = 0.34\ V$



The total V difference between Zn and Cu is 0.34 – (-0.76) = 1.1 V

Zn electrode at standard state

Cu electrode at standard state

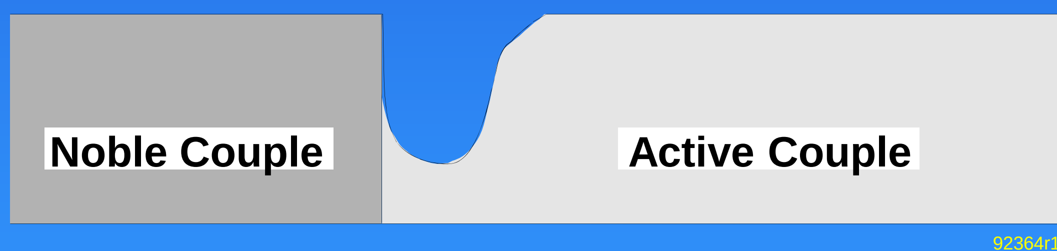
Galvanic Corrosion Factors

- Anode and cathode (initially) defined by the materials selection or by factors that occur in service
- Electromotive series is a good predictor, but kinetic factors can overpower the relative position in the series
- Area effects/current density are huge factors
- Conductivity

Major industries are based on galvanic corrosion

Effect of Conductivity on Galvanic Corrosion

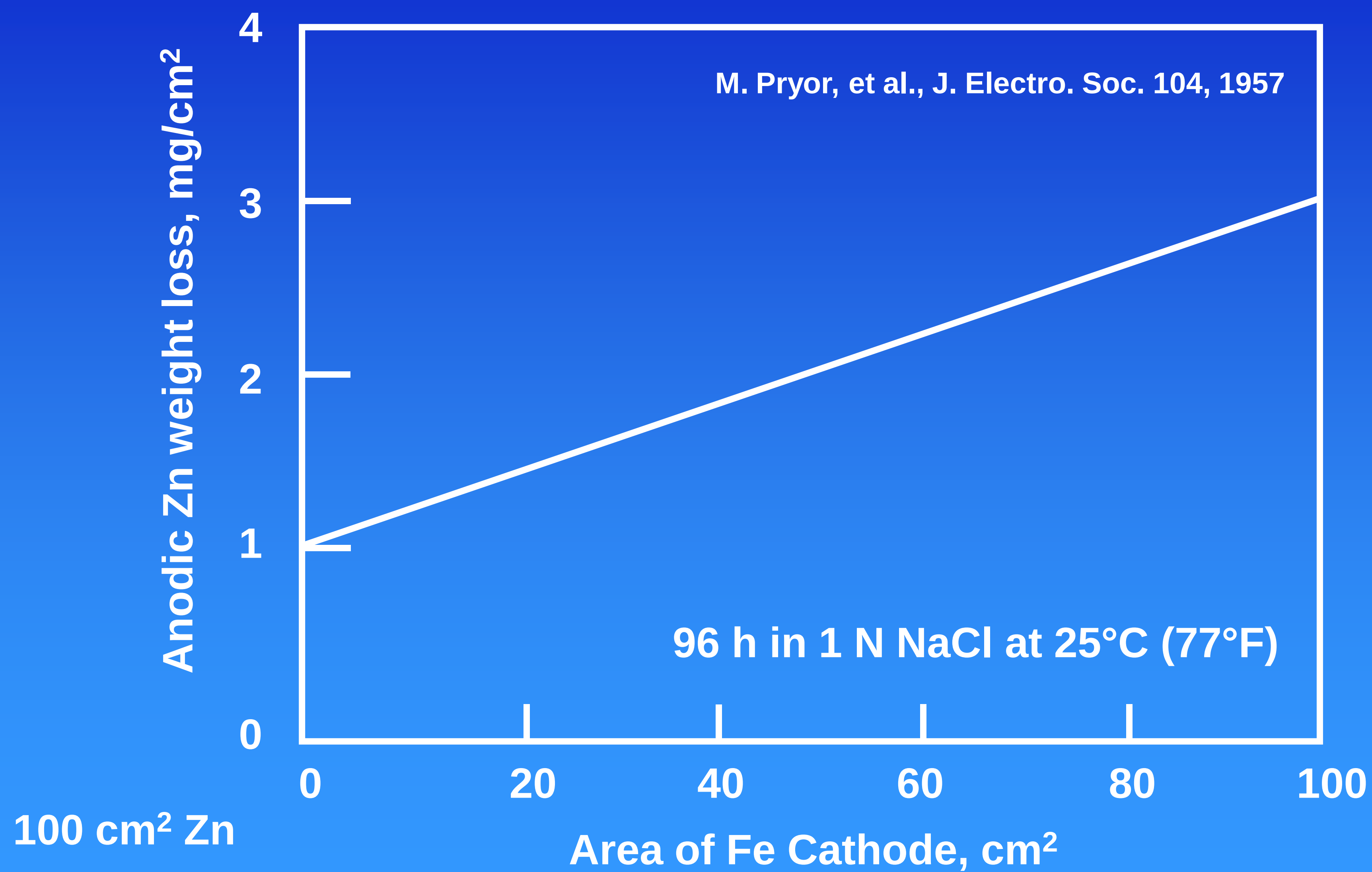
Galvanic Corrosion in High Conductivity Environment



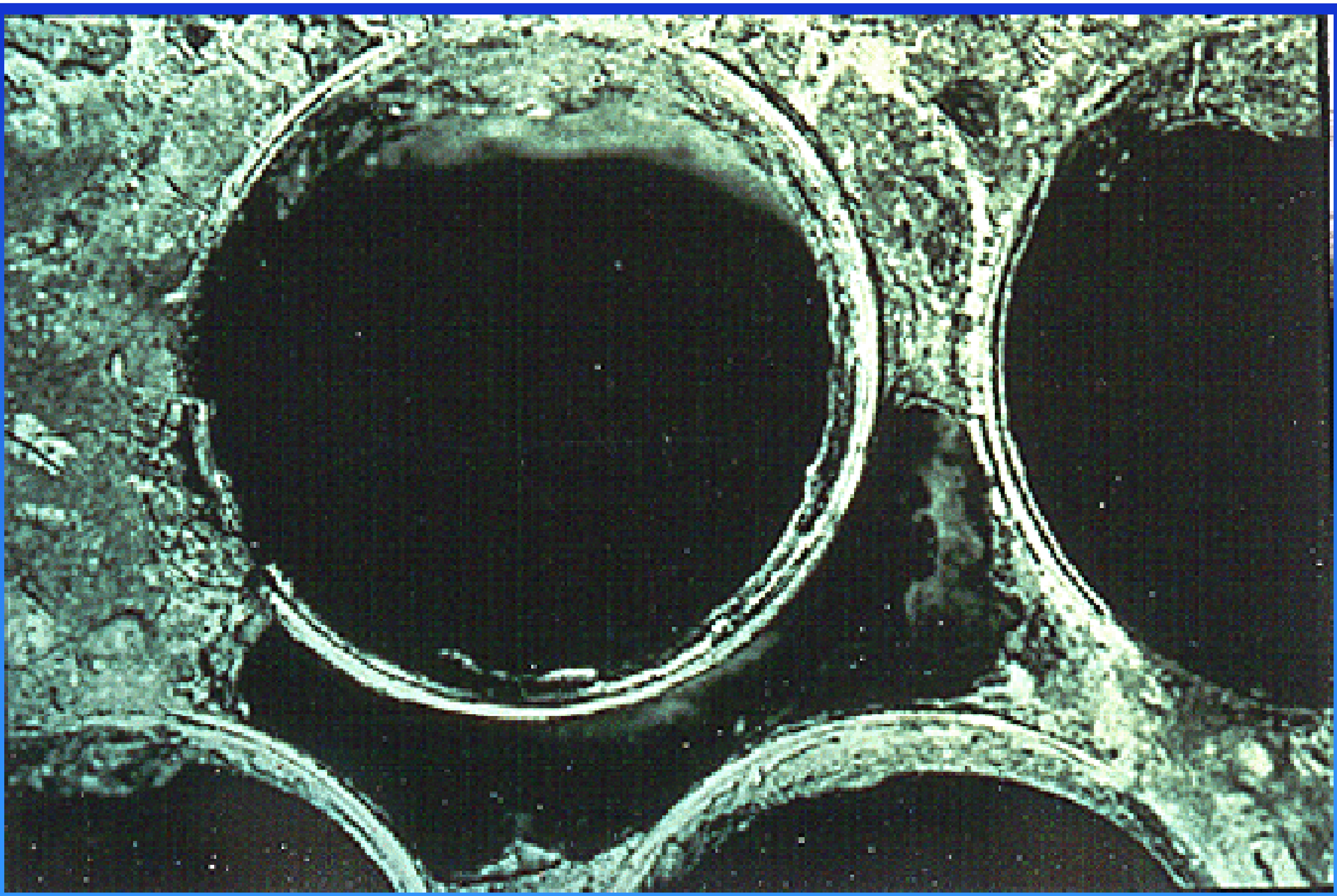
Can be worse in low conductivity water!

Galvanic Corrosion in Low Conductivity Environment

Effect of Relative Anodic and Cathodic Areas on Galvanic Corrosion



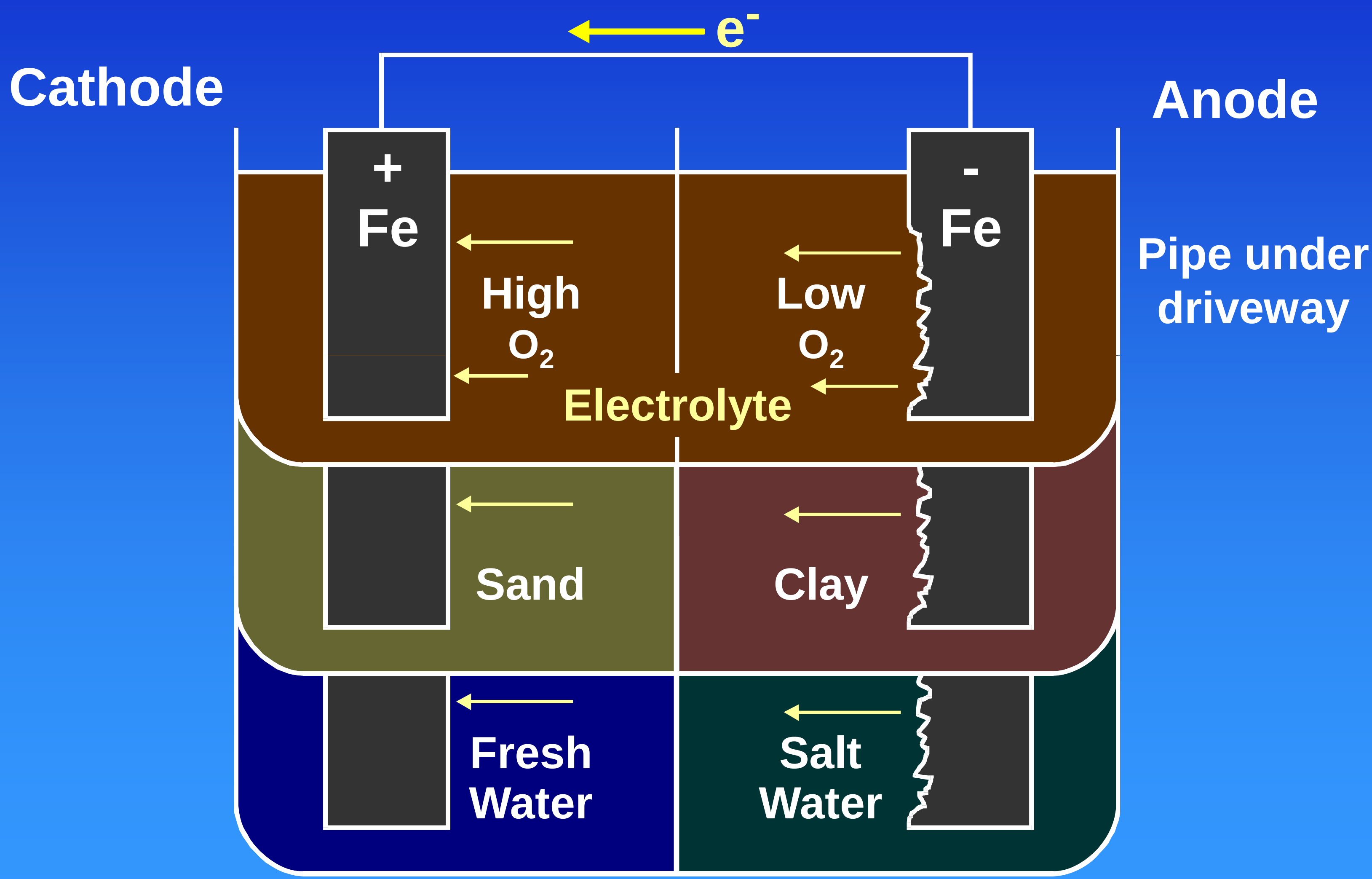
AL-6X Condenser Tubes in 60 Cu - 40 Zn (Muntz Metal) Tube Sheet



One year after retubing with AL-6X!
Electrolyte = seawater

B.Syrett and R. Coit, 2nd ASME/ANS, 1982

Dissimilar Electrolytes/ Concentration Cells



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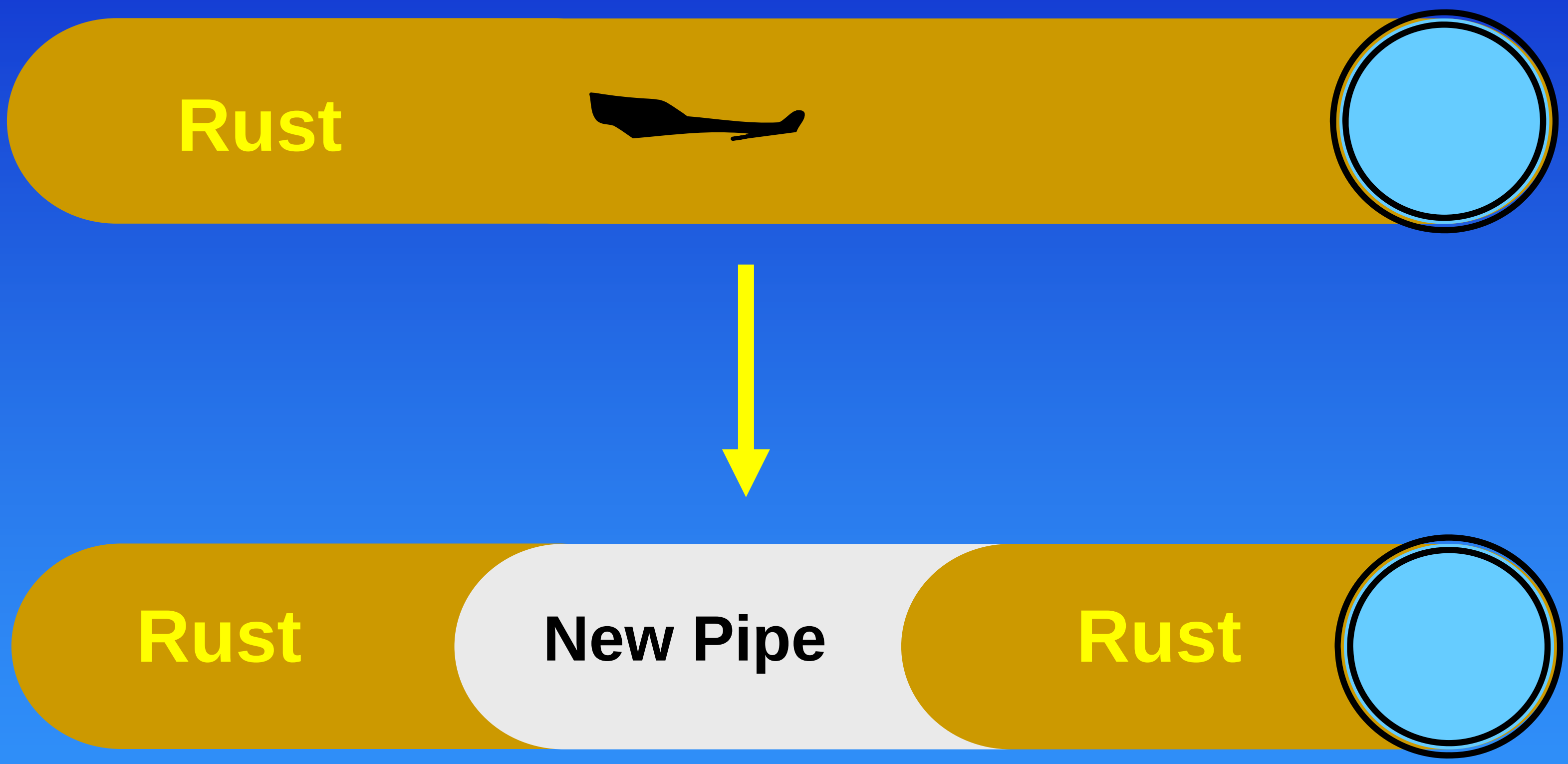
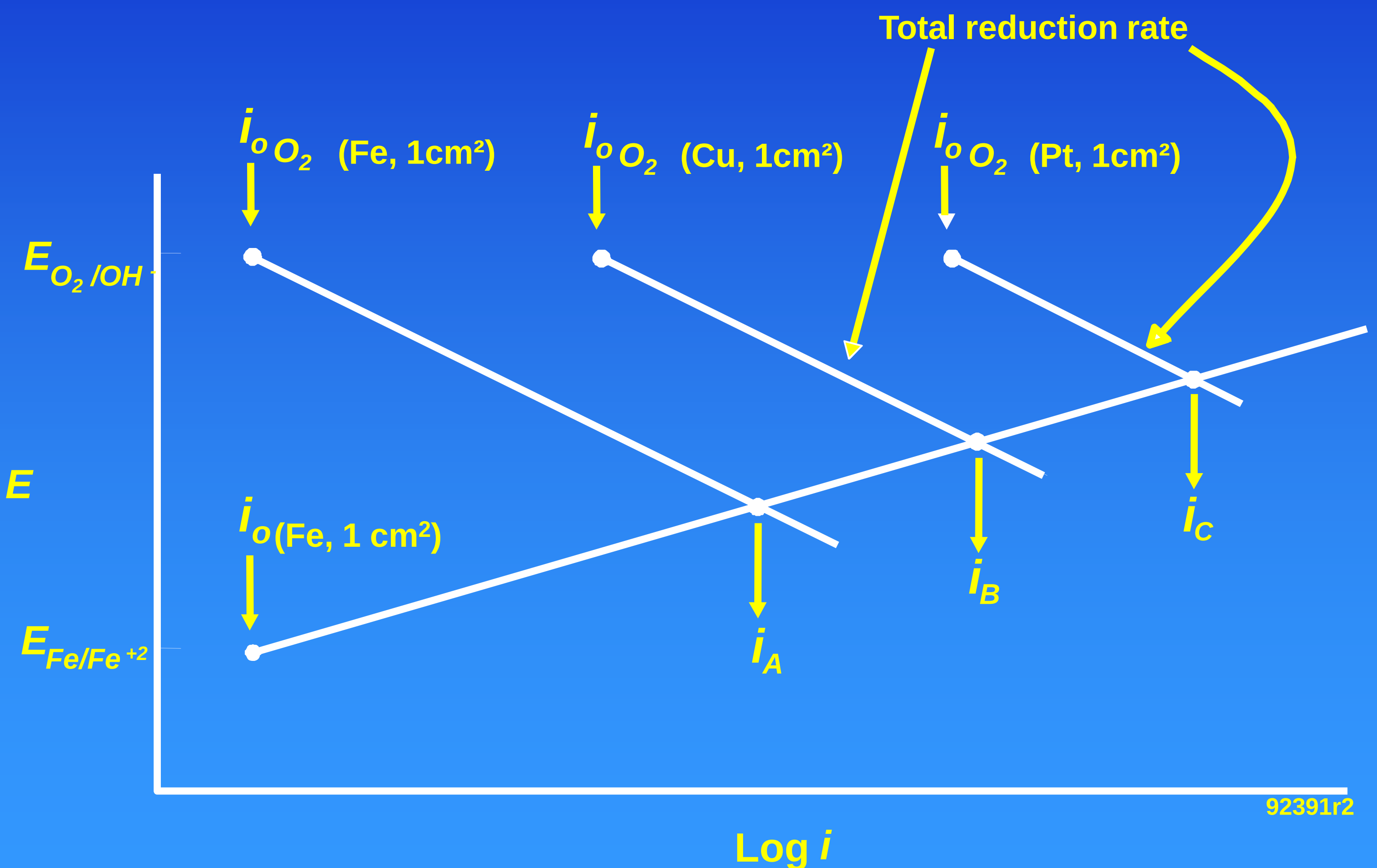
Structural Integrity Associates

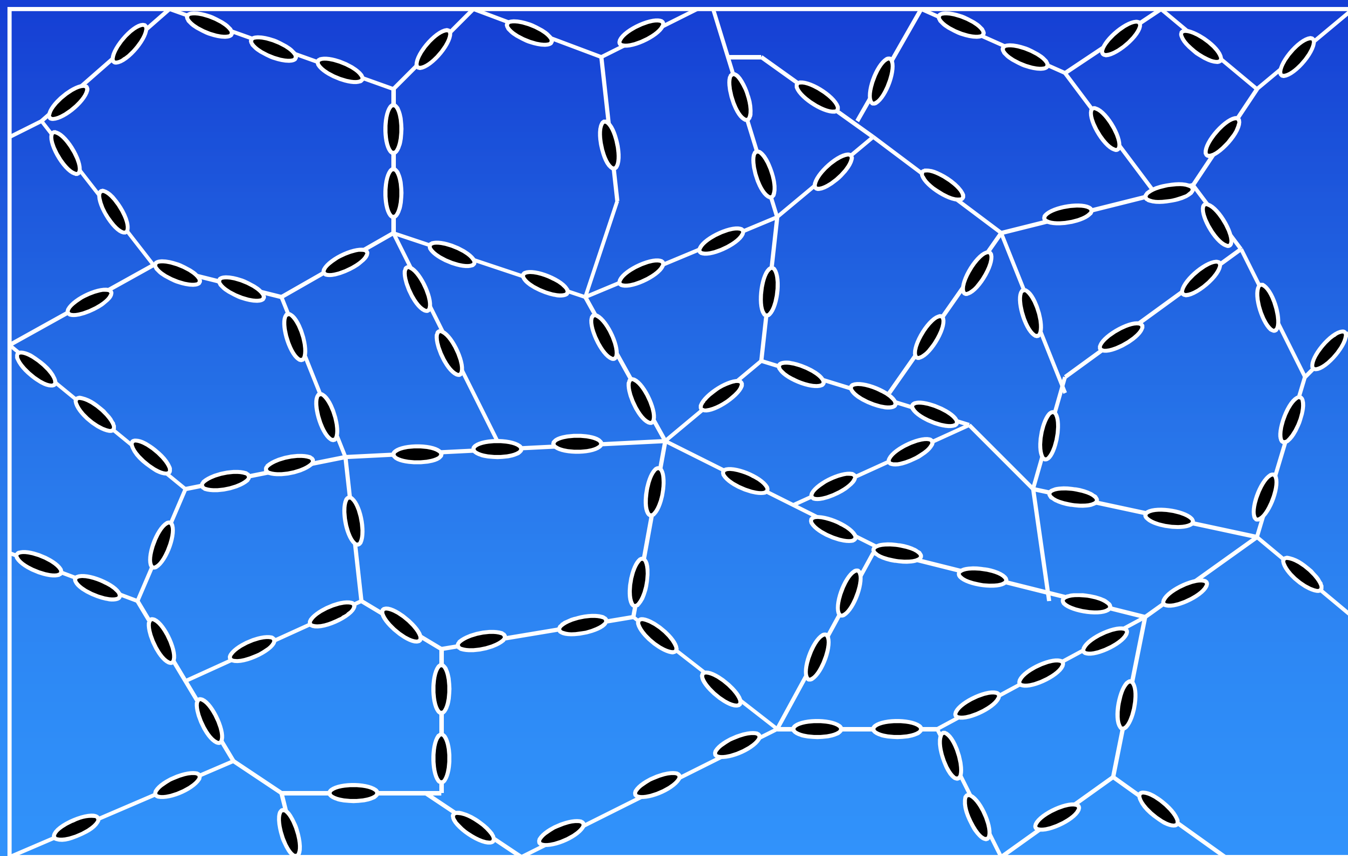
Buried Pipe Replacement



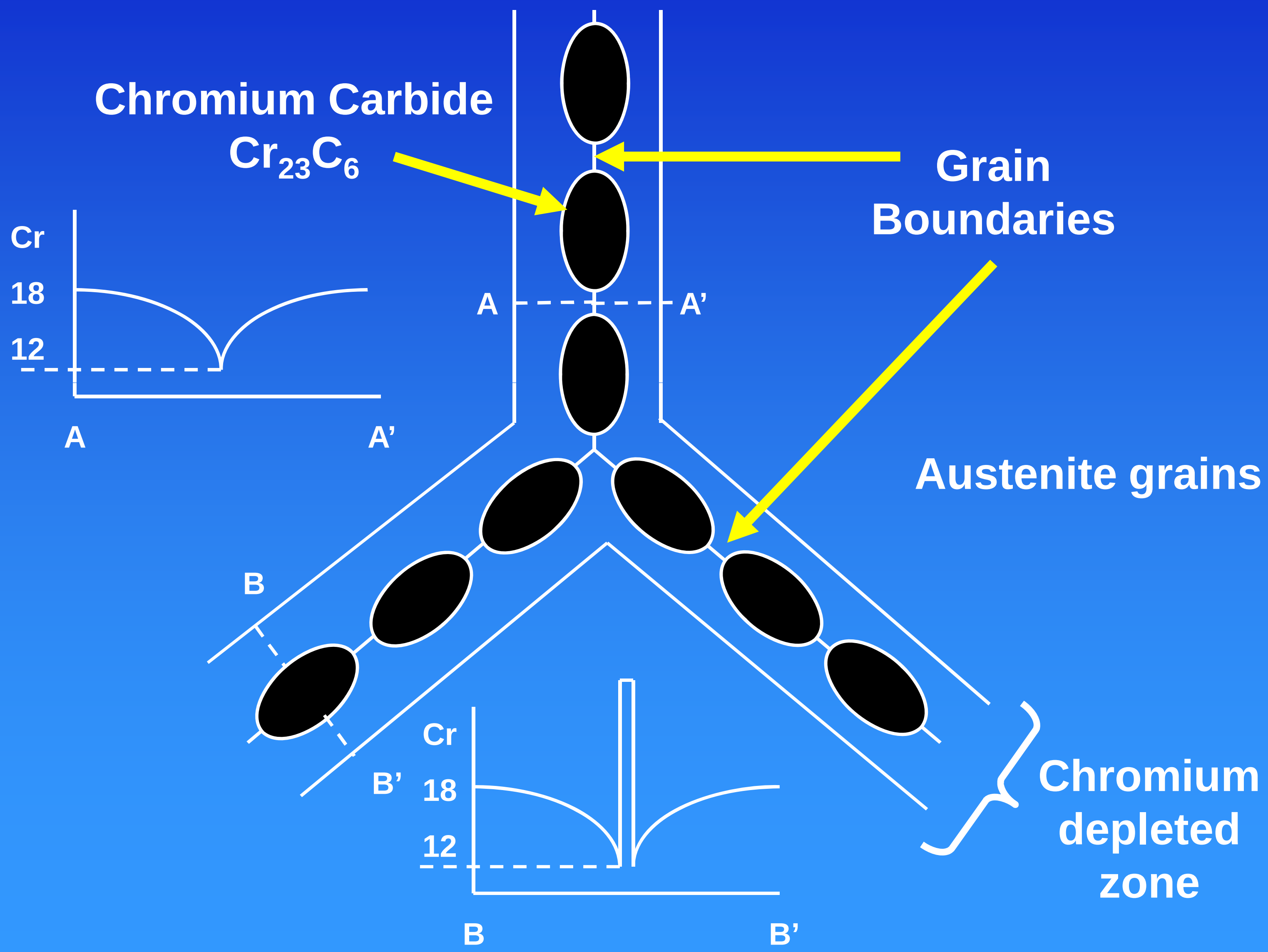
Effect of Exchange Current Density on Galvanic Corrosion of Fe-Cu and Fe-Pt Couples



Galvanic Micro-cell



Grain Boundary Sensitization



Structural Integrity Associates

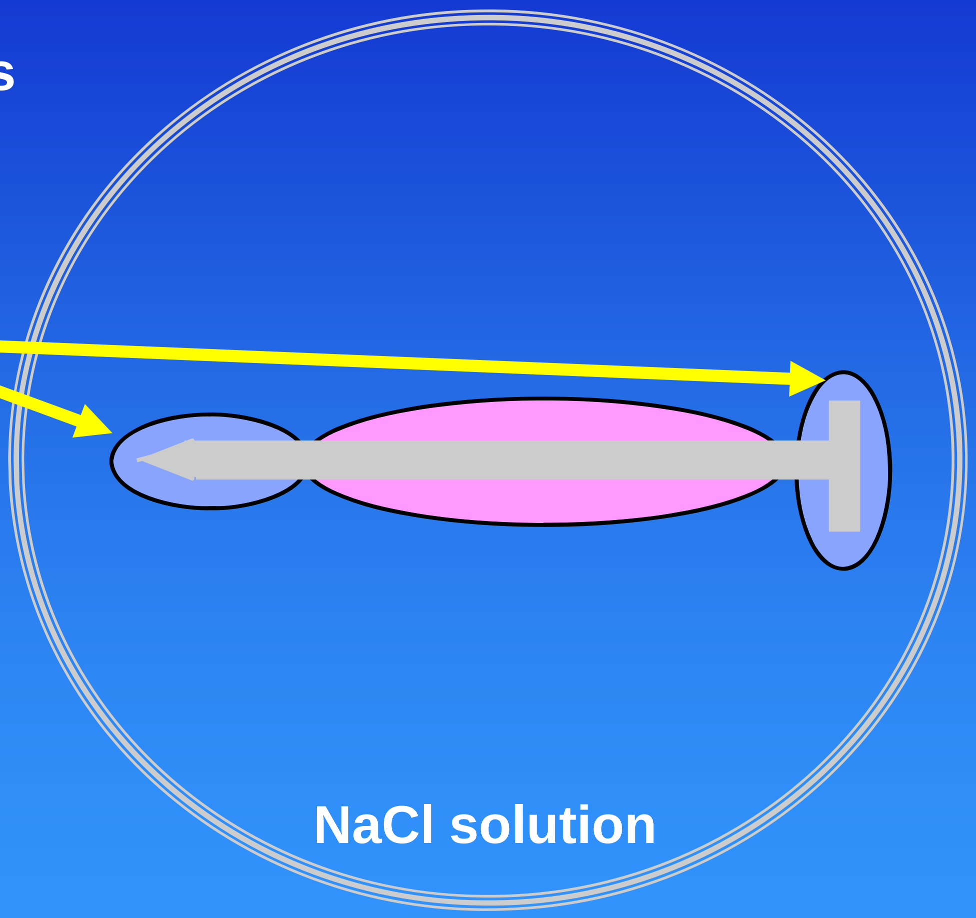
Cold Work Galvanic Cell Example

Phenolphthalein turns pink in contact with hydroxyl (OH^-) ions

Potassium ferricyanide turns blue with ferrous ions (Fe^{2+})

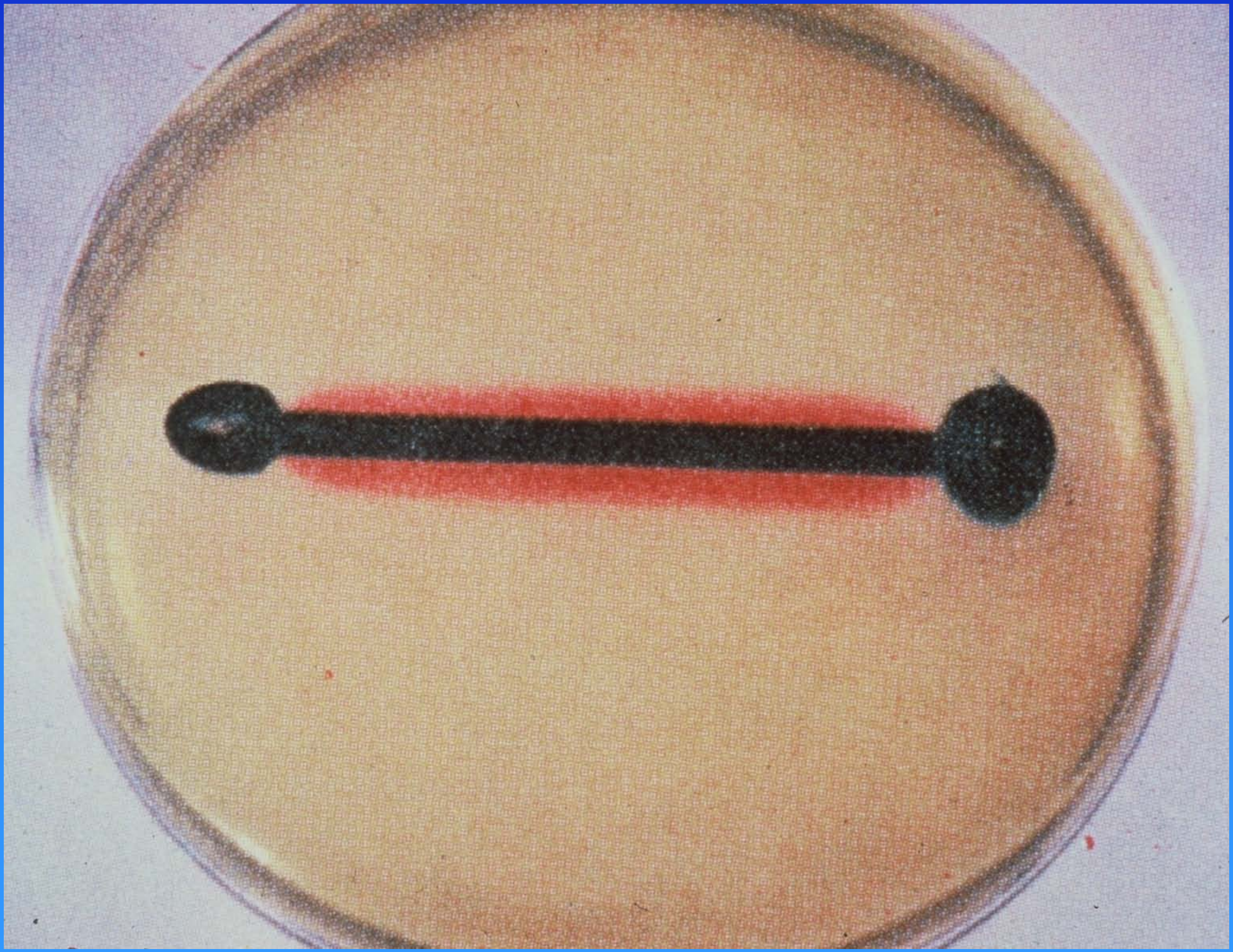
Cold worked nail head and tip corrode preferentially, i.e., become anodes

Cold work increases internal stored energy due to an increased defect structure



Anode: $Fe \rightarrow Fe^{2+} + 2e^-$ Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4(OH)^-$

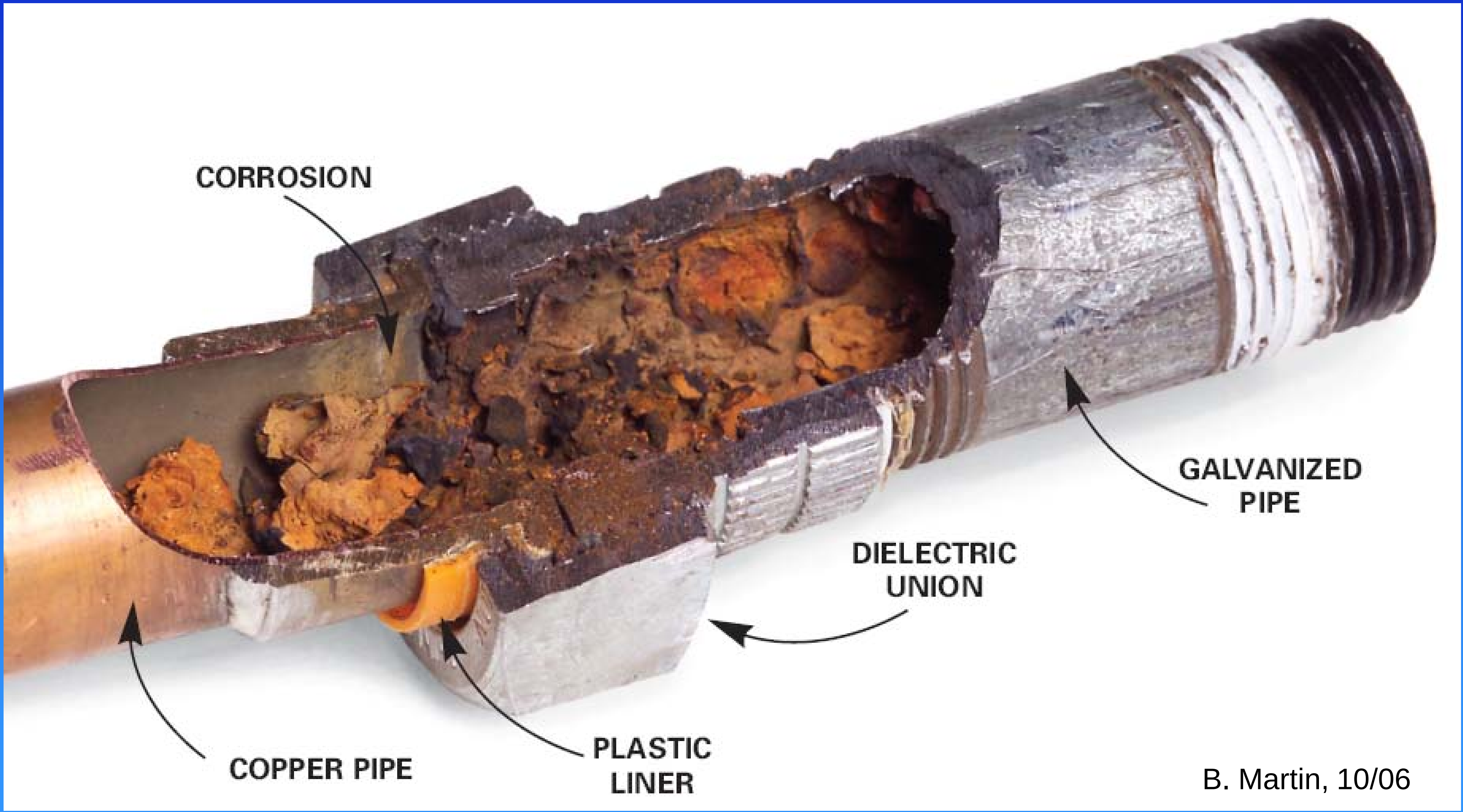
Cold Worked Nail Galvanic Cell



Mitigation of Galvanic Corrosion

- Electrically insulate the two metals (e.g., plastic coupling)
- Insert a coupling that has a average corrosion potential in the same environment (e.g., bronze inserted between copper and steel)
- If galvanic coupling is unavoidable, have a high anode surface to cathode surface ratio (e.g., Cu rivets on Fe plate)
- Use sacrificial anodes (e.g., cathodic protection) to protect entire system

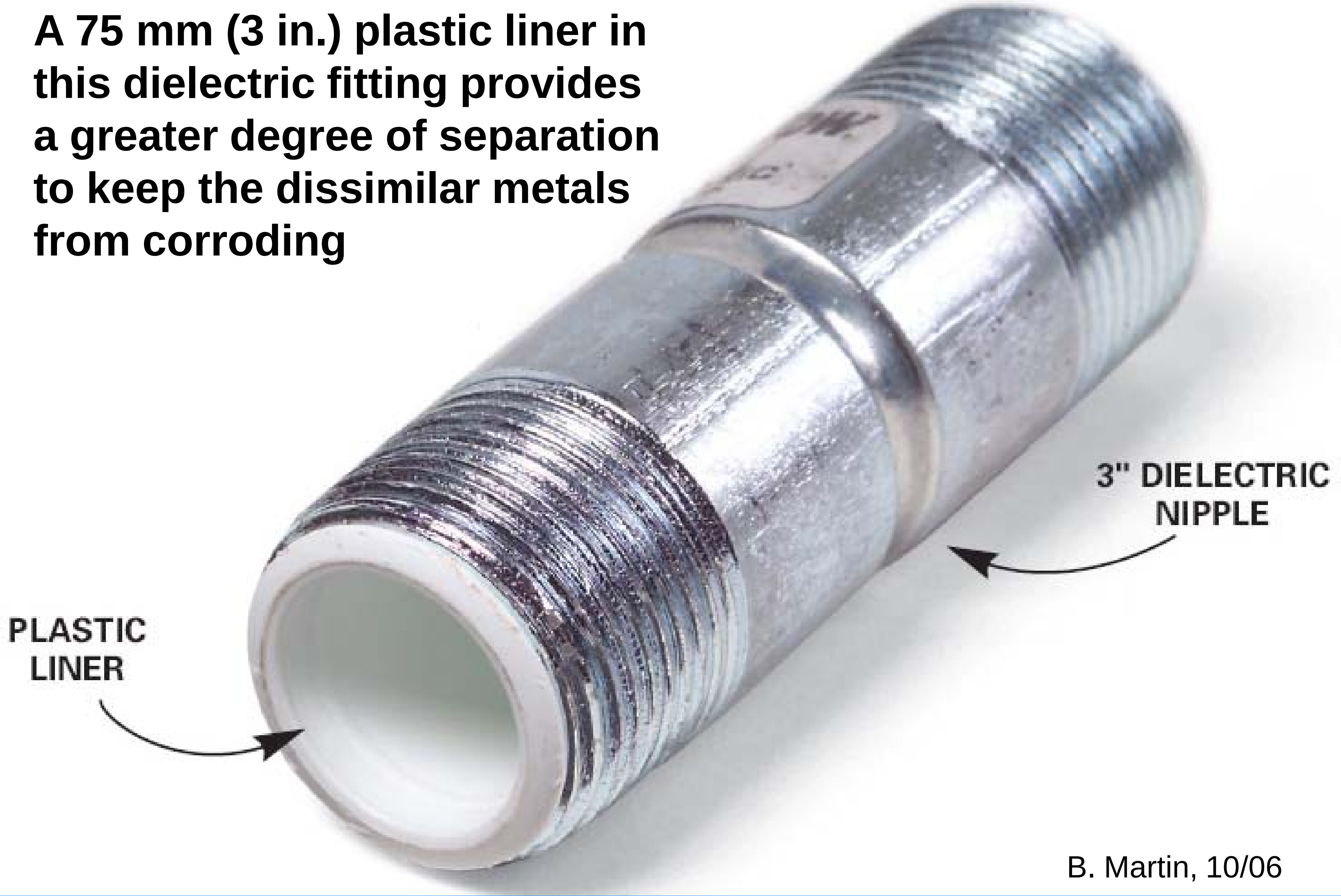
Separating Galvanic Couples - Bad



This dielectric fitting did not provide enough separation between the Cu and Fe allowing the Fe pipe to corrode and clog

Separating Galvanic Couples - Better

A 75 mm (3 in.) plastic liner in this dielectric fitting provides a greater degree of separation to keep the dissimilar metals from corroding



B. Martin, 10/06

Lasagna Cell Corrosion

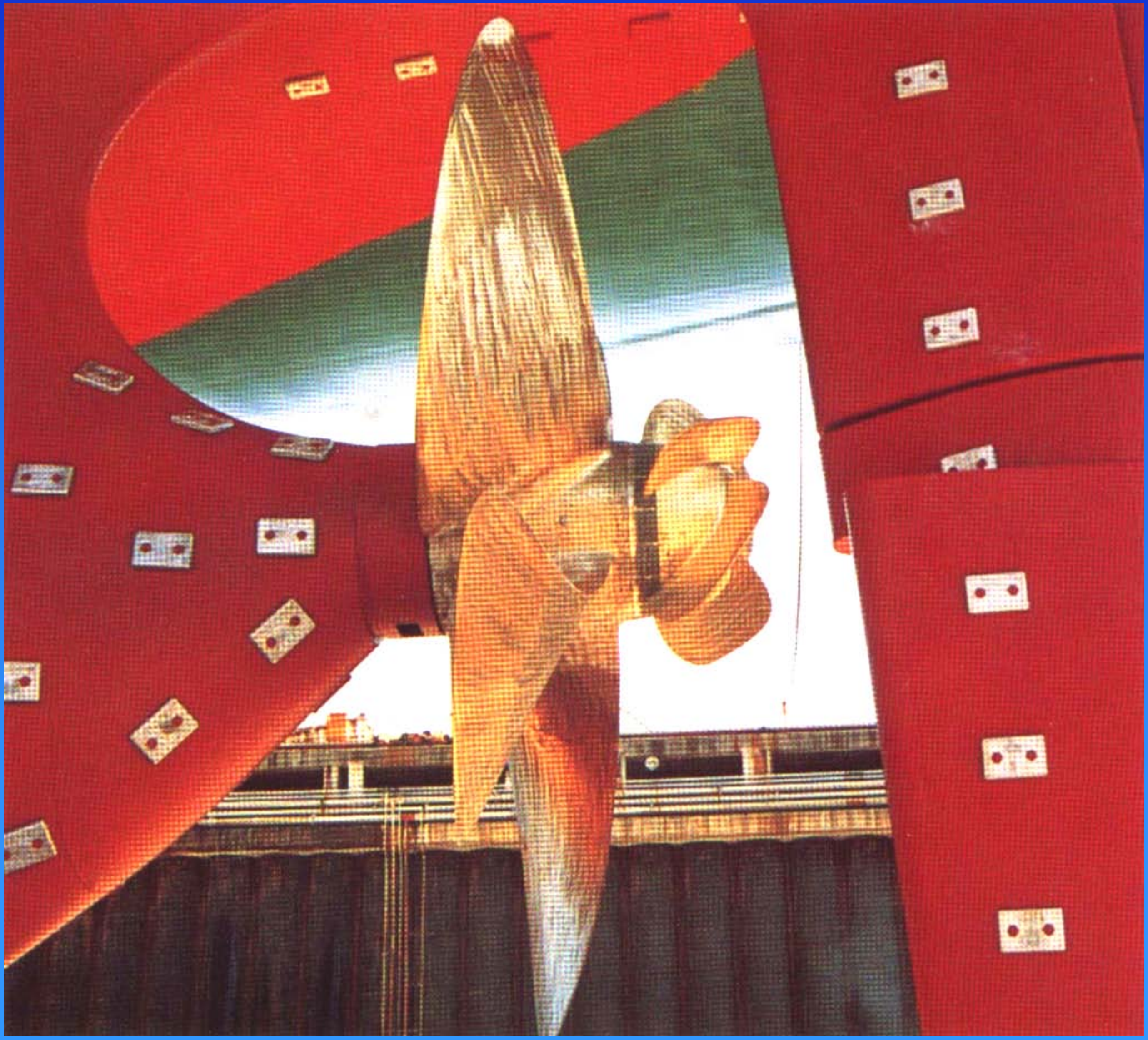
Produced when salty lasagna is stored in a steel baking pan and covered with Al foil

After a few hours foil develops small holes where it touches the lasagna and the food surface becomes covered with small spots of Al_2O_3

Mitigation of Lasagna Corrosion

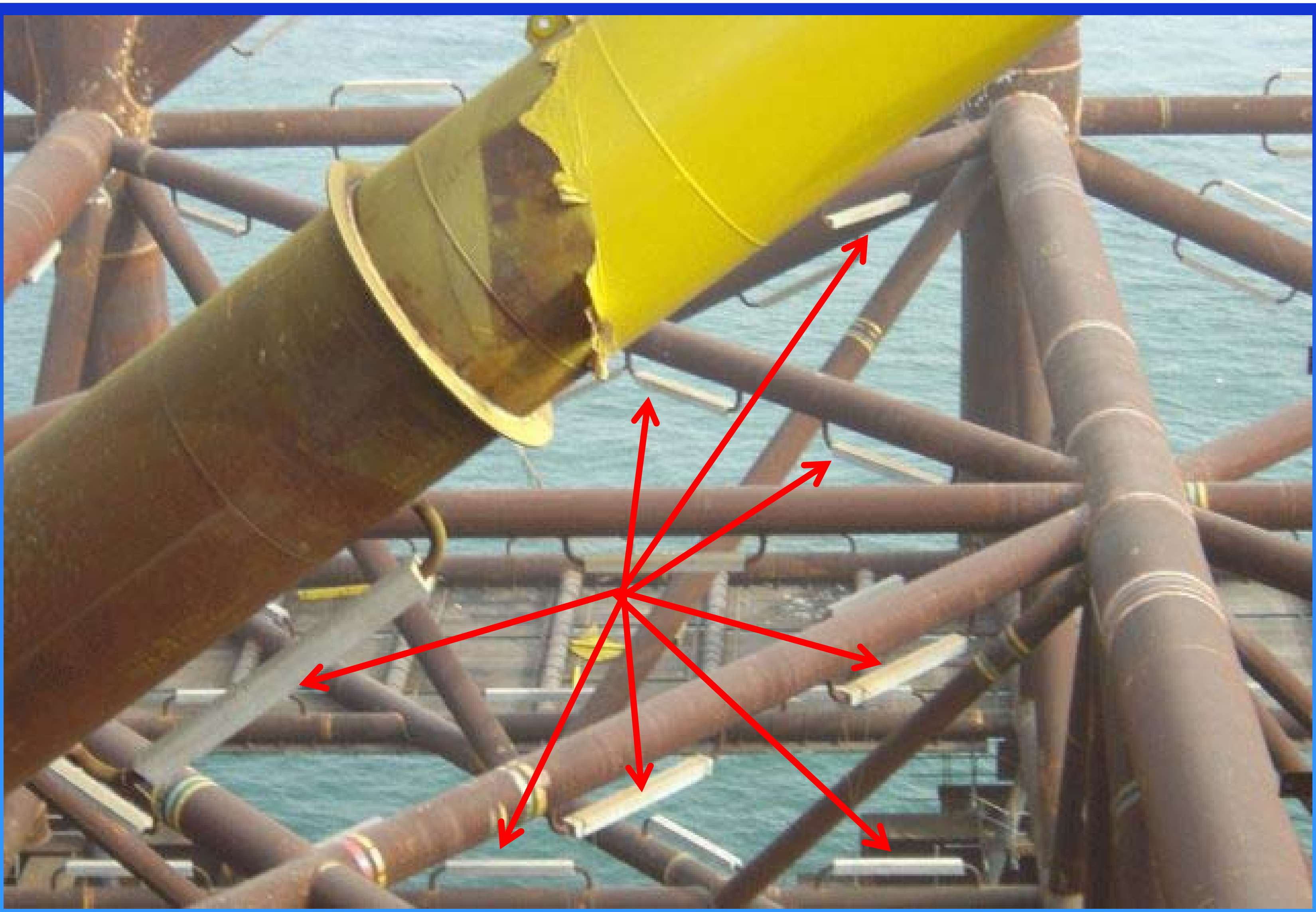
- **Use Al pan and Al foil**
- **Use Pyrex® glass pan and Al foil**

Sacrificial Anodes - Ship's Hull

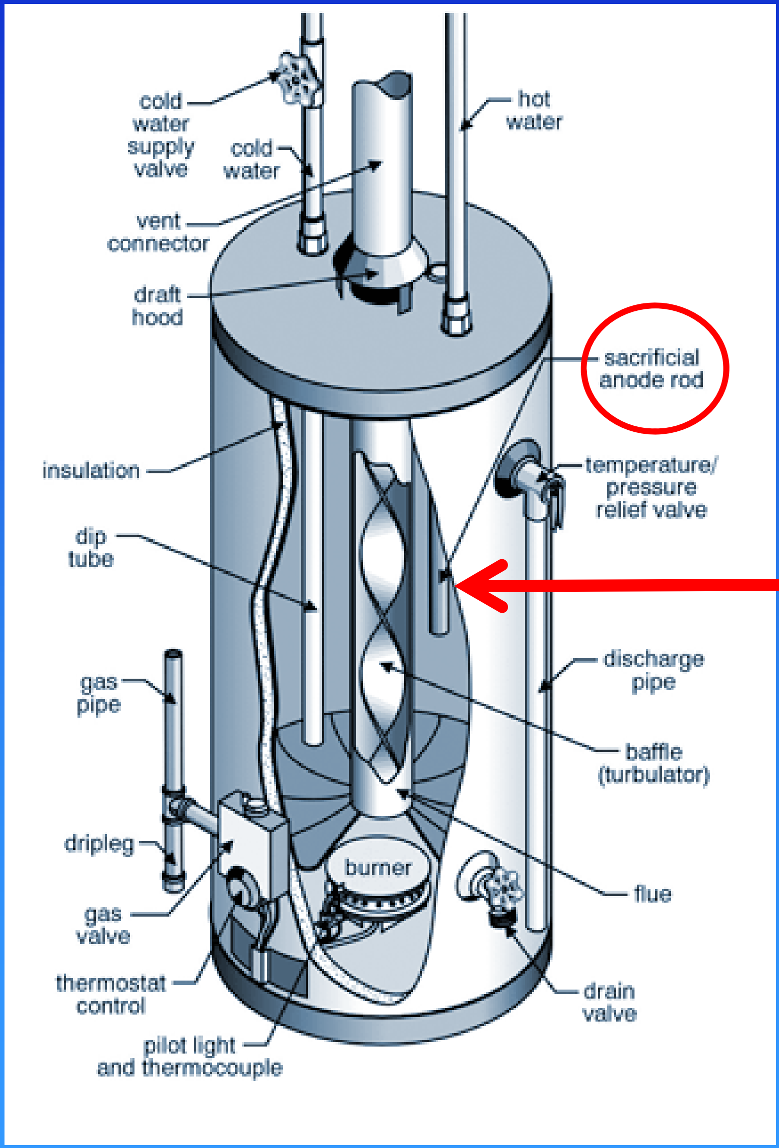


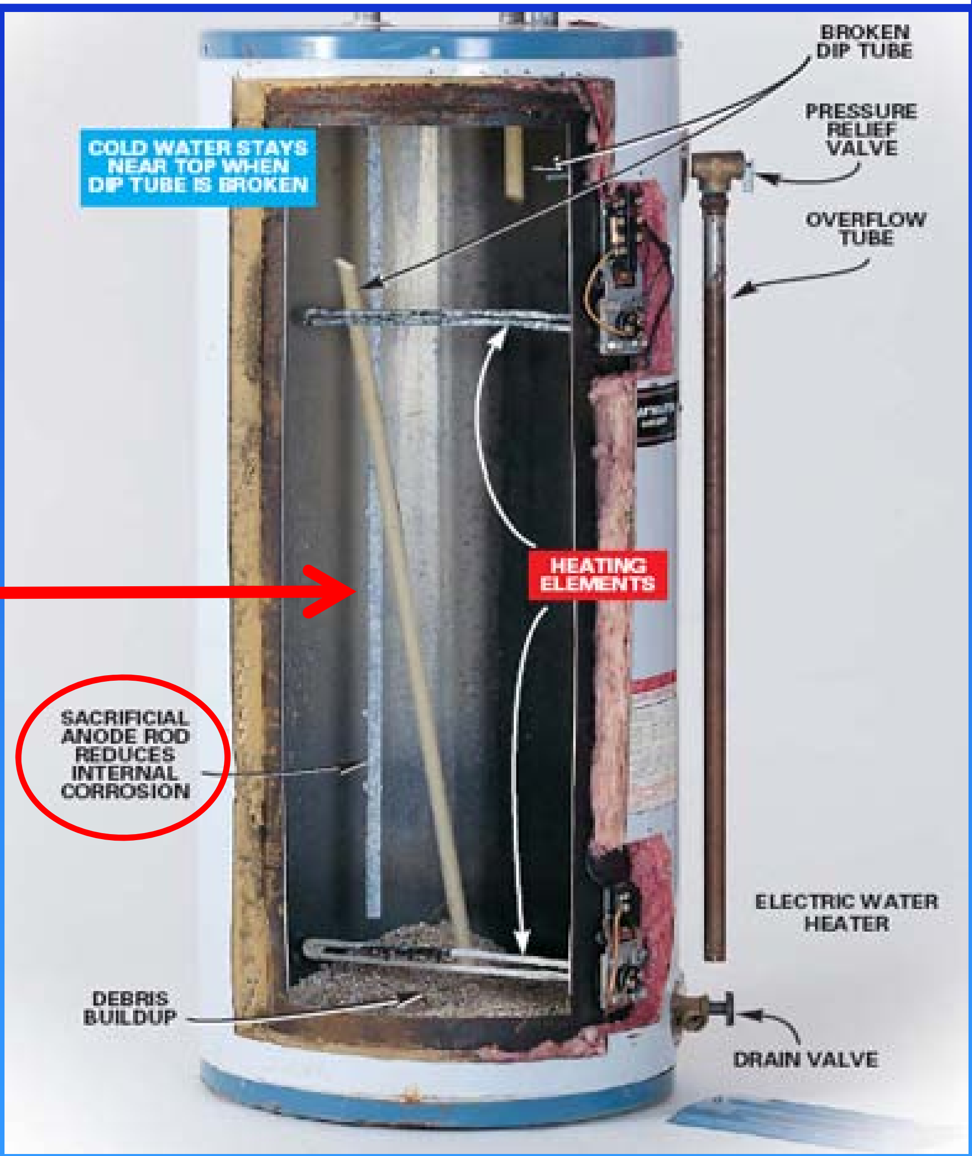
NiDi, Vol. 4, No. 2, 12/88

Sacrificial Al Anodes - Steel Structure



Sacrificial Anodes - Water Heaters



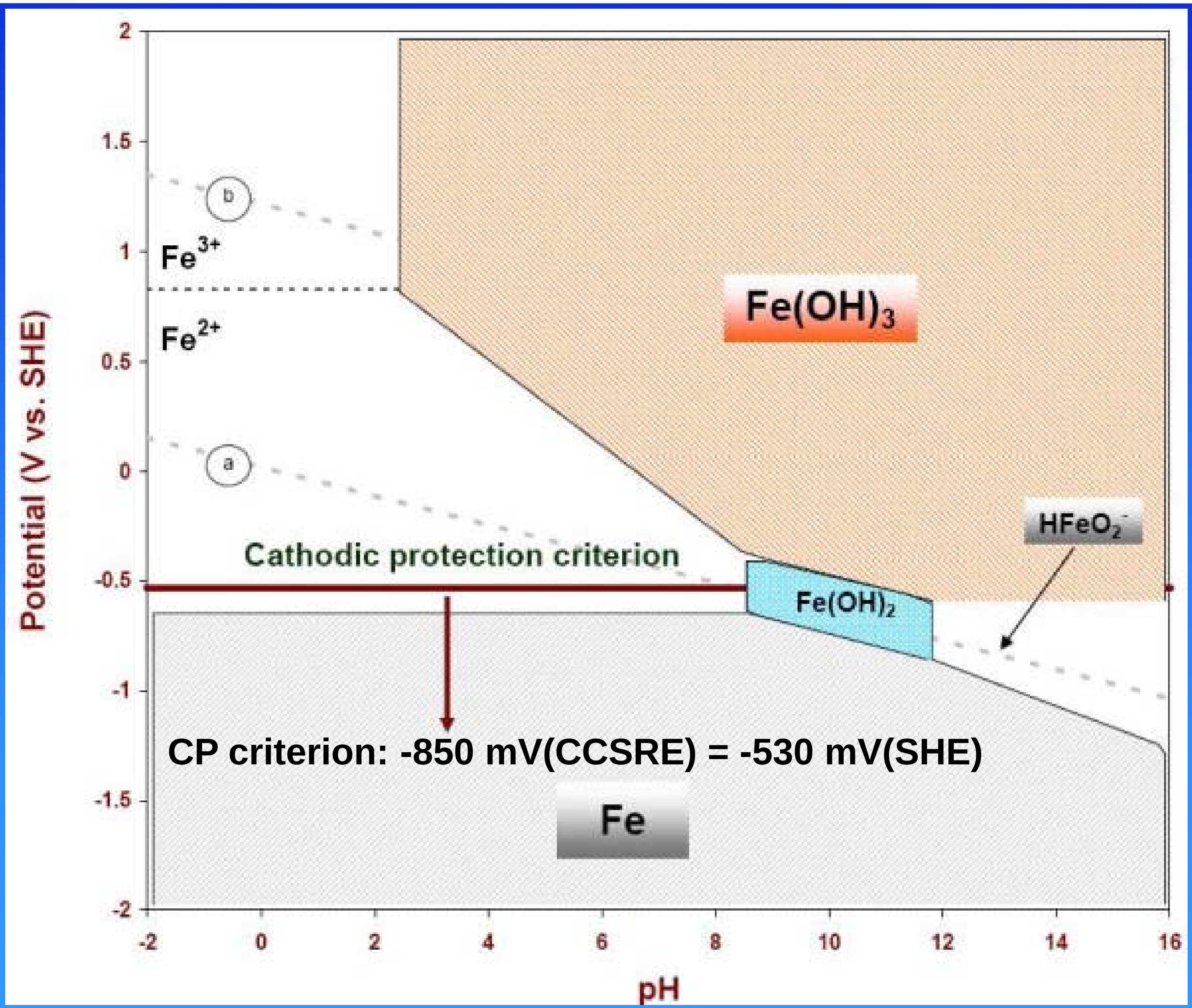


Structural Integrity Associates

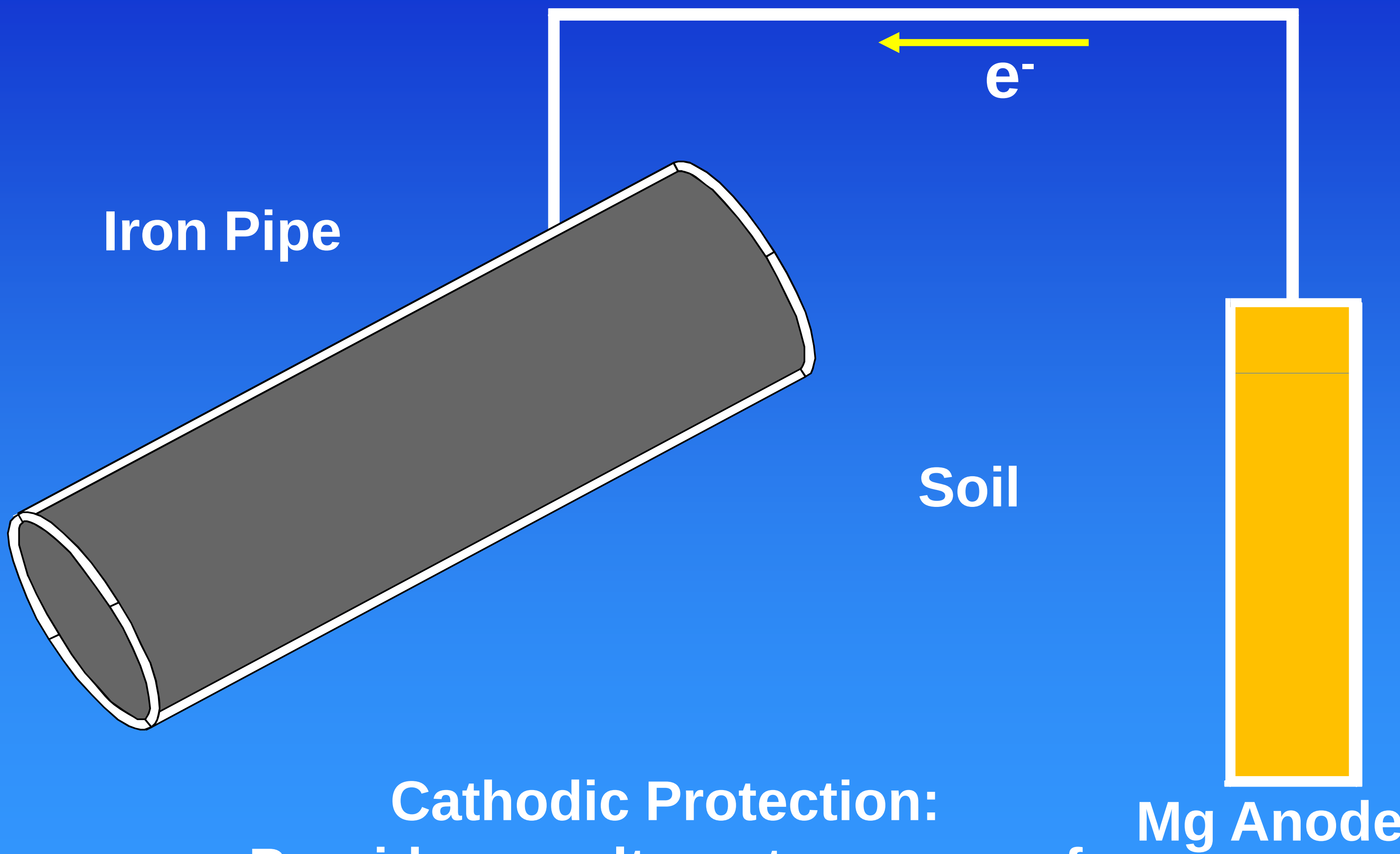
Cathodic Protection

- It's all about electrons – pump the electron "glue" into the structure
- Uniform current distribution is critical
- Objective of CP is to force the entire structure to be cathodic to the environment
- Main criterion to determine if a steel structure has adequate protection:
  - Voltage of -850 mV versus Cu-$CuSO_4$ reference electrode (CCSRE)

Pourbaix Diagram of Fe with the Cathodic Protection Criterion

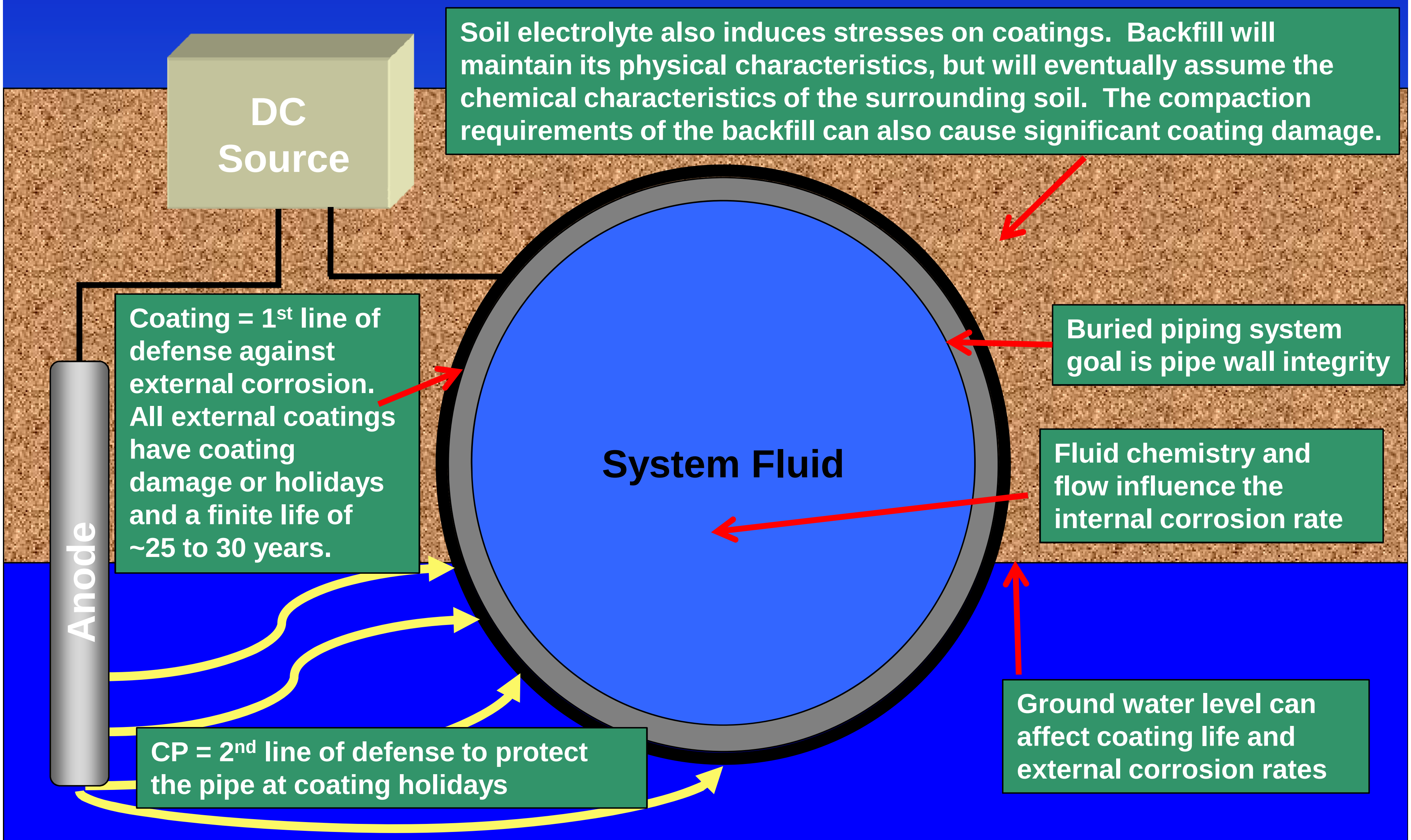


Sacrificial Anode on a Buried Pipe

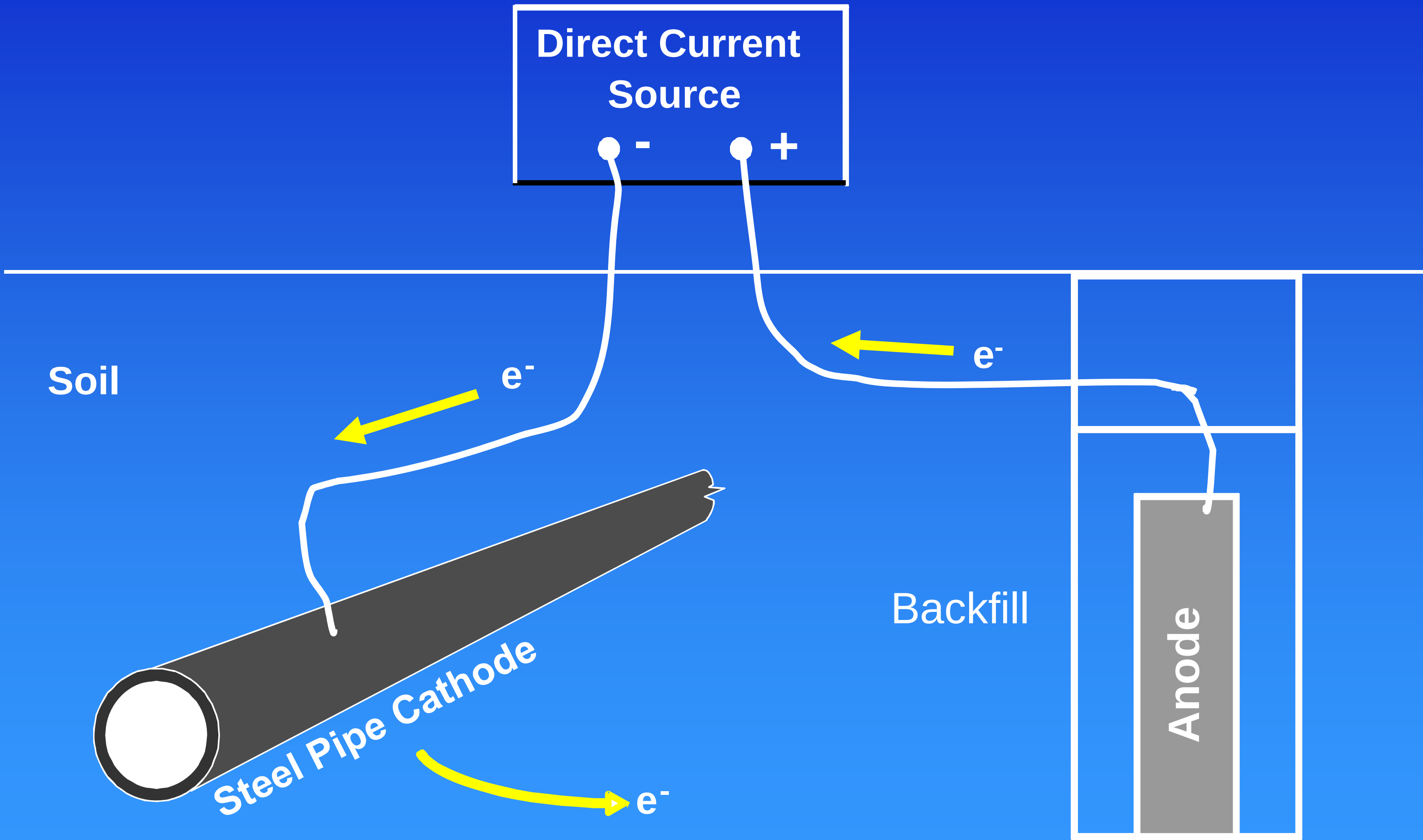


Cathodic Protection:
Provides an alternate source of electrons for oxygen reduction

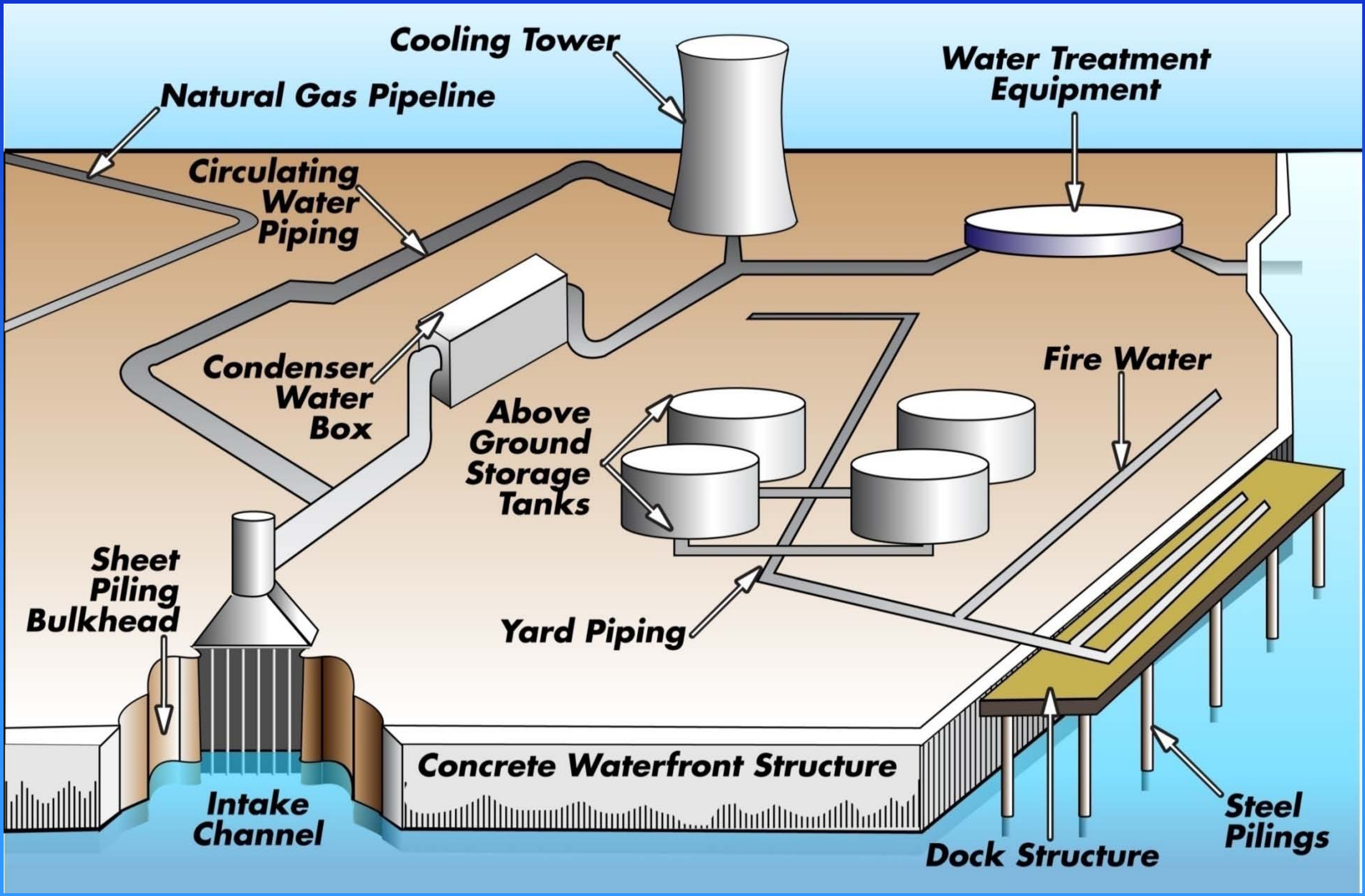
Buried Piping System



Cathodic Protection- Impressed Voltage



Designing CP Systems is Challenging

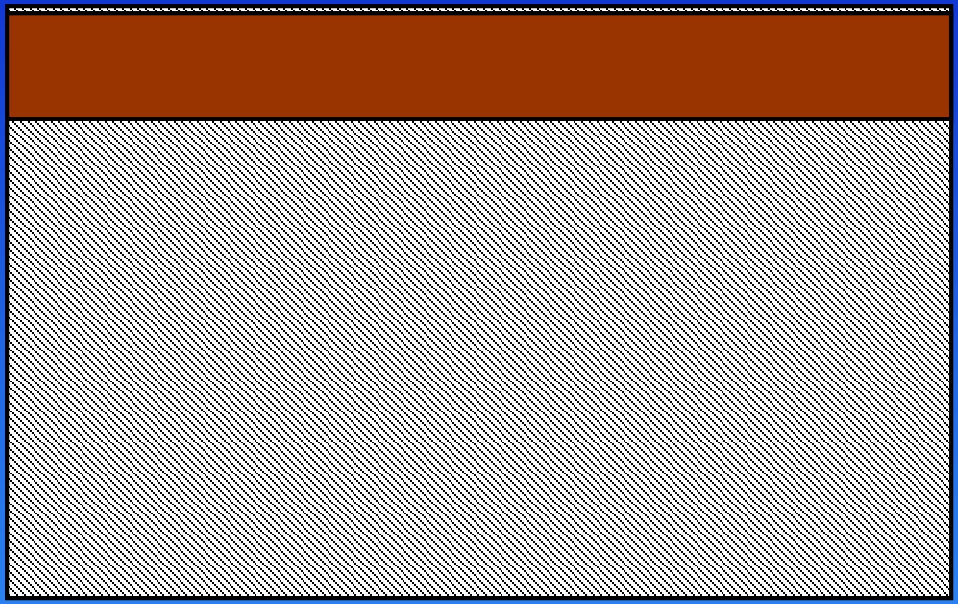


Dealloying Corrosion

NRC Dealloying Corrosion Document

- **IN84071 - Graphitic Corrosion of Cast Iron in Salt Water**

Dealloying Corrosion



- Mechanism
- LWR Case Study Example
  - Condensers
  - BWR recirc seal

Dealloying Corrosion

(Selective Leaching/Parting Corrosion)

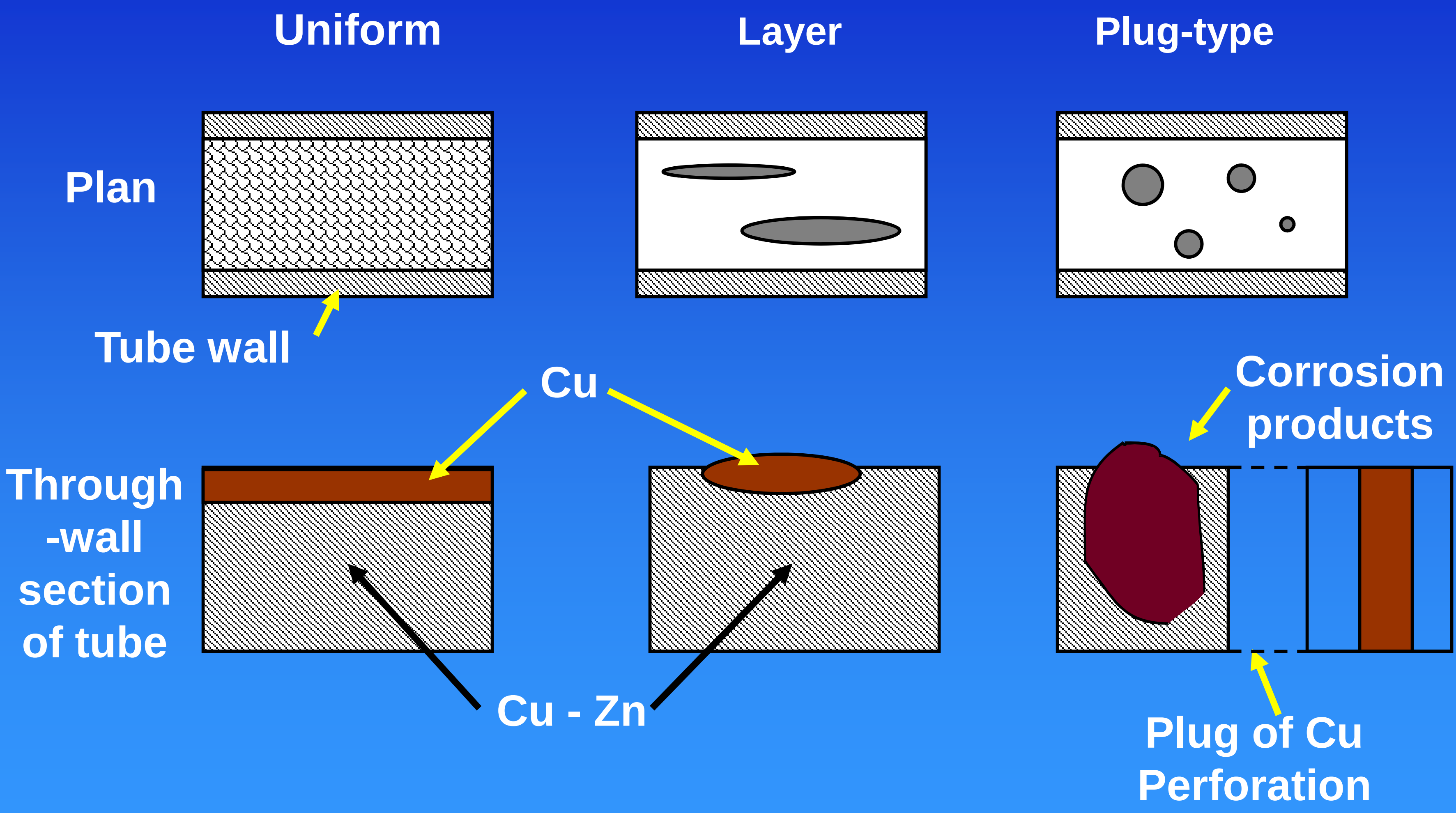
- Preferential dissolution of more active metal in an alloy, which leads to the enrichment of the remaining alloying elements
- No net loss of section, but a dramatic loss of strength/hardness as spongy material is left behind
  - Uniform dealloying
  - Banded or layer type dealloying
  - Plug dealloying
- Susceptible Copper Alloys ("dezincification"):
  - Brasses (>15% zinc)
  - Bronzes (Al bronze/Ni Al bronze)
  - Copper-Nickels
  - Many of the Cu alloys are formulated to resist dealloying
- Cast iron ("graphitization" or "graphitic corrosion")

Environmental Conditions for Dealloying Corrosion

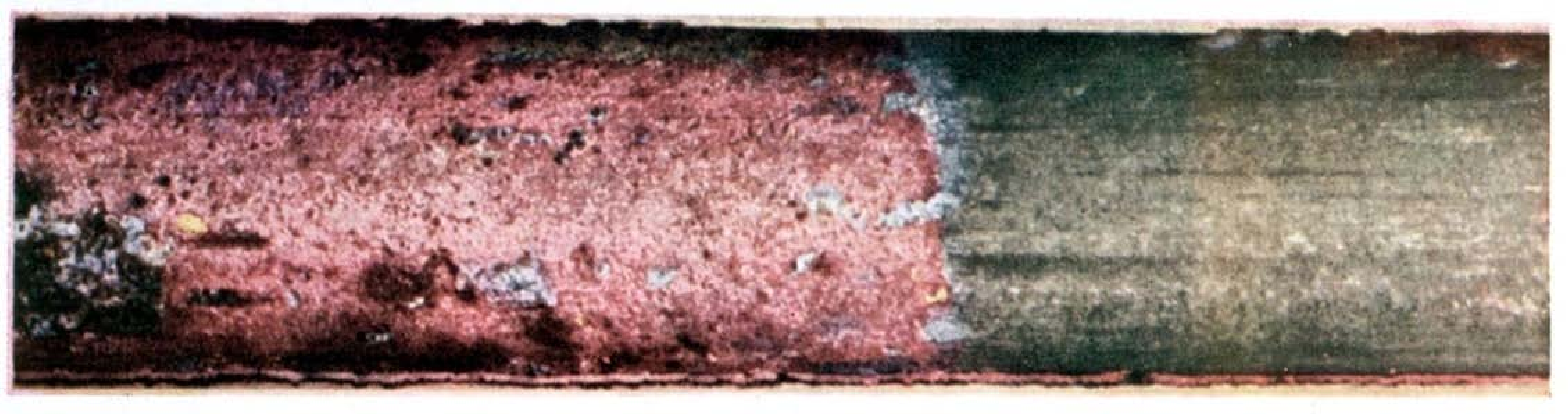
- Slow corrosion process
- High temperatures, stagnant-flow conditions and "corrosive" environment
  - Acidic solutions for brasses with high Zn and dissolved oxygen are conducive to dealloying corrosion
- Monitoring of water chemistry to control pH and concentration of corrosive contaminants and treatment with hydrazine to minimize dissolved oxygen are effective in reducing dealloying corrosion

NUREG-1801, Rev 1, 9/05

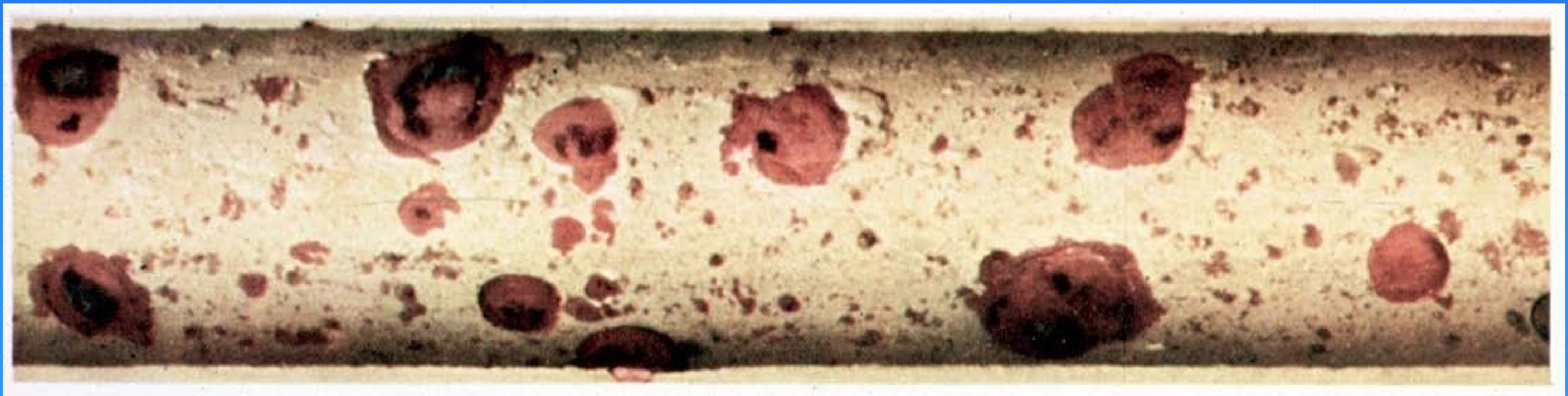
Dealloying Corrosion of Brass (Dezincification)



Dealloying Corrosion of Cu Alloys

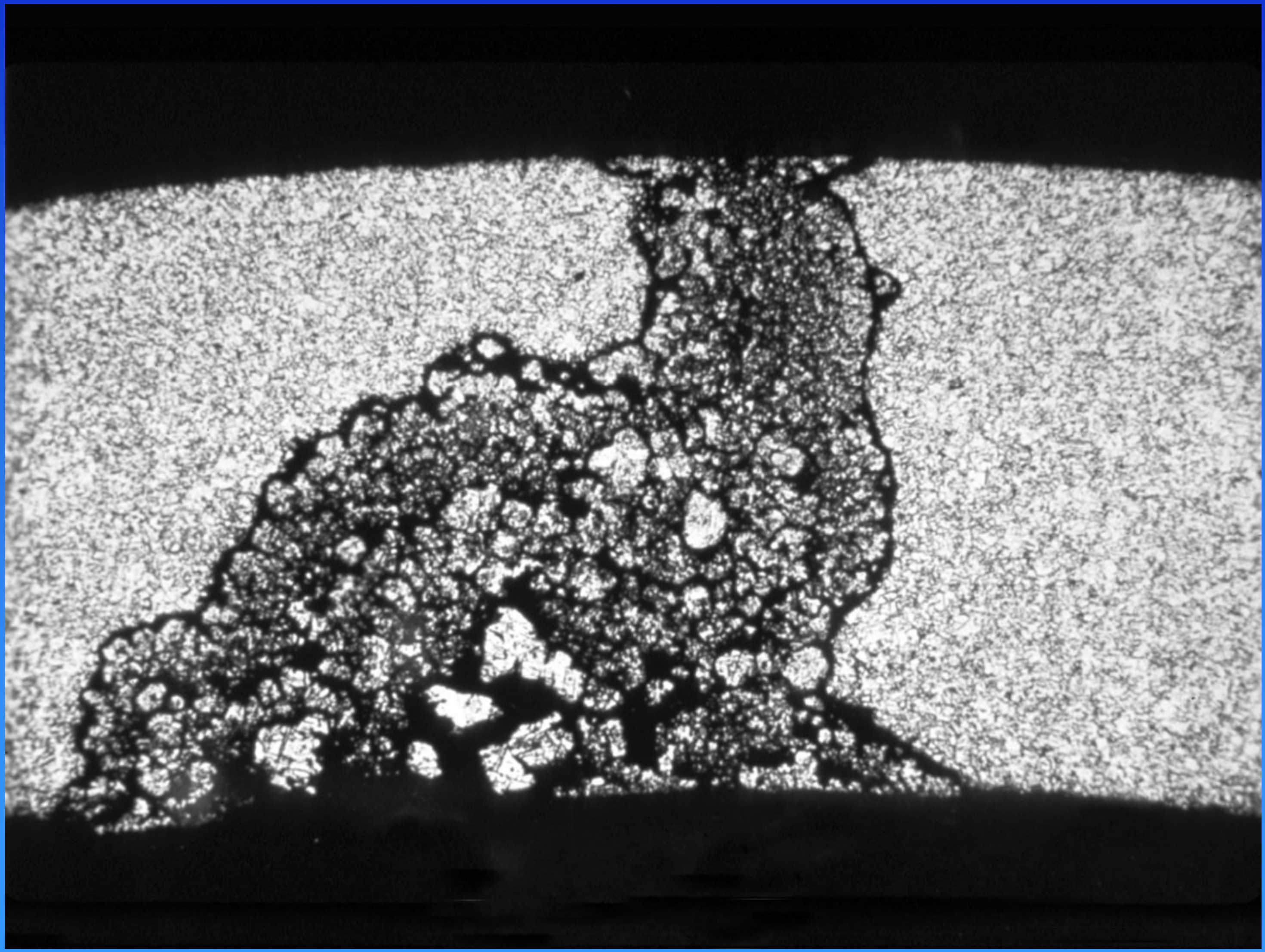


Layer type dealloying – Muntz Metal



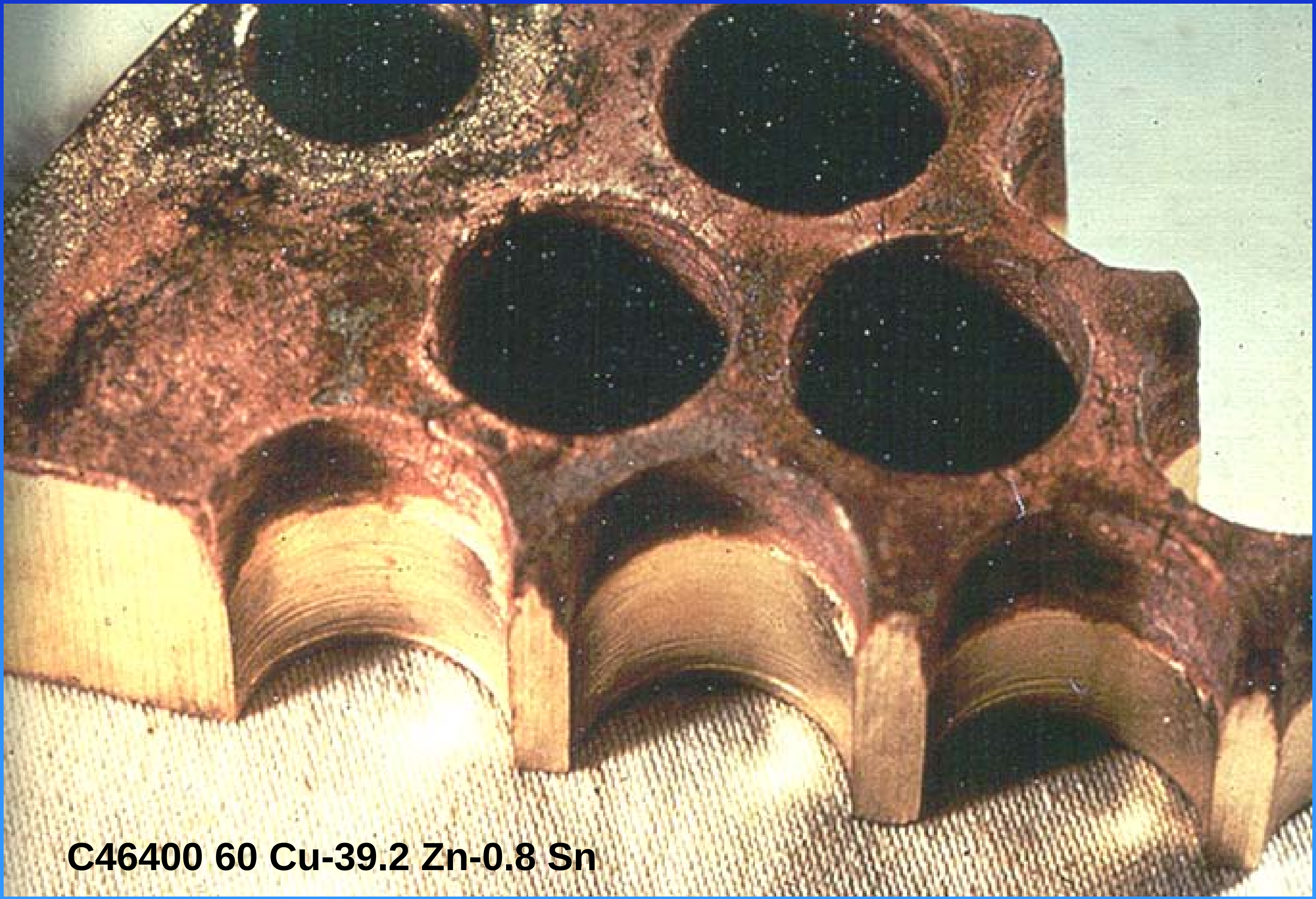
Plug type dealloying – Alumnium Brass

Plug Type Dealloying



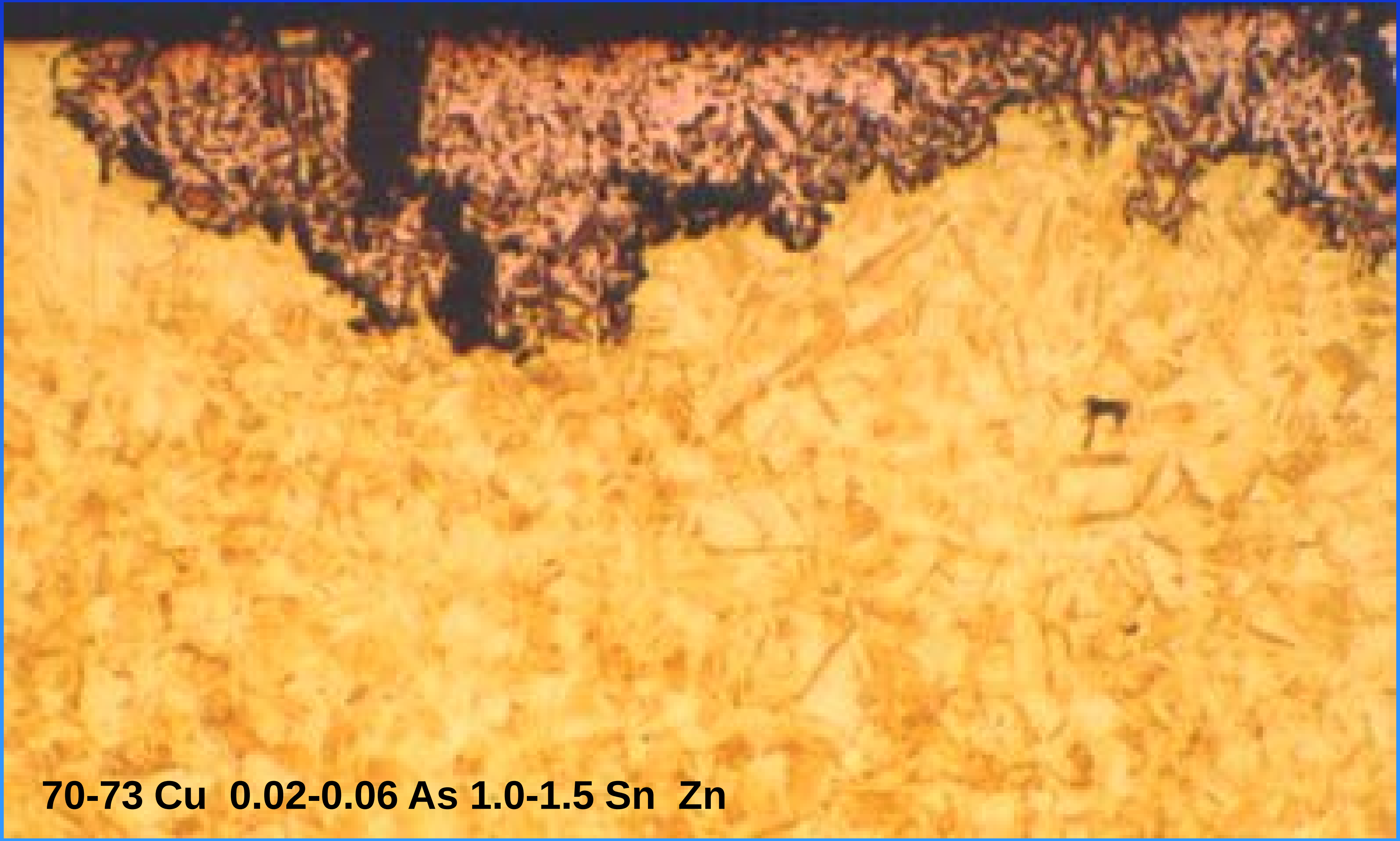
C. Gaffoglio CDA

Layer Dealloying of Naval Brass Condenser Support Plate



B.Syrett and R. Coit, 2nd ASME/ANS, 1982

Dealloying of Admiralty Brass



Dealloying Corrosion in the Courts

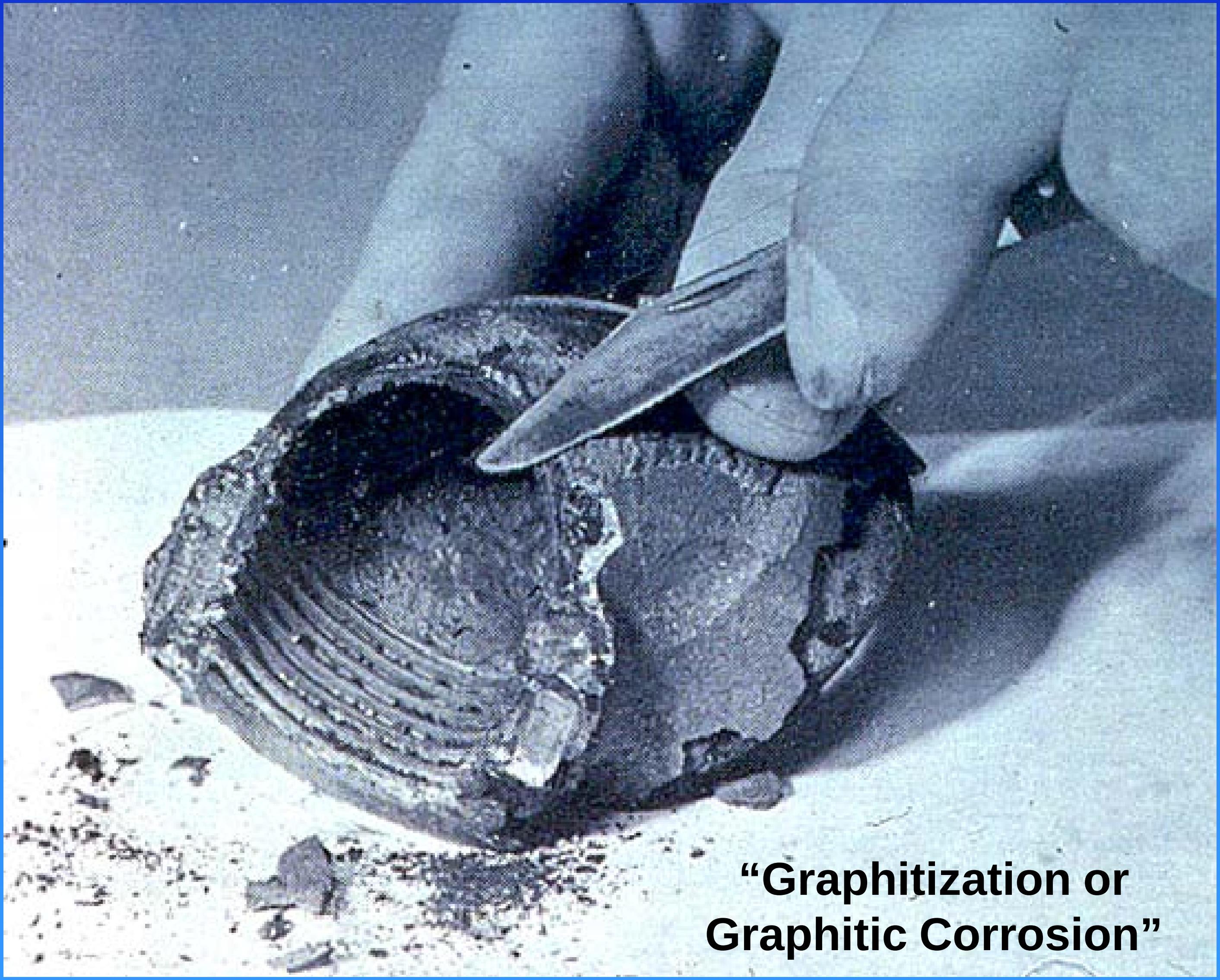
New Kitec® Fitting

Corroded Kitec® Fitting

Kitec™ Fitting Litigation

"Class Counsel to provide information to class members of the class action lawsuit involving brass KITEC® plumbing fittings that was certified by the Nevada District Court on October 16, 2006, which alleges that KITEC® Fittings are defective because they dezincify and fail when exposed to water."

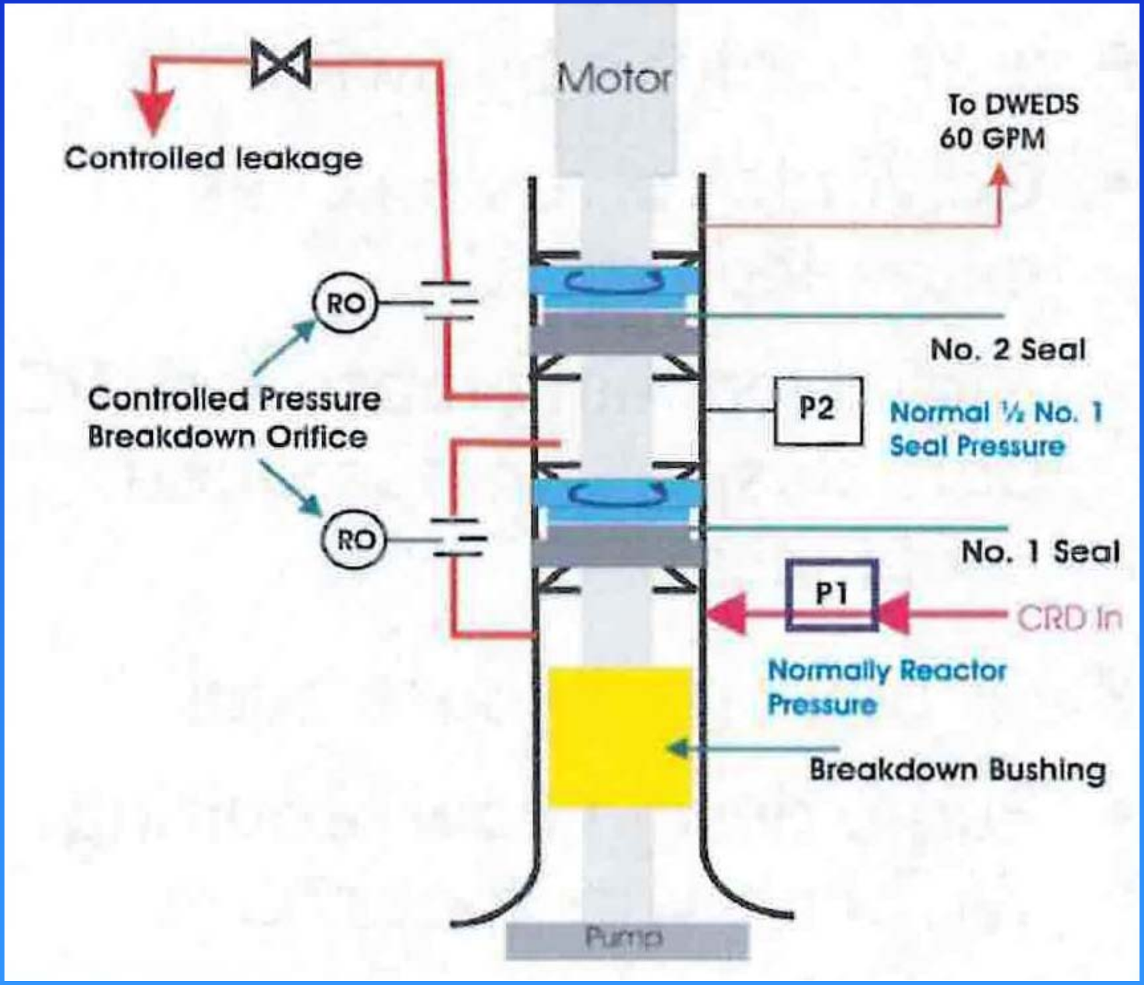
Dealloying of a Cast Iron Elbow



"Graphitization or Graphitic Corrosion"

Dealloying of a Cast Iron Pipe

“Dealloying”* of BWR Recirc Seal



River Bend recirc pumps have design issues that allow axial motion of the shaft during down powers

• Seals are replaced at each outage

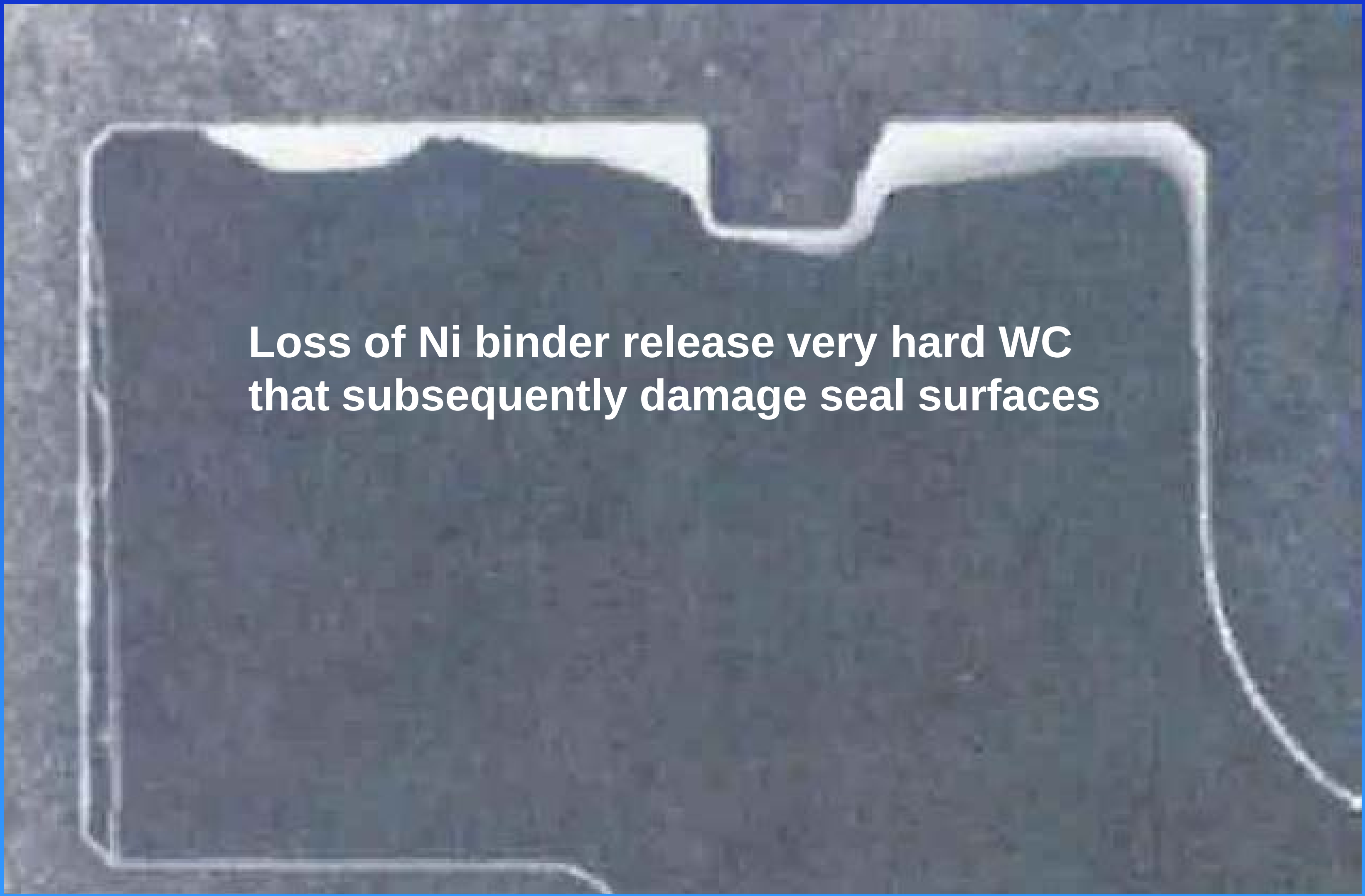
• Seals have tungsten carbide (WC) faces for greater durability

- WC in Ni binder is susceptible to “dealloying corrosion”*

*** It’s not really dealloying since the Ni binder/WC is not an alloy, per se**

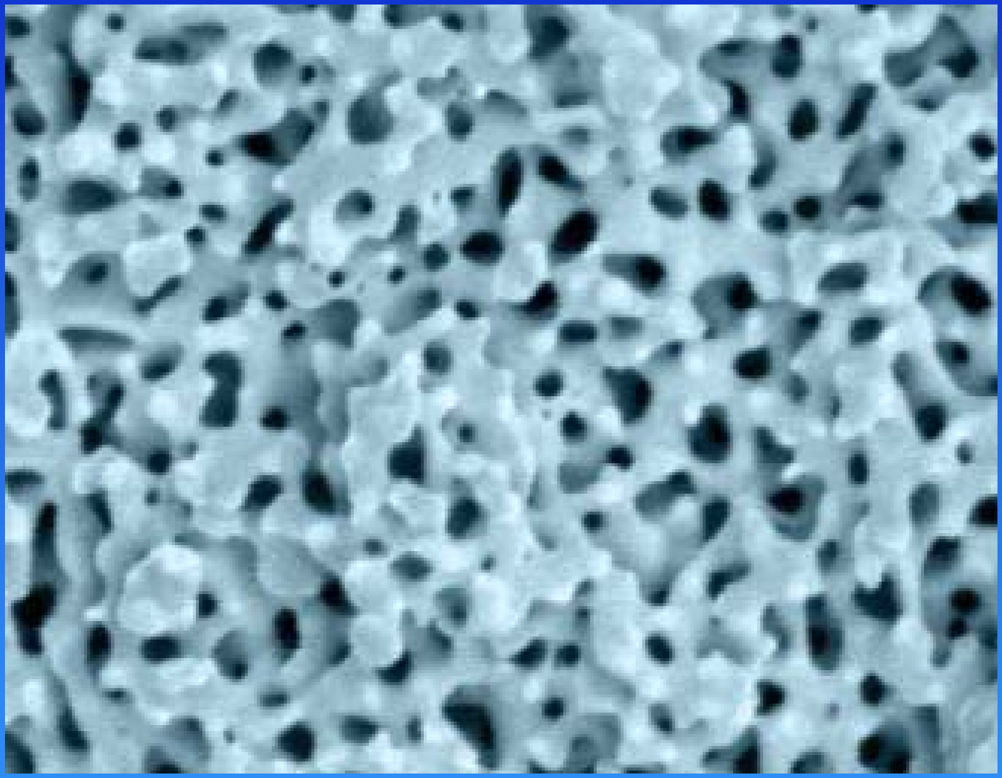
T. Caine, BWRVIP, 12/10

"Dealloying" of Tungsten Carbide

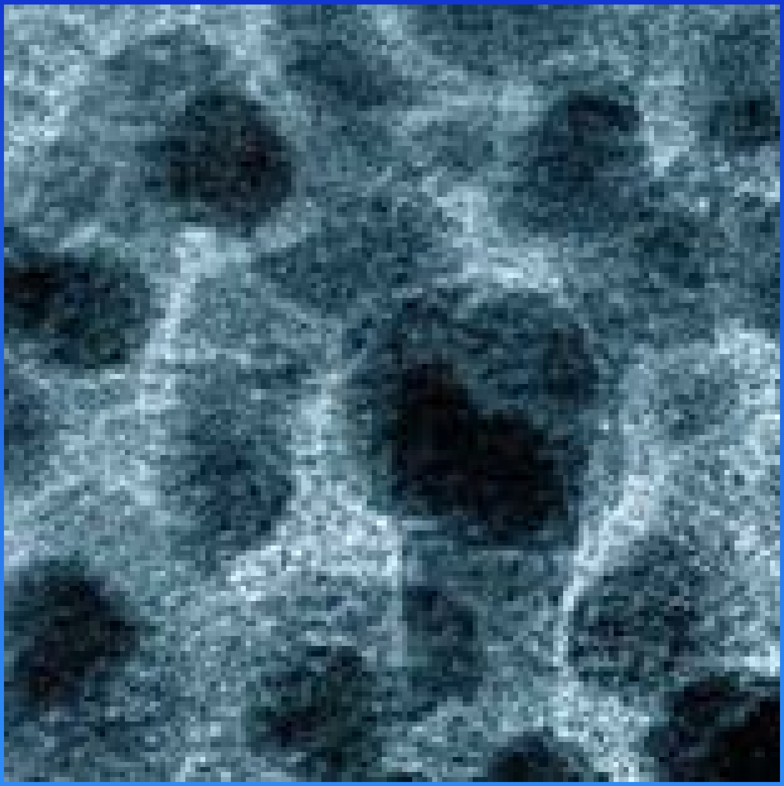


T. Caine, BWRVIP, 12/10

Synthesis of Nanoporous Metal Foam via Dealloying Corrosion



SEM of a synthesized porous Au with a the sponge-like morphology after dealloying of Ag



High-resolution TEM shows foam of nanocrystalline Au with <10 nm grain size

Velocity Phenomena

Velocity Phenomena

Velocity Phenomena Background

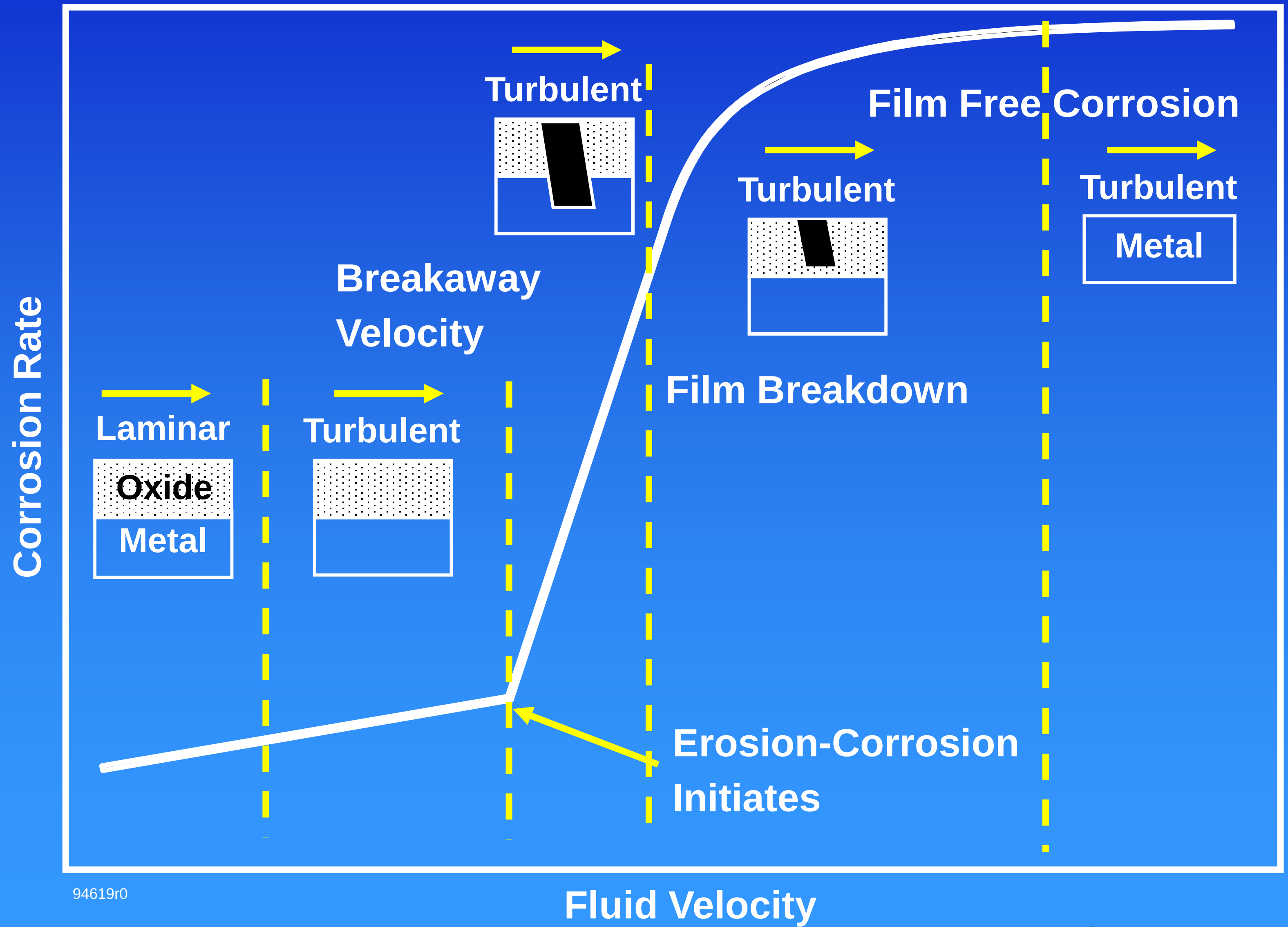
- Erosion-Corrosion
- Cavitation/Impingement
- Fretting
- Flow-accelerated corrosion (FAC)
- Very complex
- Electrochemical and mechanical aspects

Effect of Flow on Corrosion

- Disturbs equilibrium and increases dissolution
- Supplies dissolved oxygen to form passive film, minimizes differential aeration cells
- Supplies aggressive ions or could increases concentration of inhibitors
- Carries solid particles - removes protective layers, enhances corrosion
- Prevents deposition of material, minimizes differential-aeration cells

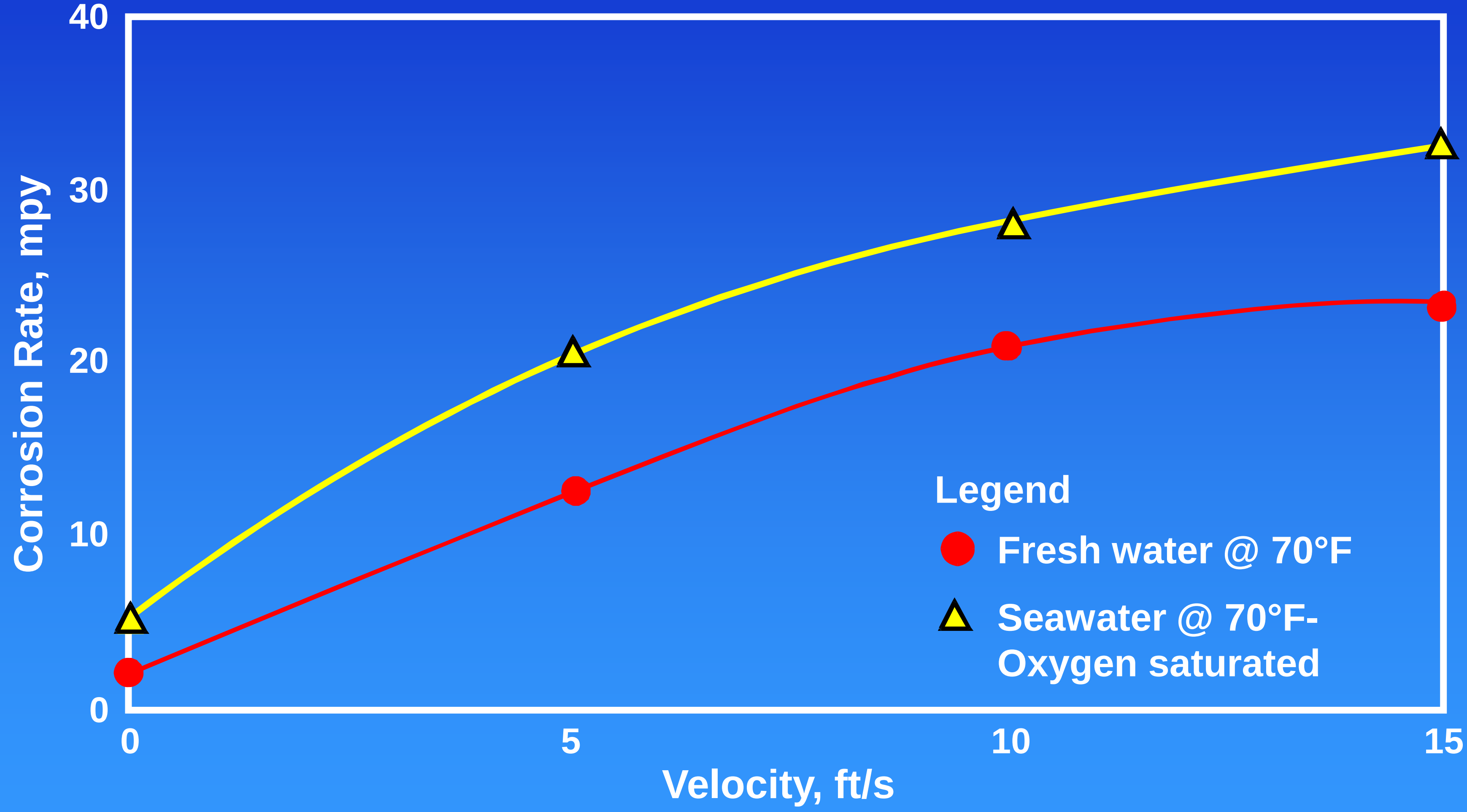
The effects of flow rate are unpredictable!

Effect of Velocity on Corrosion Rate



B. Gordon, NEDO-24819A, 1984

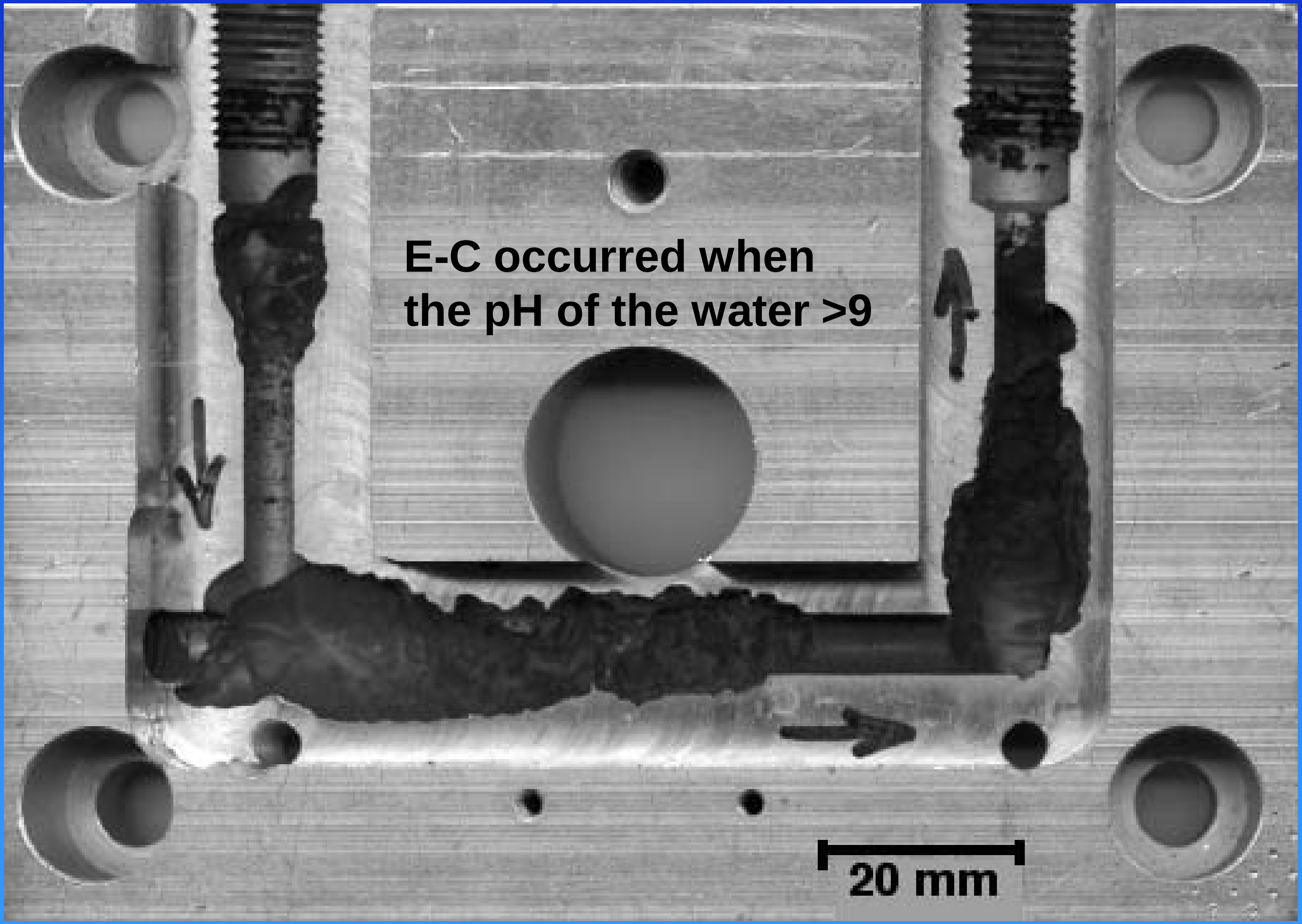
Effect of Velocity on the Corrosion Rate of Carbon Steel



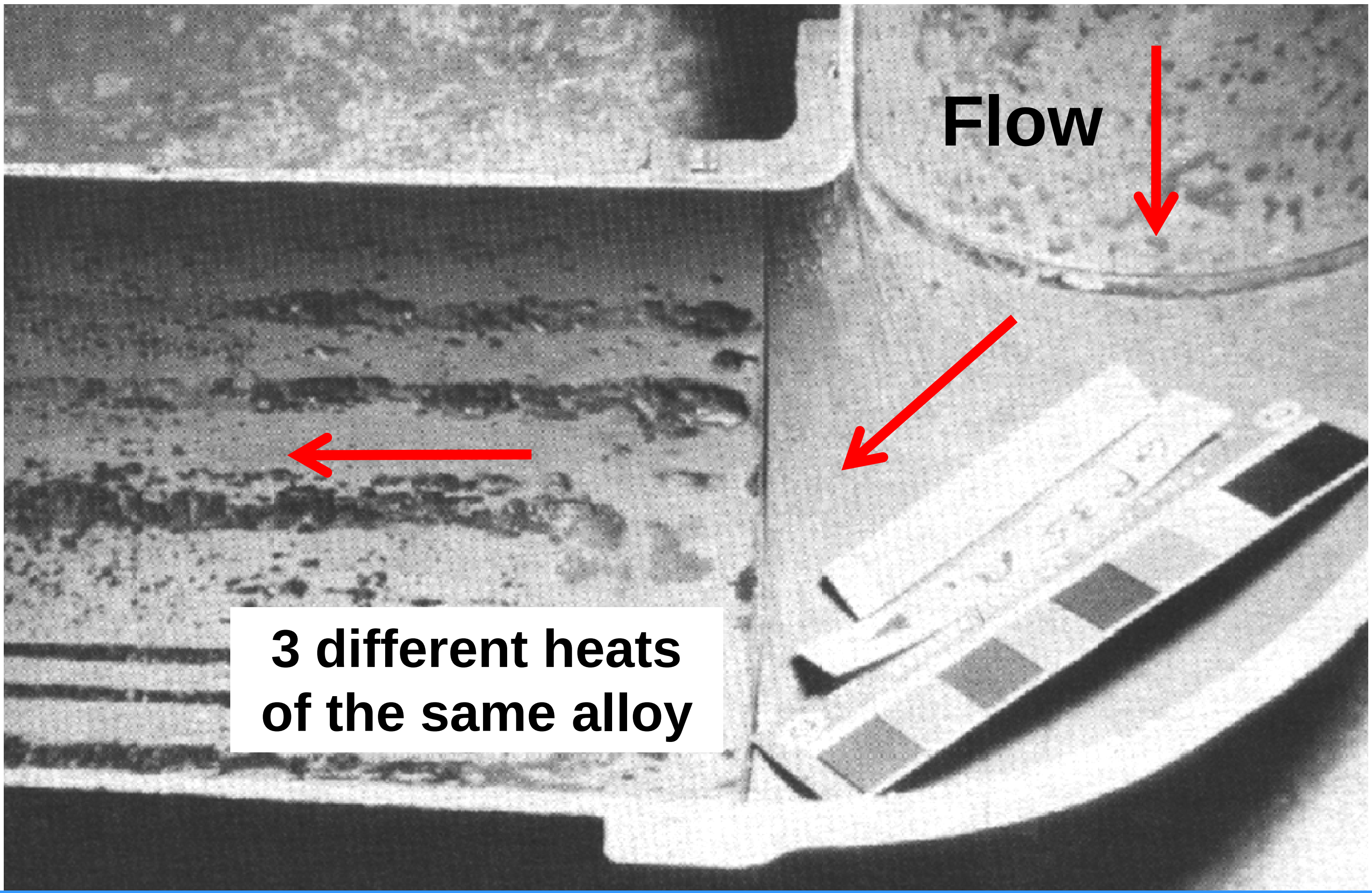
94618r0

Moss, NACE Western Region Meeting, 1966

Erosion-Corrosion of Al Heat Sink

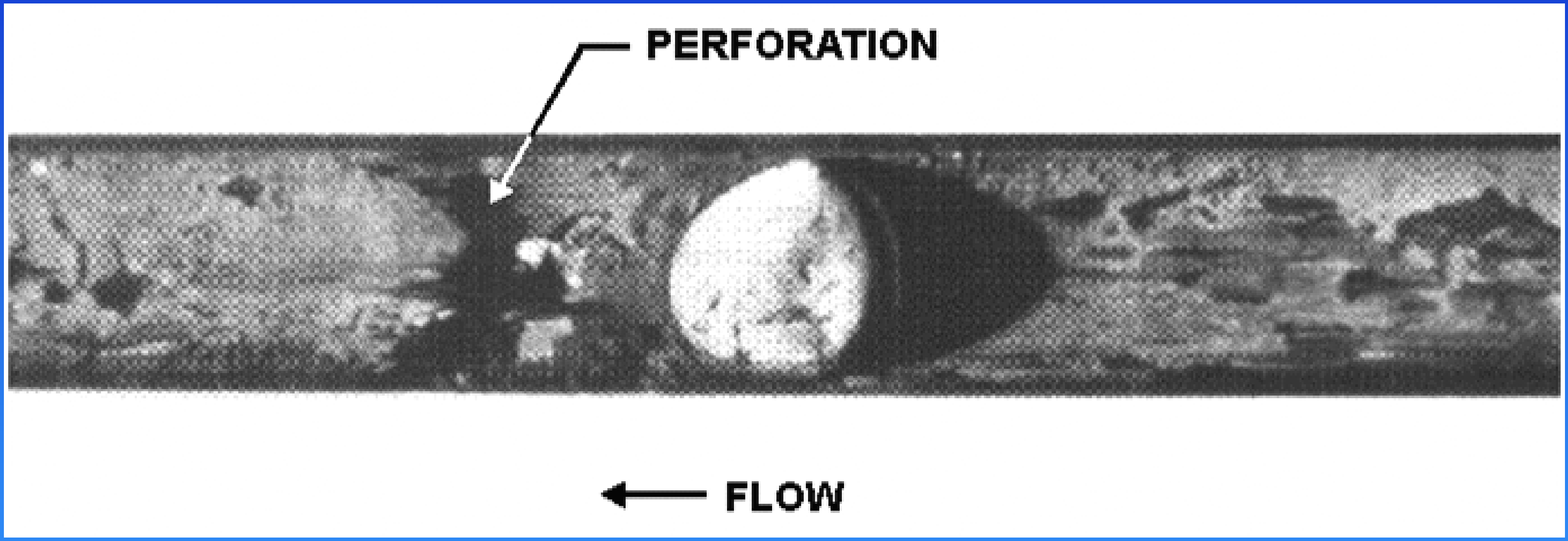


Erosion-Corrosion of 90-10 Copper-Nickel Piping in Sulfide Polluted Seawater



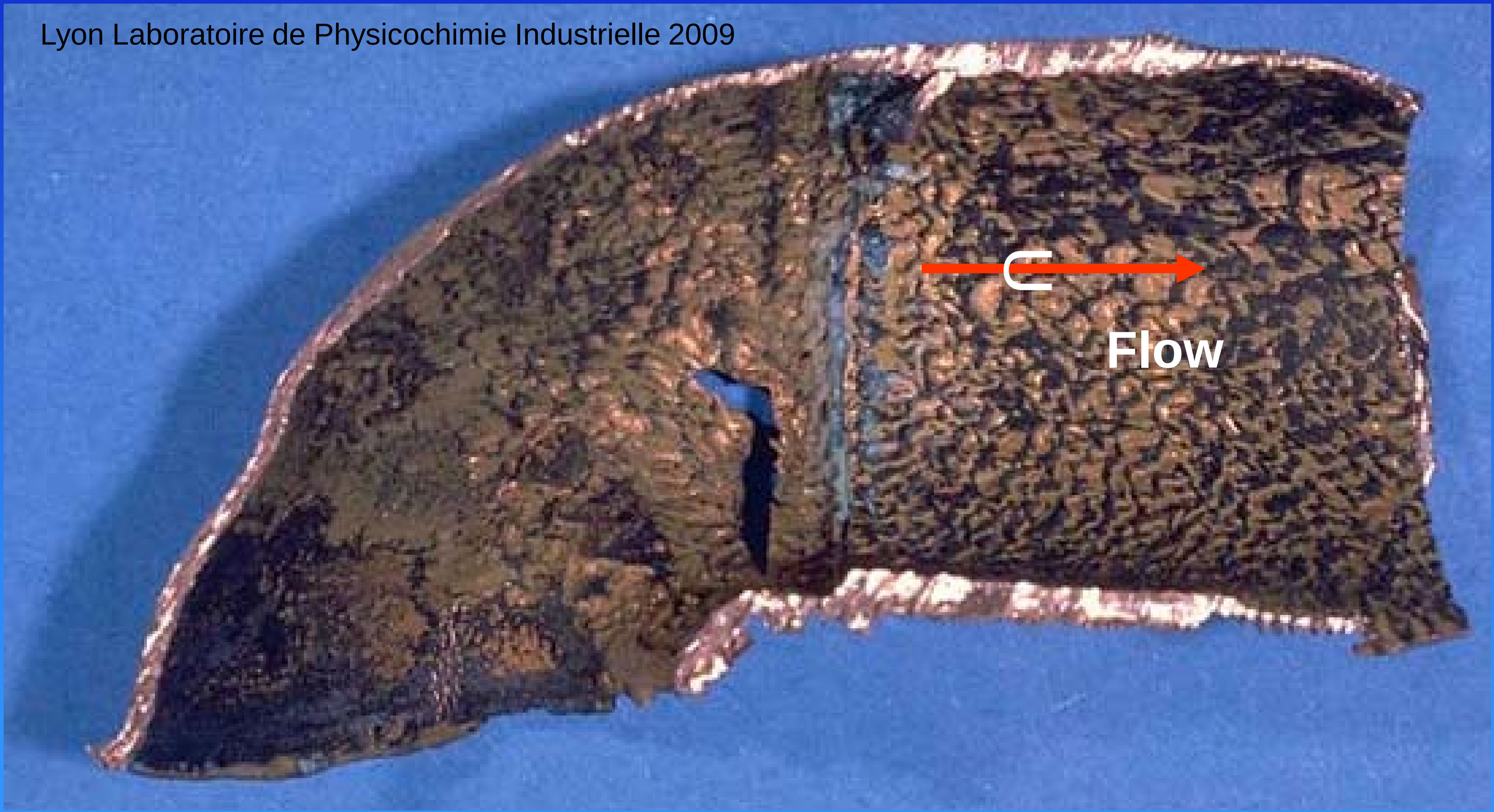
B.Syrett and R. Coit, 2nd ASME/ANS, 1982

Erosion-Corrosion of a Copper Alloy Condenser Tube Due to Blockage of Flow by a Pebble



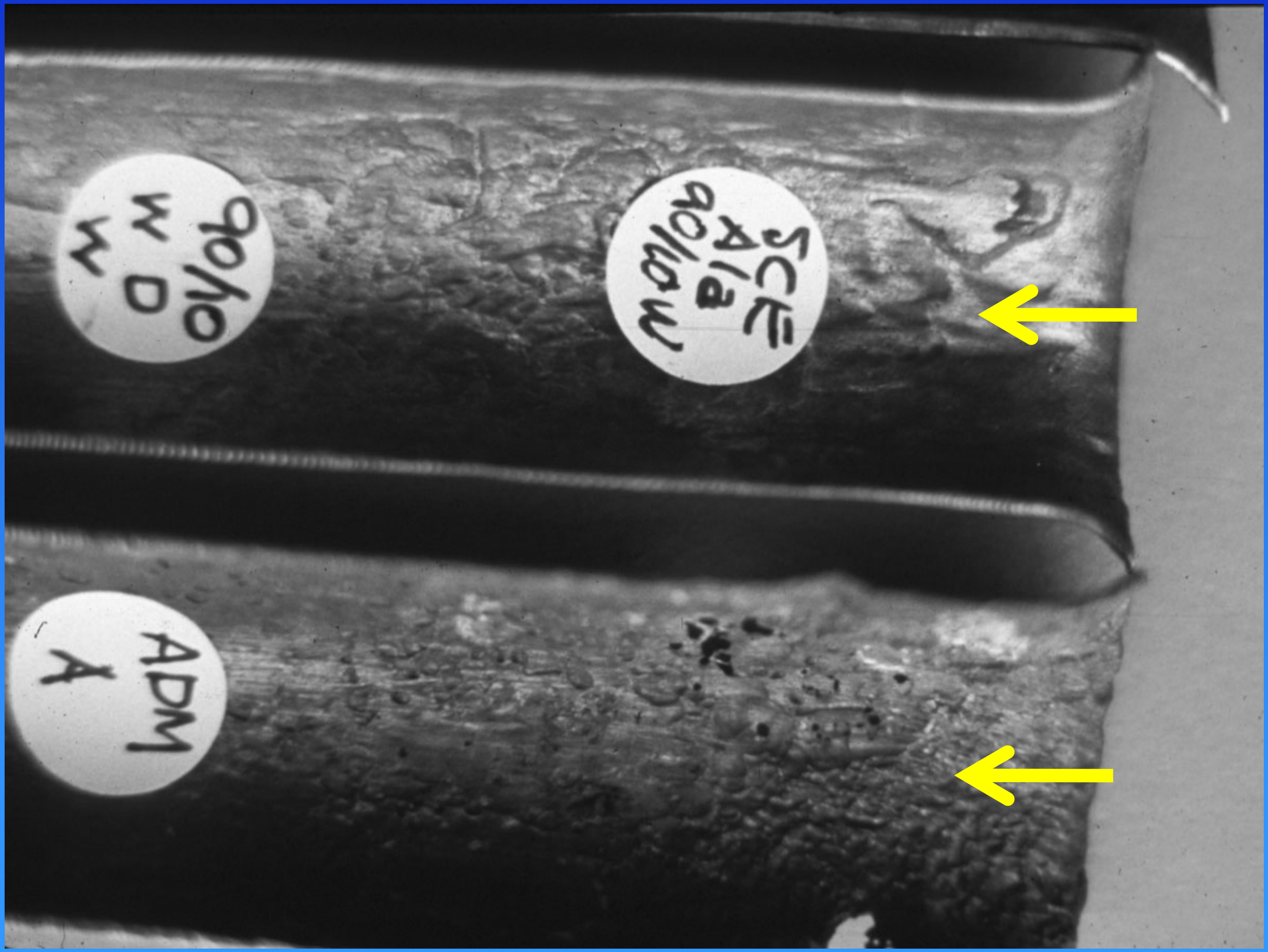
B.Syrett and R. Coit, 2nd ASME/ANS, 1982

Copper Erosion-Corrosion



"Horseshoes" are characteristic of E/C that are oriented with the closed end of the features pointing in the direction of source of flow. "Horses walk upstream."

Inlet-End E/C of 90-10 Cu-Ni and Admiralty Brass Condenser Tubes



Structural Integrity Associates

BWR Copper Cooler Leaks

Structural Integrity Associates

Condenser Bay Cooling Coil E/C

Belzona E/C Mitigation

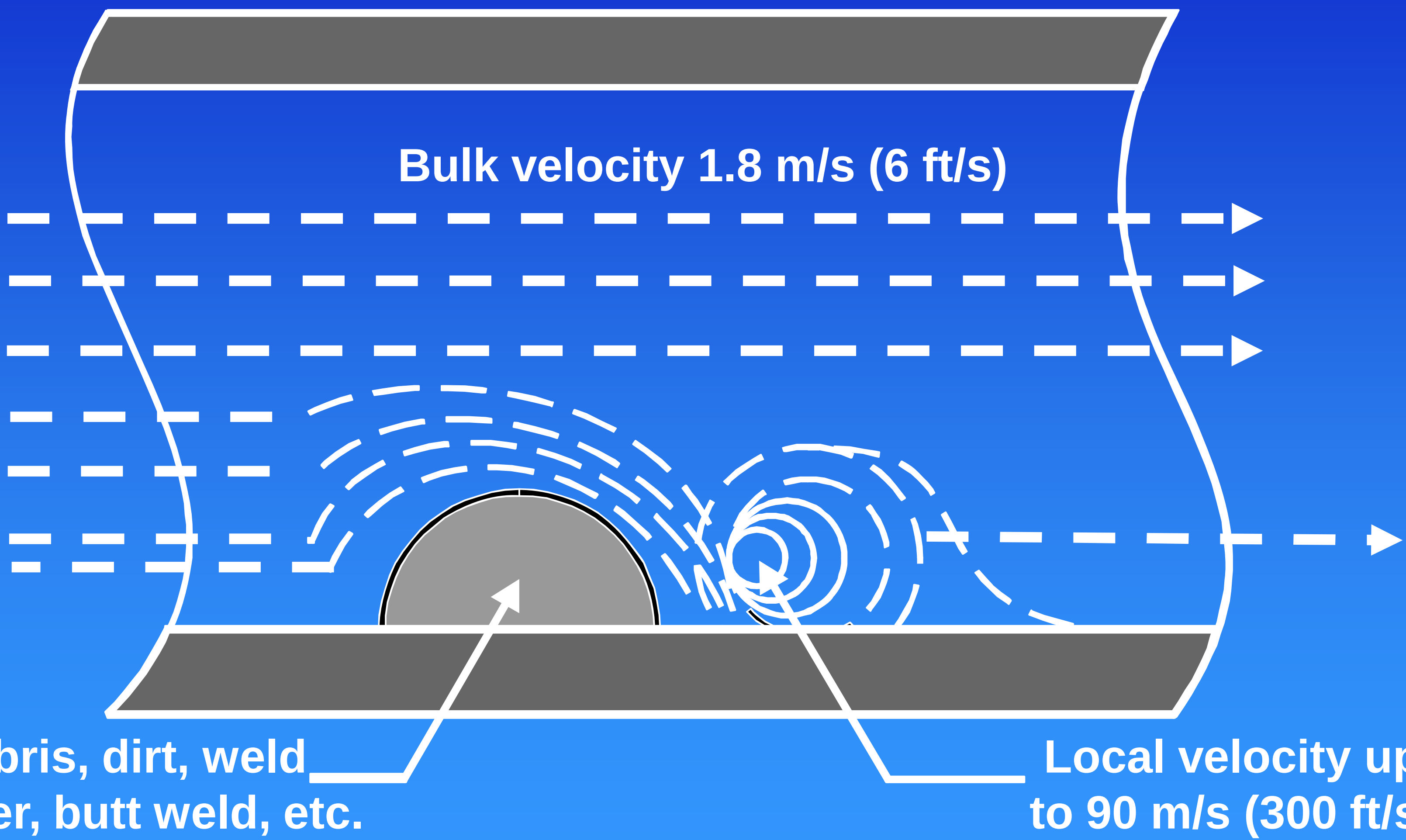
Recommended Maximum Flow Velocities for Copper Piping/Tubing

Organization	<10ºC (<50ºF)	<60ºC (<140ºF)	>60ºC (>140ºF)
ASM Committee on Corrosion of Copper (US)		0.6 – 0.9 m/s (2 – 3 ft/s)	
Copper Development Association (US)	2.4 m/s (8 ft/s)	1.5 m/s (5 ft/s)	0.6 – 0.9 m/s (2 – 3 ft/s)
Foundation for Water Research (UK)		0.5 – 1.0 m/s (1.6 – 3.2 ft/s)	0.5 – 2.0 m/s (1.6 – 6.4 ft/s)
Canadian Copper and Brass Development Association		1.5 m/s (5 ft/s)	0.9 – 1.2 m/s (3 – 4 ft/s)

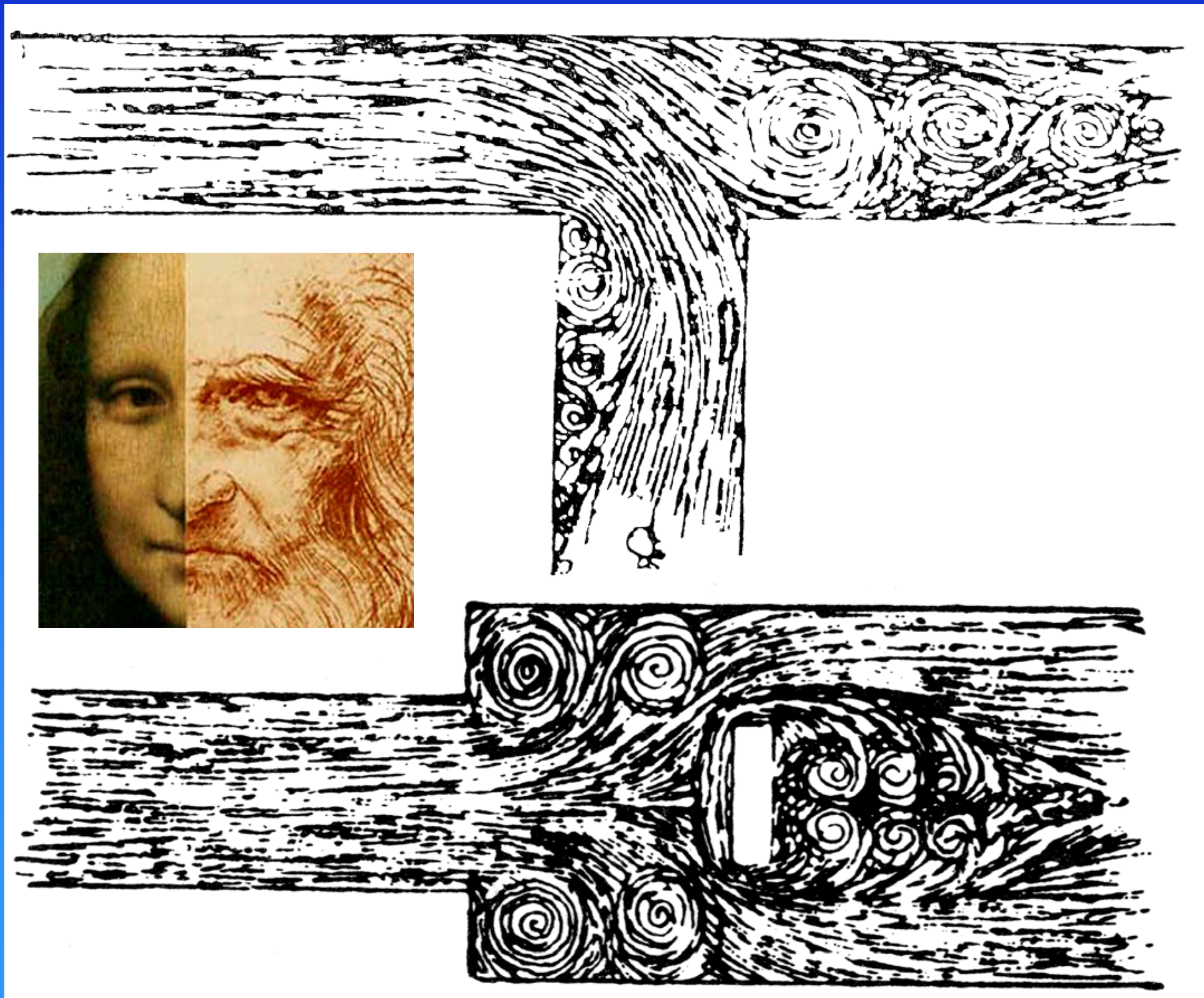
E/C of Cu Alloys in LWRs

- **E/C of Cu alloys (e.g., Cu-Zn Admiralty brass) used in condensers and heat exchangers can be a significant problem elsewhere in the circuit**
  - **Release of Cu cations introduces another reduction reaction that can raise the corrosion potential and exacerbate various corrosion modes:**
    - **BWR fuel cladding**
    - **HWC effectiveness**
    - **Secondary side of PWR steam generators**
- **Led to the replacement of Cu-Zn, Cu-Ni or Cu-Al condenser and heat exchanger tubing with stainless steels or for seawater cooled stations, super stainless steel (e.g., AL-6X) or titanium tubing**

Blockage Induced Erosion-Corrosion



Flow Separations, Reattachment and Eddies

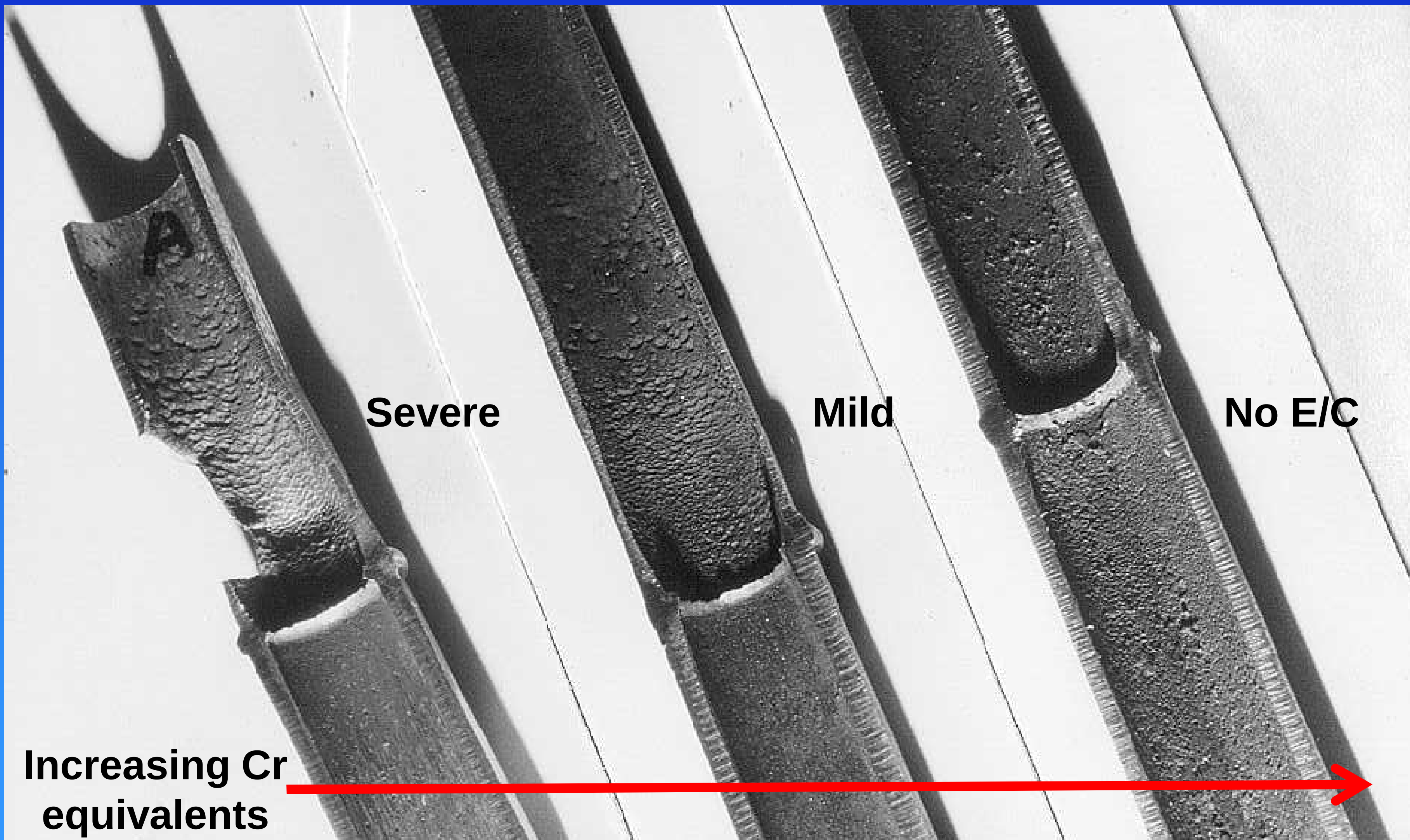


In branched channel

Expansion and blocking

L. da Vinci, ~1500

Erosion Corrosion after Butt Welds



LWR Flow-Accelerated Corrosion (FAC)

- FAC = normally protective oxide layer on a carbon steel surface dissolves in a fast flowing water
- Underlying metal corrodes to re-create the oxide and, thus, the metal loss continues at a constant rate
- FAC was distinguished from erosion corrosion:
  - FAC does not involve impingement of particles, bubbles, or cavitation
  - By contrast to E/C, FAC involves dissolution of normally poorly-soluble oxide by combined electrochemical, water chemistry and mass-transfer phenomena

LWR FAC

- **FAC is frequently localized at areas of high turbulence that are associated with:**
  - ♦ **Geometrical discontinuities or abrupt changes in flow direction**
- **Electrochemical and mechanical aspects for FAC. The water or steam flow past the carbon steel component may increase the kinetics of corrosion:**
  - ♦ **Corrosion kinetics may increase under both laminar and turbulent flow**
    - ○ **Increase transport of DO to the carbon steel surface**
    - ○ **Increase removal rate of oxidized species from the carbon steel surface**

Some NRC FAC Documents

- BL-87-01 - Thinning of Pipe Walls in Nuclear Power Plants
- GL89008 - Erosion/Corrosion-Induced Pipe Wall Thinning
- IN97084 - Rupture in Extraction Steam Piping as a Result of Flow-Accelerated Corrosion
- IN92007 - Higher ... Erosion/Corrosion in Unisolable Reactor Coolant Pressure Boundary Piping Inside Containment at a BWR
- IN93021 - Summary of ... Observations Compiled During Engineering Audits or Inspections of Licensee Erosion/Corrosion Programs
- IN91087 - Rapid Flow-Induced Erosion/Corrosion of Feedwater Piping
- IN91018 - High-Energy Piping Failures Caused by Wall Thinning
- IN88017 - Summary of Responses to NRC Bulletin 87-01, "Thinning of Pipe Walls in Nuclear Power Plants"
- IN87036 - Significant Unexpected Erosion of Feedwater Lines

LWR FAC Factoids

- FAC is a corrosion mechanism that degrades carbon steel pipes and fittings (not LAS, SS, etc.)
- Normally protective magnetite (Fe_3O_4) oxide layer on CS dissolves and is mechanically removed in flowing water (one phase) or wet steam (two phase)
- FAC can reduce or eliminate the protective oxide layer and lead to a rapid removal of the base material
- FAC has caused leaks, catastrophic and deadly failures in nuclear and fossil power plants
- Utilities are conducting large inspection programs to avoid FAC related problems in BOP piping and vessels

FAC Rate

- **The rate of metal loss depends on a complex interplay of many parameters including:**
  - **Dissolved oxygen content and pH**
  - **Material composition (e.g., minor alloying elements Cr, Cu and Mo)**
  - **Fluid hydrodynamics (e.g. velocity, geometry, steam quality, temperature and mass transfer)**
- **Suggested reading: EPRI TR-106611, 1996**

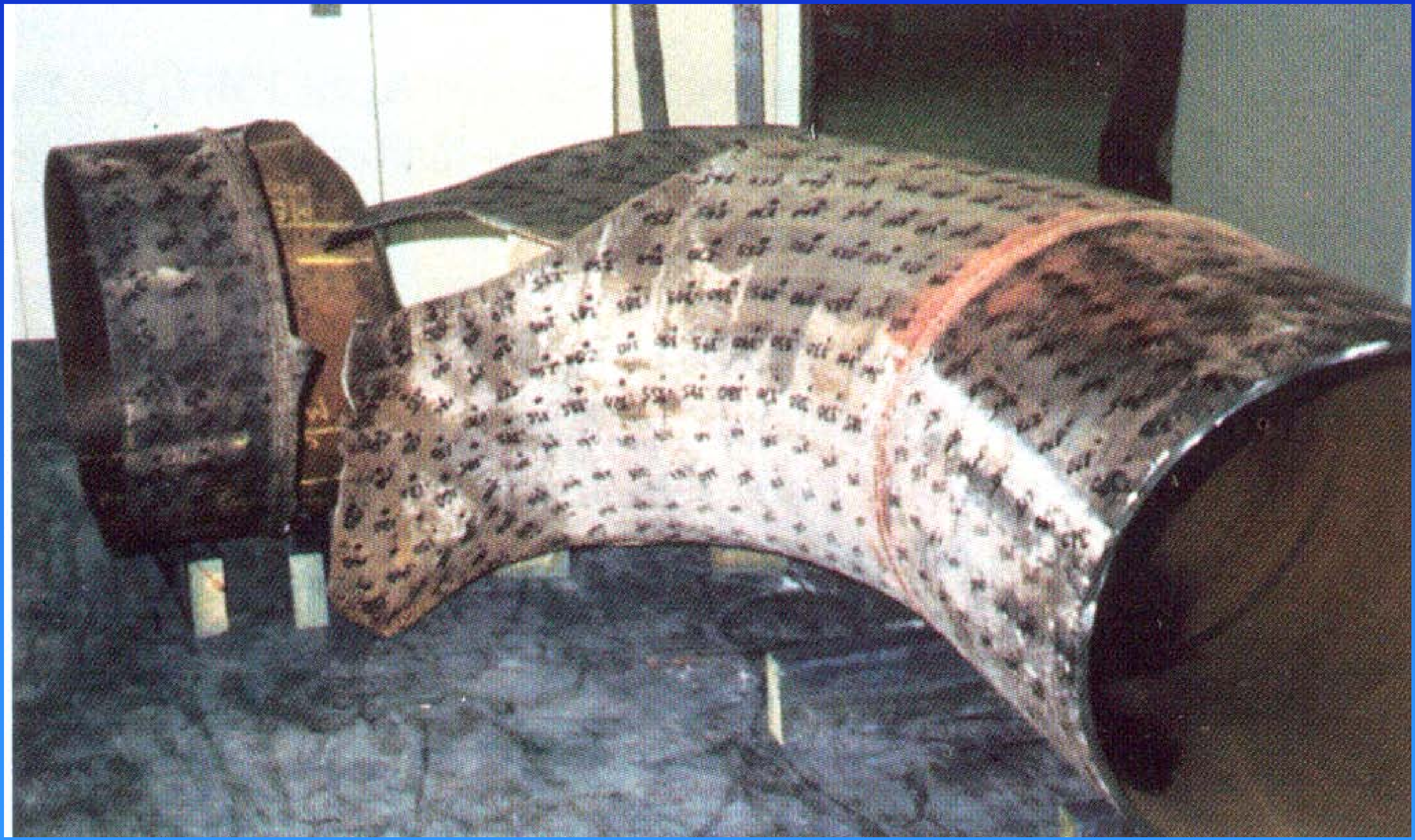
Consequences of FAC

- In addition to degrading piping and vessels, the iron oxides removed by FAC;
  - Form the majority of the feedwater iron
  - Can foul flow measurement devices
  - Can foul polishers
  - Increase the radiation levels in the BOP

LWR FAC History – Surry 2 – 1986

- **12/9/86: 46 cm (18”) carbon steel condensate system elbow rupture in the secondary side of the Surry 2 PWR <u>kills</u> 4 and <u>injures</u> 4**
- **Surry 2 was the first time “E/C” in single phase system was observed in a US LWR**
- **US LWRS have since included inspections of single phase flow carbon steel in their ISI programs**
- **EPRI subsequently develops CHEC™, CHECMATE™ and CHECWORKS™ FAC codes**

Surry 2 Condensate Elbow FAC

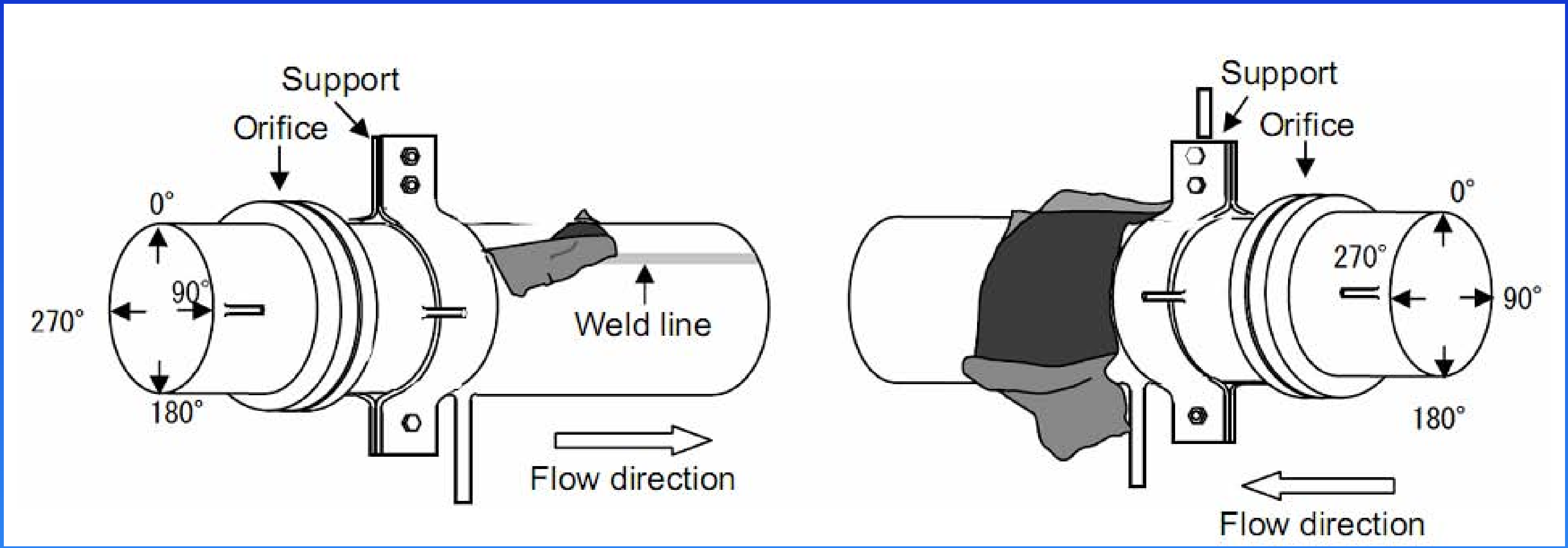


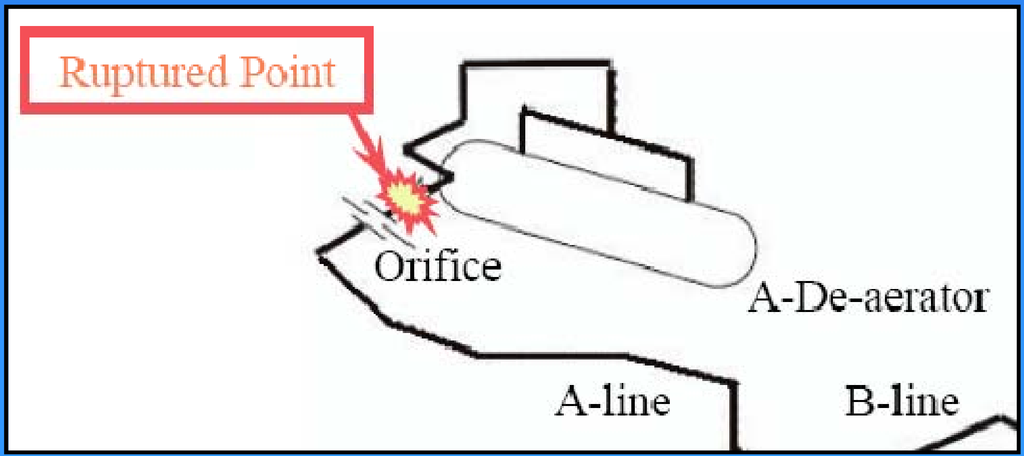
EPRI TR-106611, 1996

More Recent LWR FAC – Mihama 3 – 2004

- 8/9/04: 56 cm (22") carbon steel steam line rupture Mihama 3 PWR <u>kills</u> 5 and severely <u>injures</u> 6
- Kansai Electric Power (Kepco) admitted that it was told in 4/03 that this pipe was "a safety threat"
- The 149ºC (300ºF) steam pipe was only inspected after fitting in 1976 and not examined since because "it was not expected to corrode so quickly"
- Scheduled for re-inspection August 14 (five days after the rupture)
- Kepco admitted that the pipe had dangerously corroded 96% to just 0.4 mm (20 mils) from its original 10 mm (0.39 in) thickness

Mihama 3 FAC Location

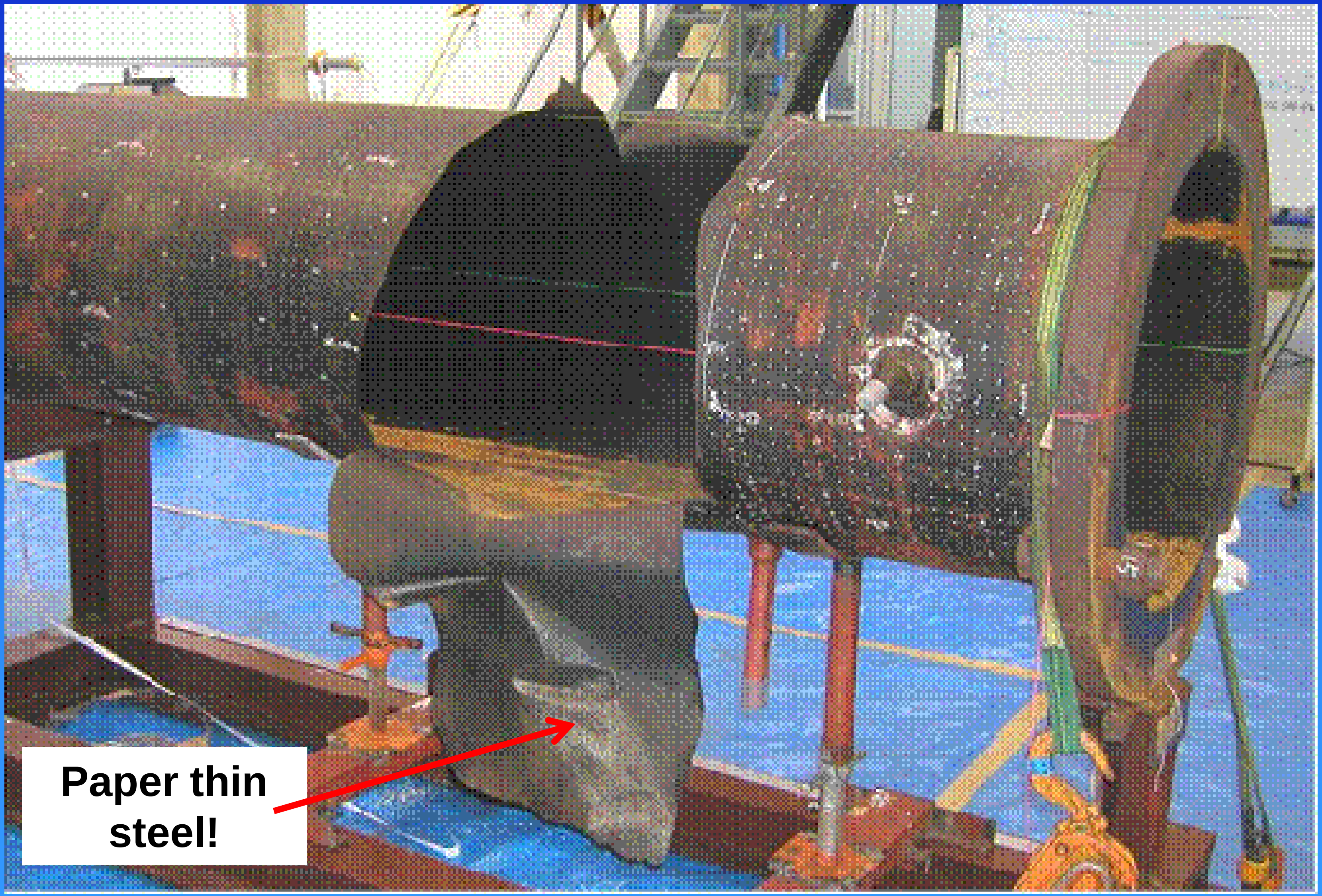




Mihama 3 FAC

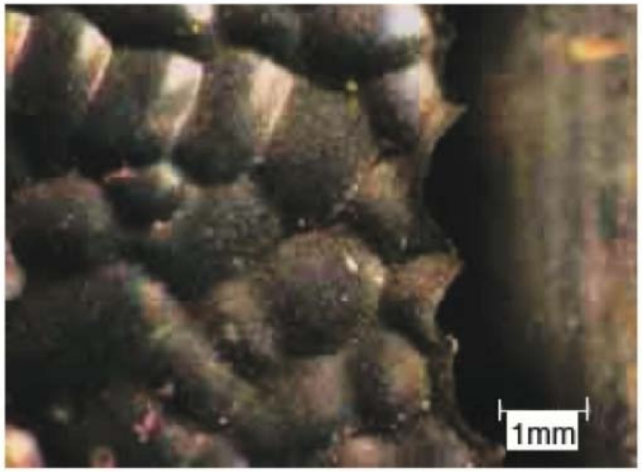
Mihama 3 FAC

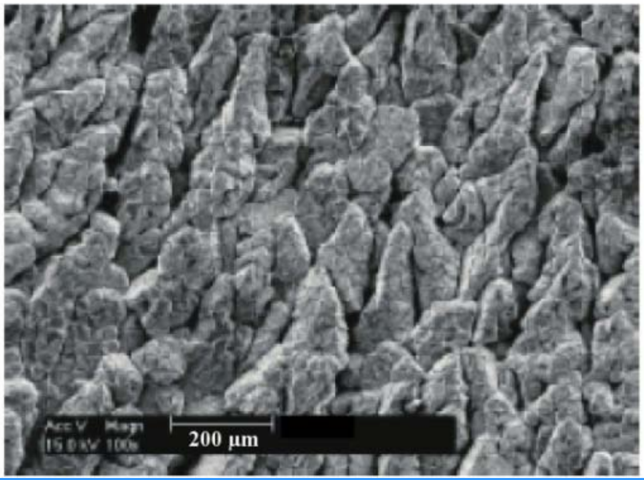
Mihama 3 FAC



Mihama 3 FAC

- Kepco spokesman Nakano-san: "We conducted visual inspections, but never made ultrasonic tests, which can measure the thickness of a steel pipe."
- Deputy plant manager Kokado-san: "We thought we could delay the checks until this month."
- Kokado-san: "We had never expected such rapid corrosion."
- Police spokesman Miyamoto-san: "Police are investigating the company on suspicion of corporate negligence resulting in death."





Structural Integrity Associates

FAC at Low Temperatures

- FAC typically occurs at ~90–230°C (200–450°F)
- FAC at lower temperatures (e.g., RT) has occurred!
  - ♦ Raised questions on CHECWORKS™ FAC model
- PWR FAC low temperature vulnerable areas and summary:
  - ♦ Between the exit of the condensate polishers and the amine injection location
  - ♦ Downstream of the blow down demineralizer
  - ♦ FAC of ~0.25 mm/y (10 mpy) observed
  - ♦ Perforations or ruptures would be likely to occur within the lifetime of a plant

EPRI, 1013474, 2006

FAC at Low Temperatures

- Damage to BWRs may be less common, but similar FAC rates observed
- FAC model predictions are quite good with no "low temperature" bias
- Utilities should:
  - Conduct inspections to determine if any FAC
  - Repairs and/or system redesign may be required
    - Change material or Cr coatings
    - PWRs move amine injection point
    - BWRs inject O_2

EPRI, 1013474, 2006

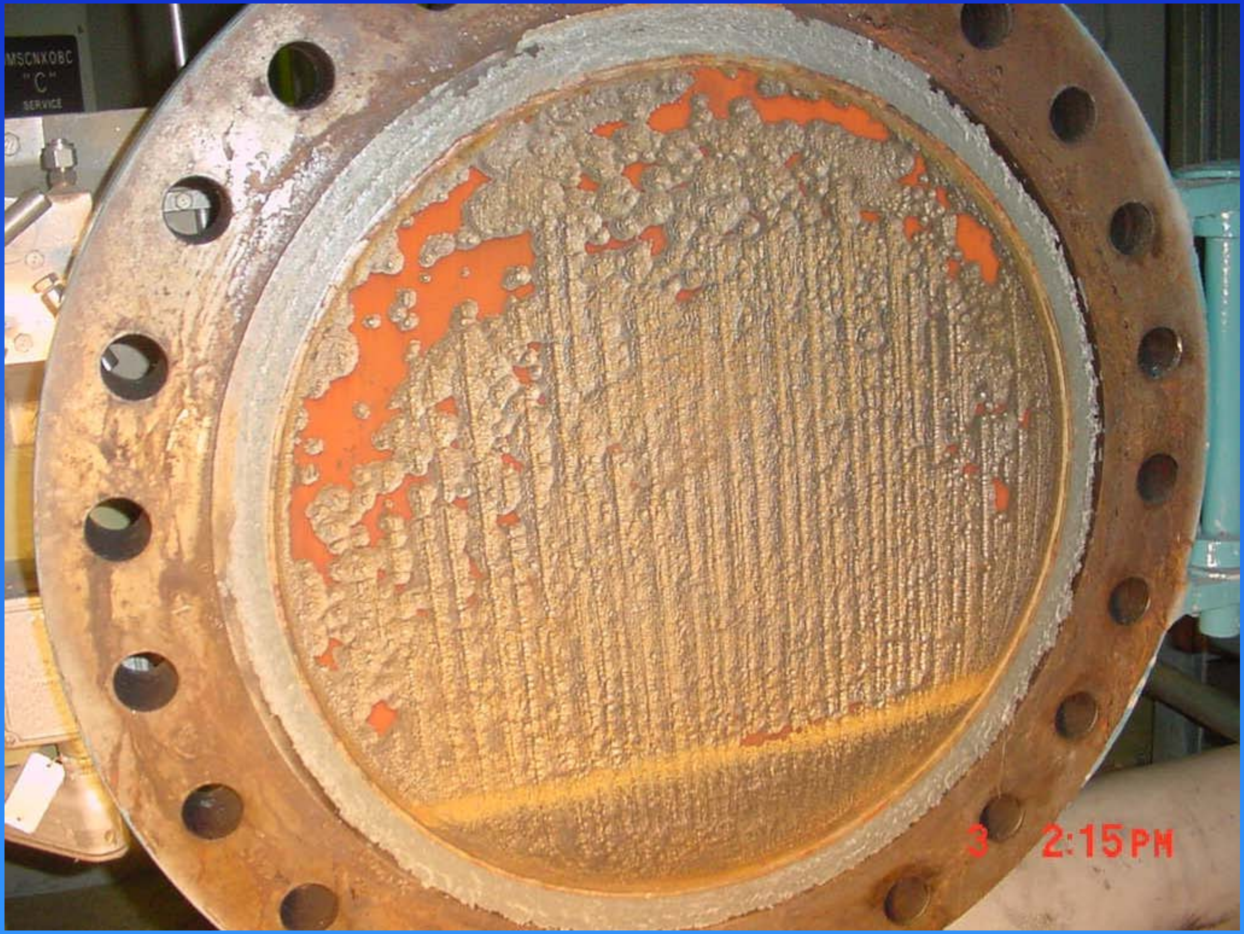
South Texas Project
Low Temperature FAC

2004 - Piping downstream of the condensate polisher

32 – 54°C (90 – 130°F)
2.7 m/s (8.9 f/s)
pH 7
5 ppb DO

EPRI, 1013474, 2006

Palo Verde Unit 1 Low Temperature FAC



2003 - Resin traps downstream of the condensate polisher

57°C (135°F)
pH 7
1-3 ppb DO

EPRI, 1013474, 2006

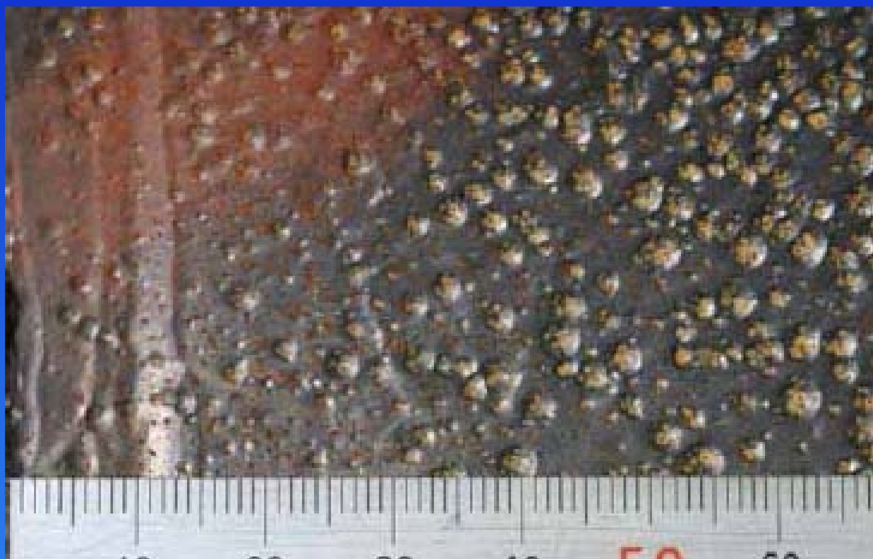
Surry Unit 1 Low Temperature FAC

2006 – 1st elbow downstream of the demineralizers

24 – 52°C (75 – 125°F)
2.78 m/s (9.1 f/s)

EPRI, 1013474, 2006

Fukushima Daini Unit 1
Low Temperature FAC



35°C (95°F)
1 m/s (3 f/s)
<10 ppb DO

2005 – CRD straight pipe downstream of an orifice

EPRI, 1013474, 2006

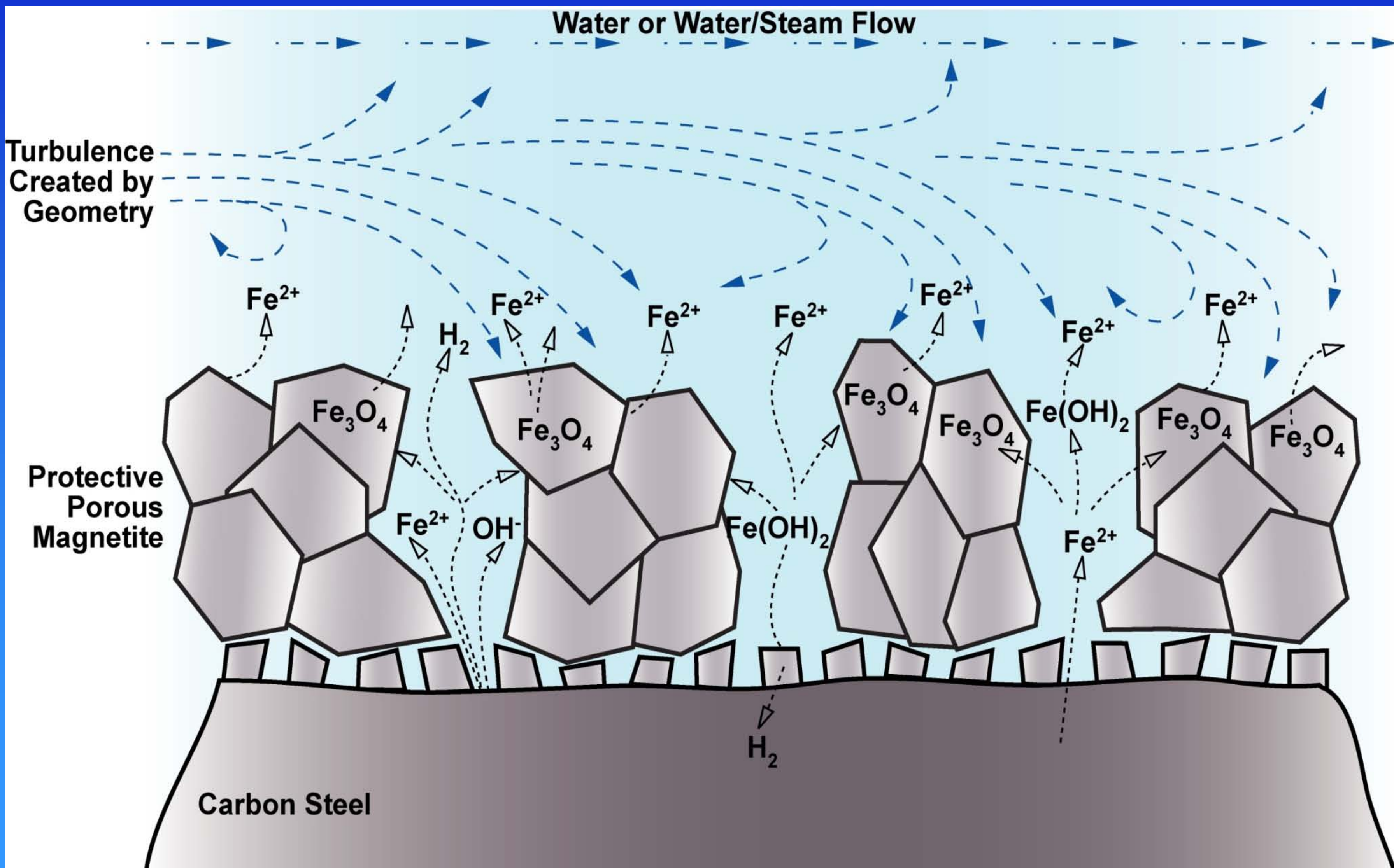
Nine Mile Point Unit 1
Low Temperature FAC

2002 – Reactor building closed loop cooling system (RBCLC) small-bore CS piping with threaded fittings

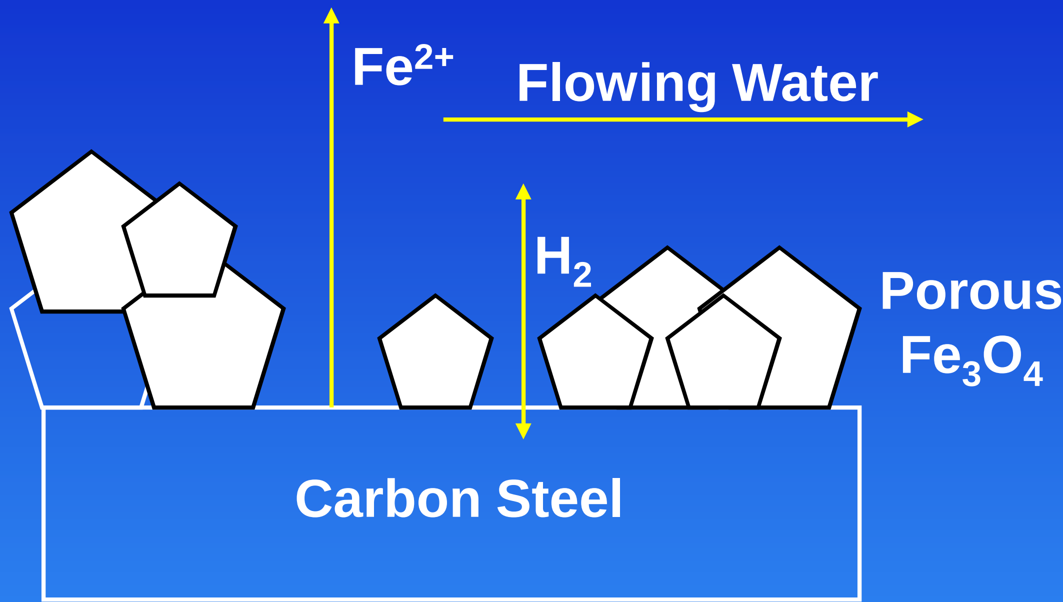
49°C (120°F)
pH 6.5
~0 ppb DO

EPRI, 1013474, 2006

Mechanism of FAC in Flowing Turbulent Flow



Basic FAC Mechanism Details



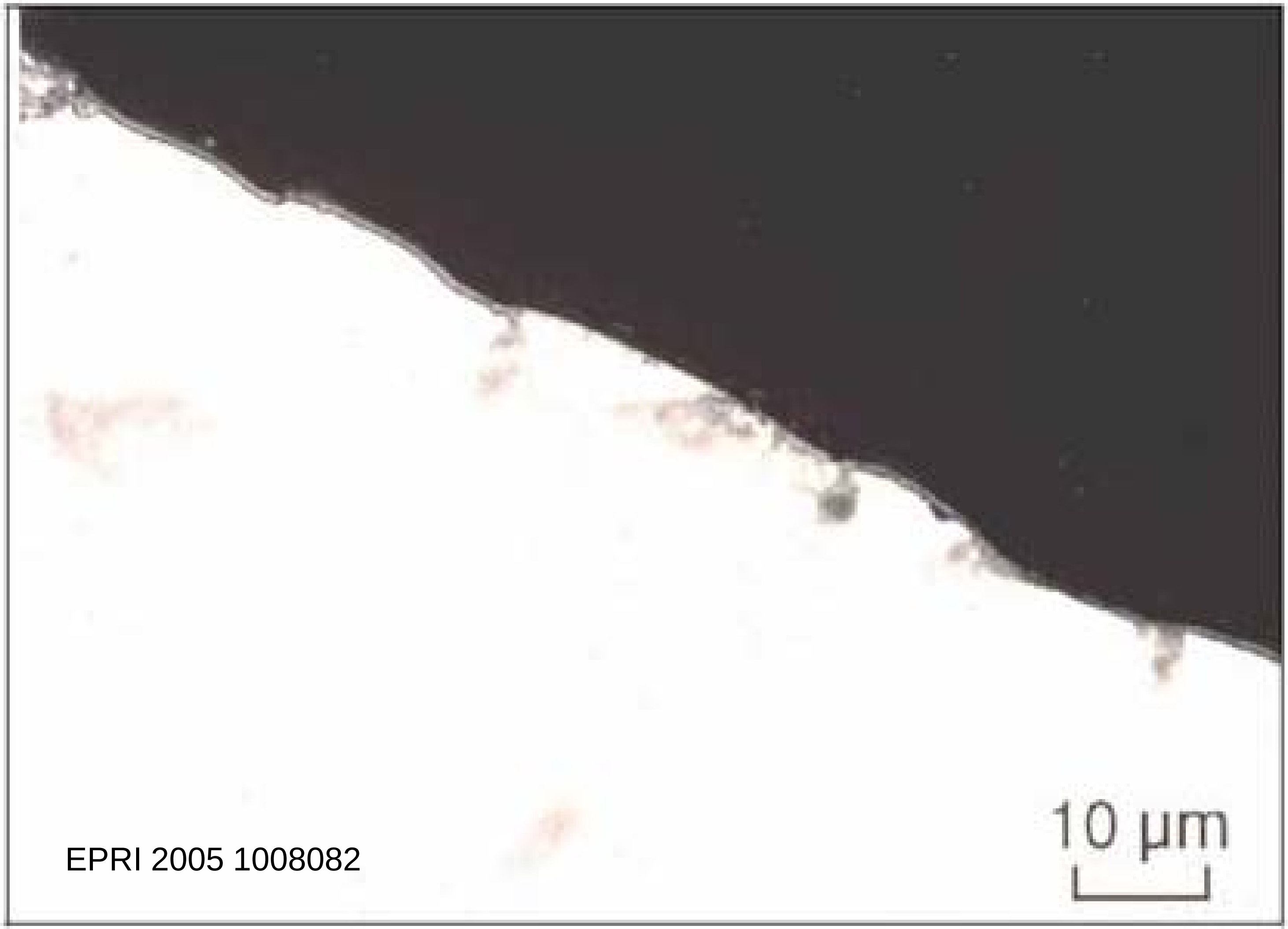
Carbon steel corrosion occurs at the iron-magnetite interface in oxygen-free water by the following reactions:

$$Fe + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_2 \rightarrow Fe(OH)_2 + H_2$$

and

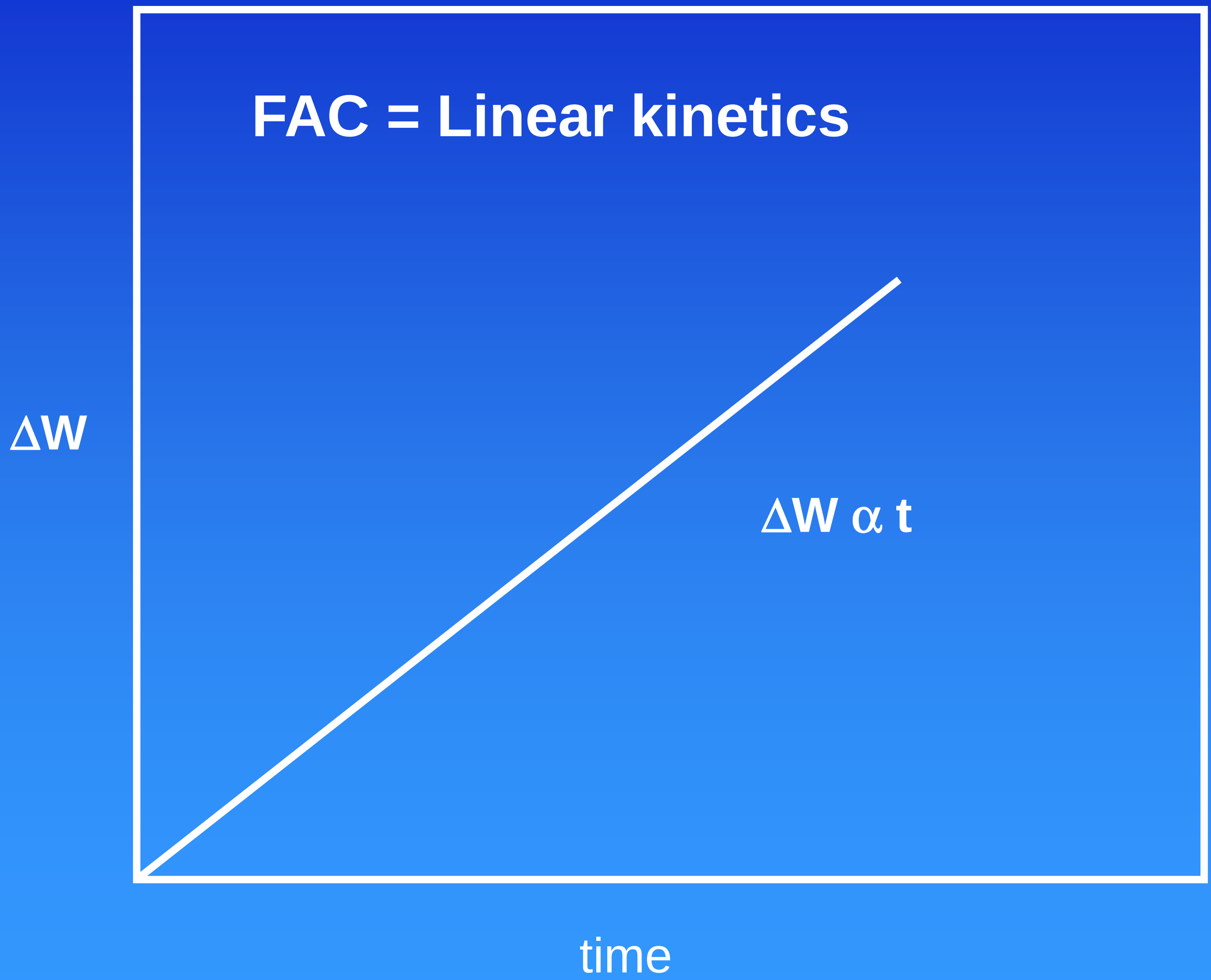
$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

FAC Produces Thin Oxide Films



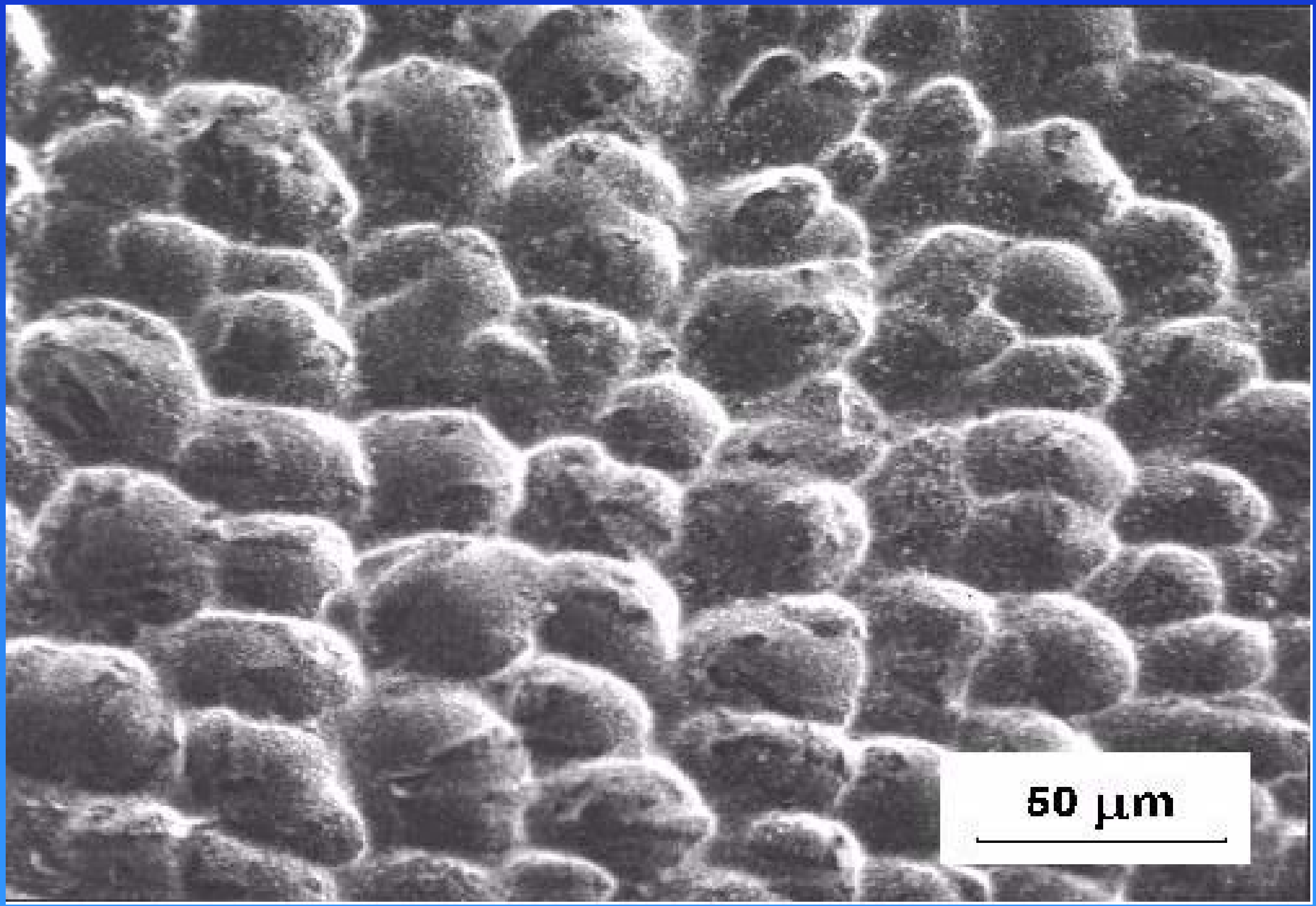
EPRI 2005 1008082

FAC Kinetics



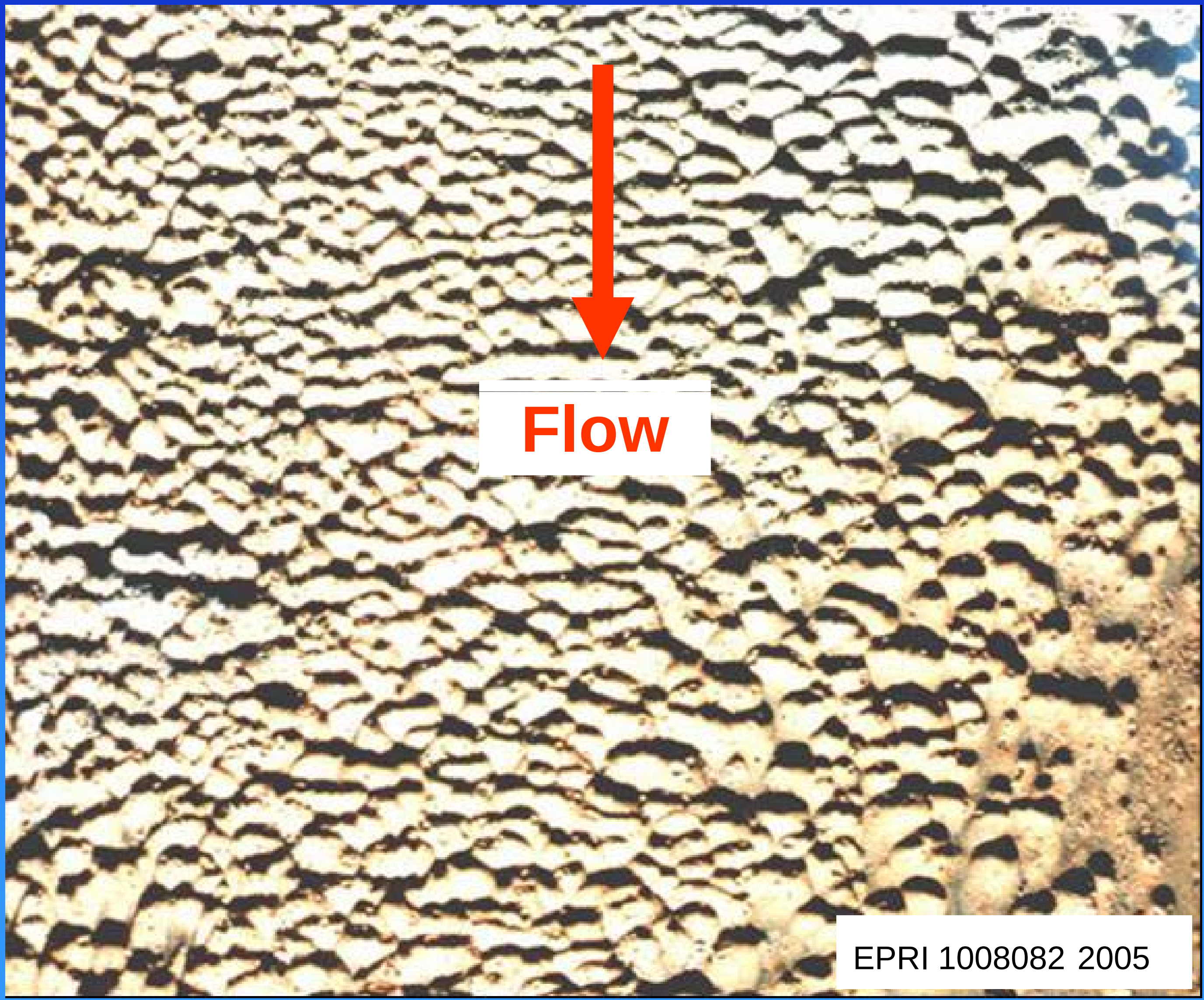
Single-Phase FAC

Single-phase FAC often appears as small scallops or horseshoe-shaped "pits"



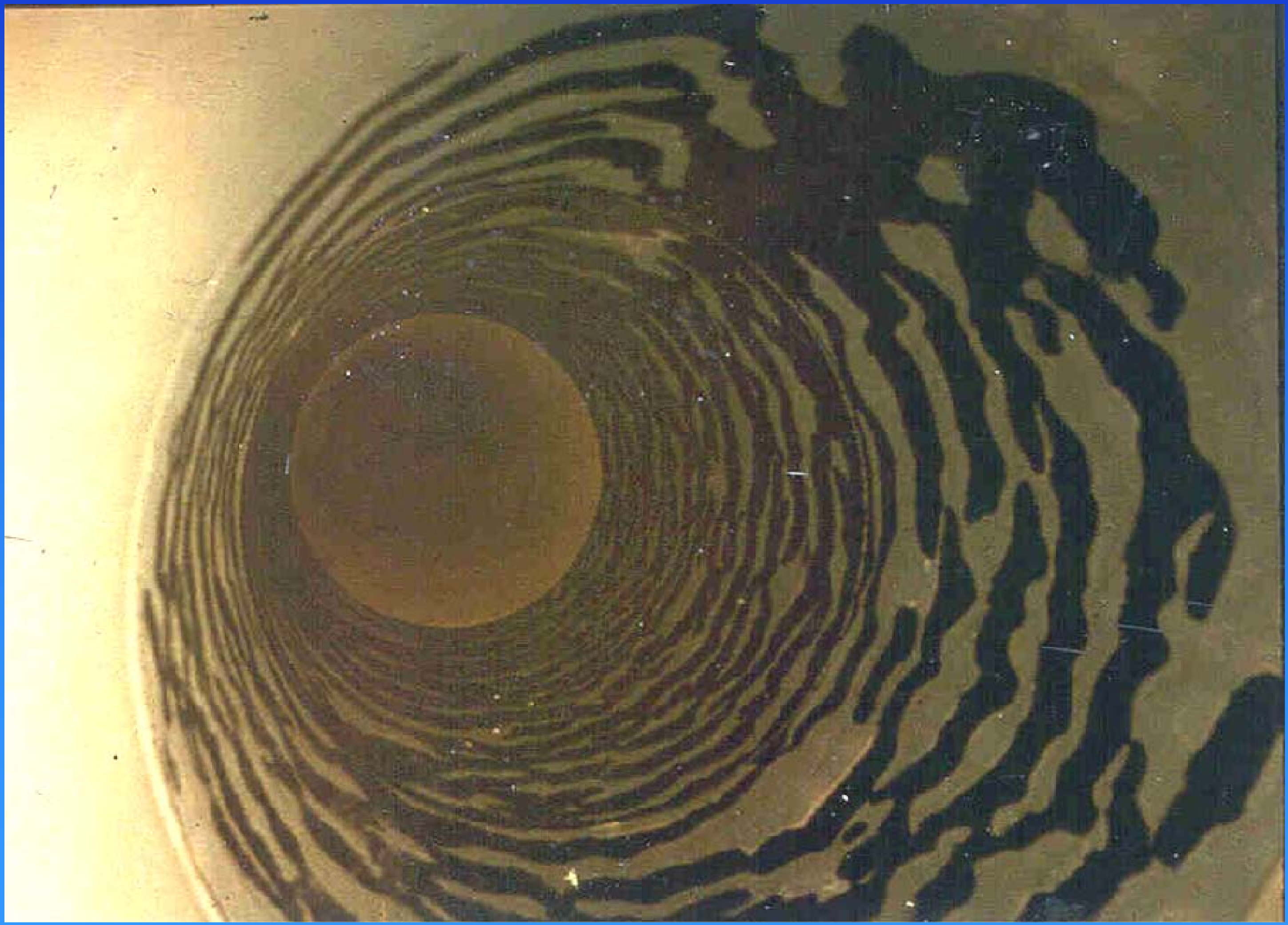
EPRI TR-106611, 1996

Typical Surface Appearance of FAC



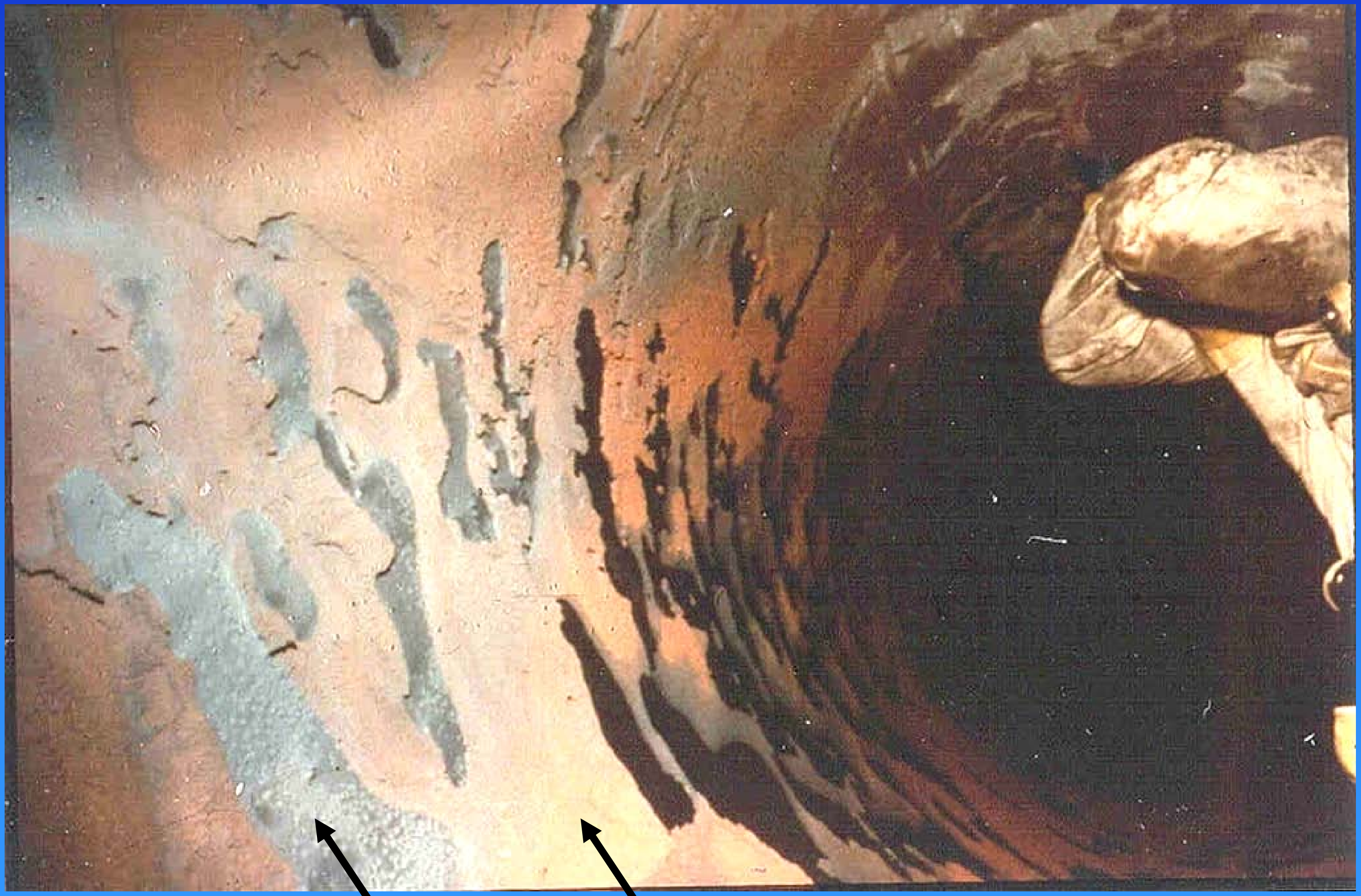
Two-Phase FAC - Tiger Striping

Very disturbed, turbulent water film flow along steam pipe wall



Two-Phase FAC - Tiger Striping

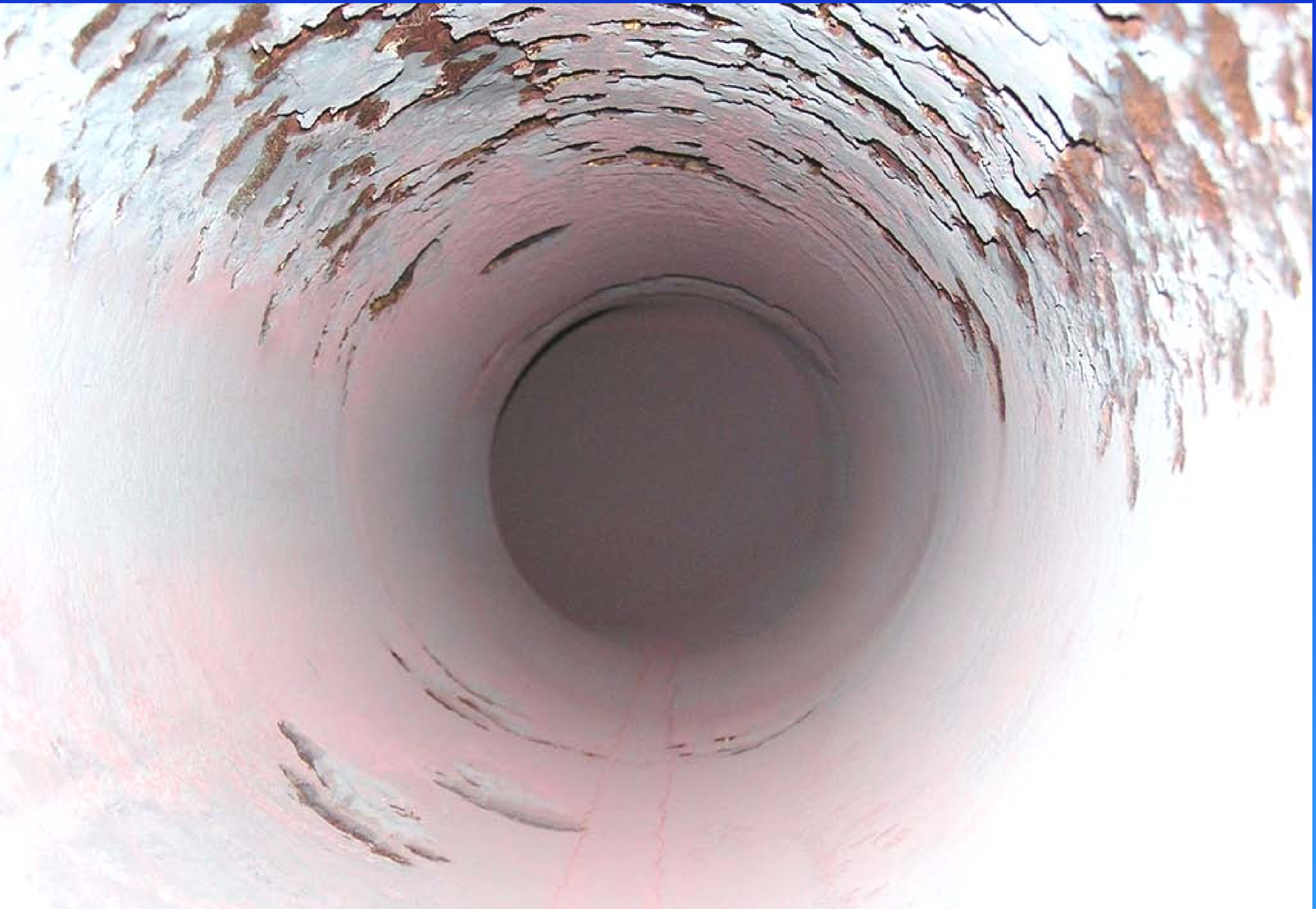
Wet steam piping



Corrosion **Oxide**

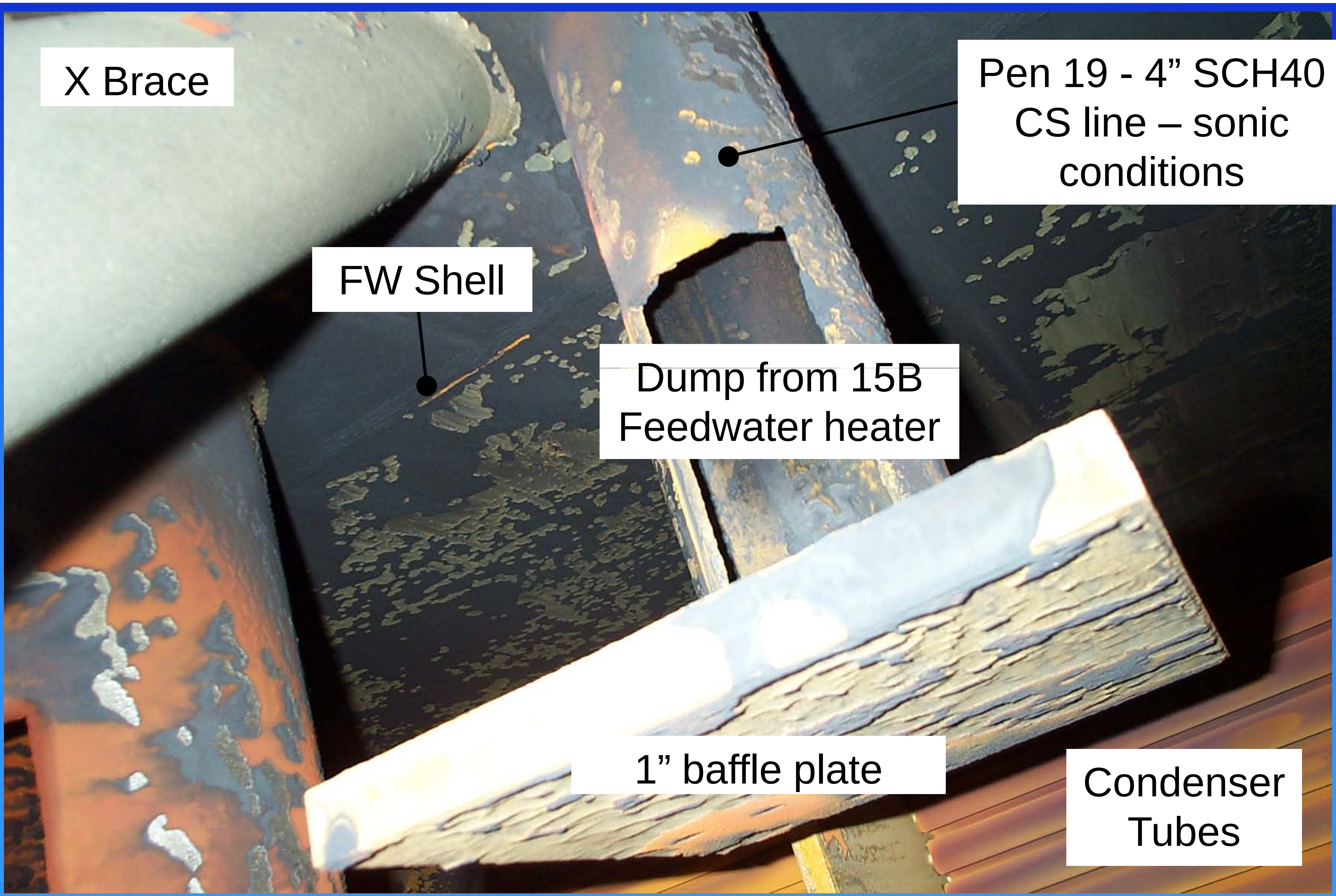
EPRI 1004924 2003

Clinton Extraction Steam Line
Two-Phase FAC - Tiger Striping



Flow rate = 72 m/s = 235 ft/s = 160 mph!

Monticello Condenser Two-Phase FAC



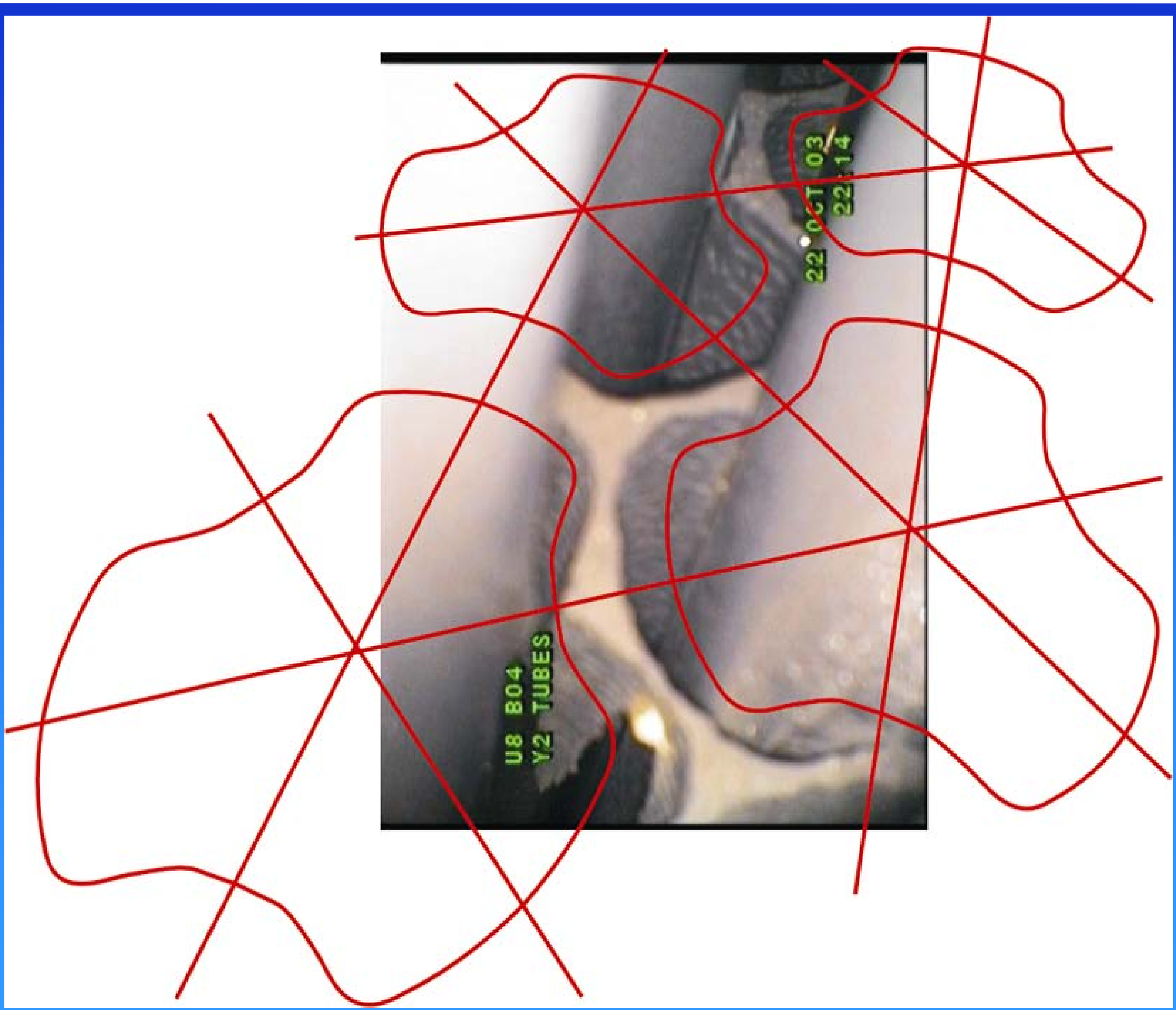
FAC of CANDU SG Tube Support Plate

Example of severe thinning on underside of broached TSP

- **Illustrates an advanced stage of FAC**
- **Thinning is uniform to ~10% remaining ligament**

P. King, 12th Env. Deg., 2005

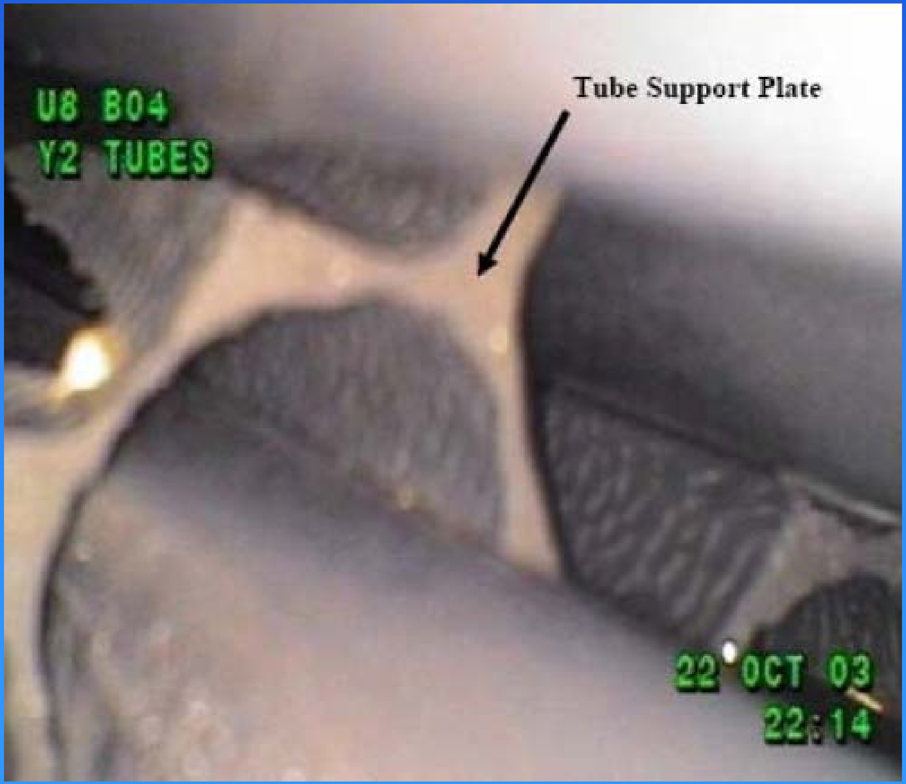
FAC of SG Tube Support Plate



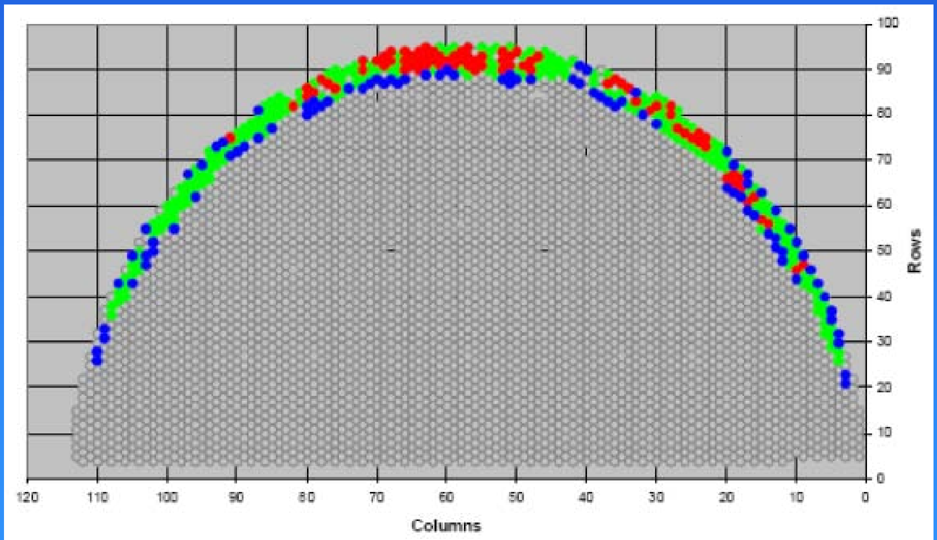
P. King, 12th Env. Deg., 2005

Additional FAC Concerns

- FAC may contribute to fretting corrosion



- Concerns regarding additional loading applied to tubes and pinching if support plates bend



- Advanced degradation
- Complete loss of support
- Partial degradation

J. Riznic, SGAM, IAEA, 6/09

FAC Degradation of SG Scalloped-bars

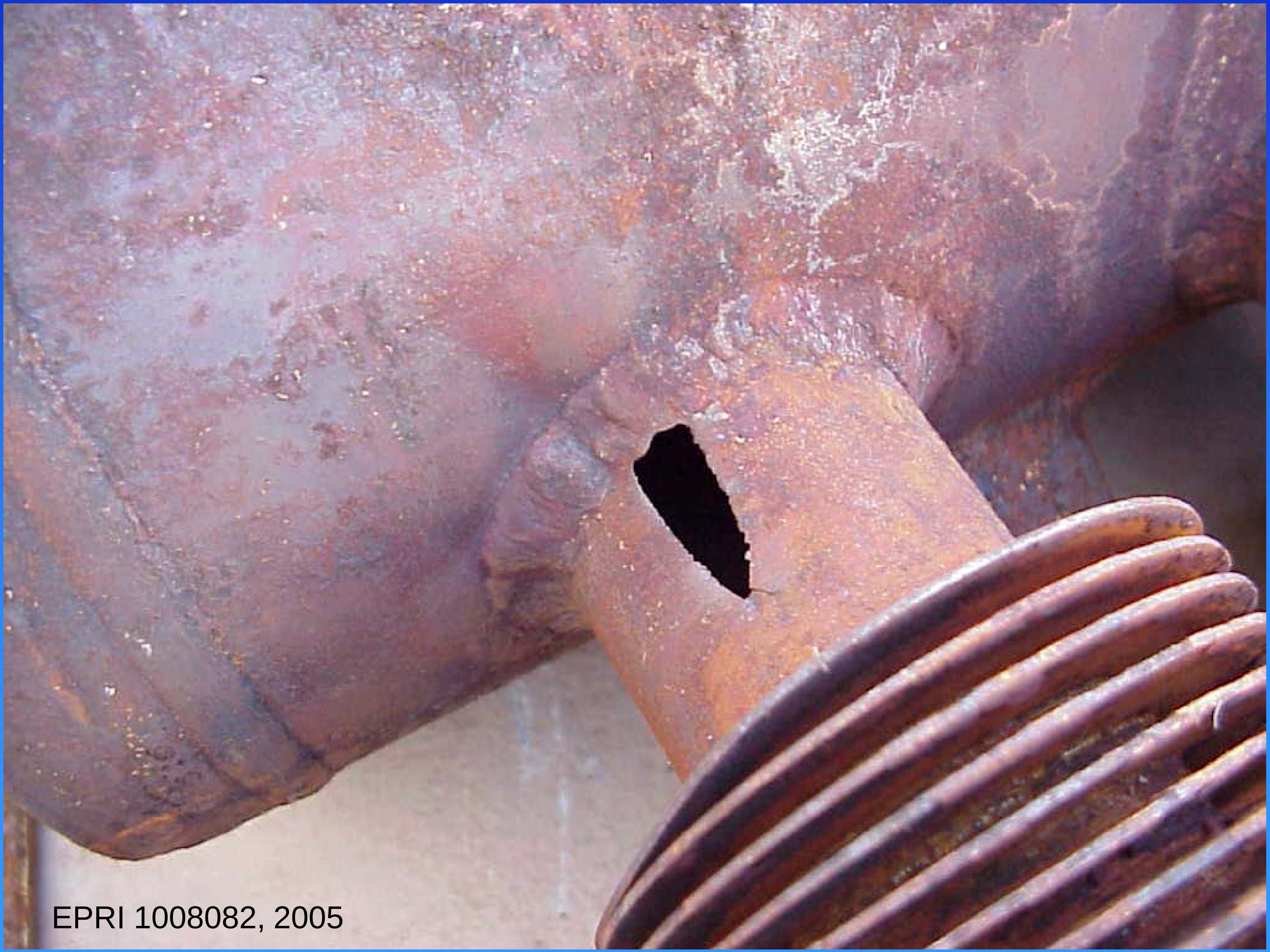
Fossil Economizer Inlet Header Tube FAC

EPRI 1008082, 2005

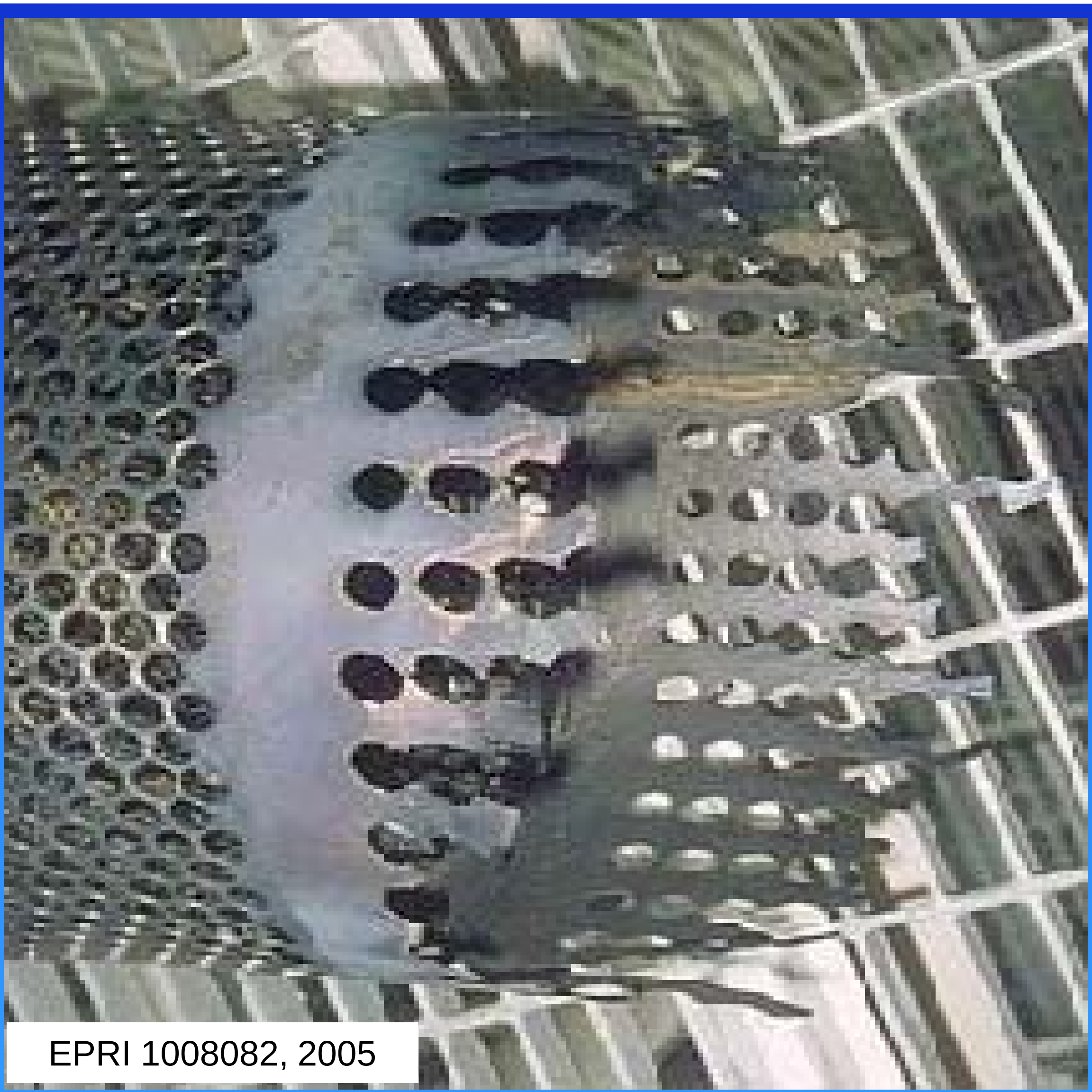
Fossil Drain Line FAC

EPRI 1008082, 2005

Fossil LP Evaporator Tube FAC



Fossil HRSG* Drum Separating Device FAC



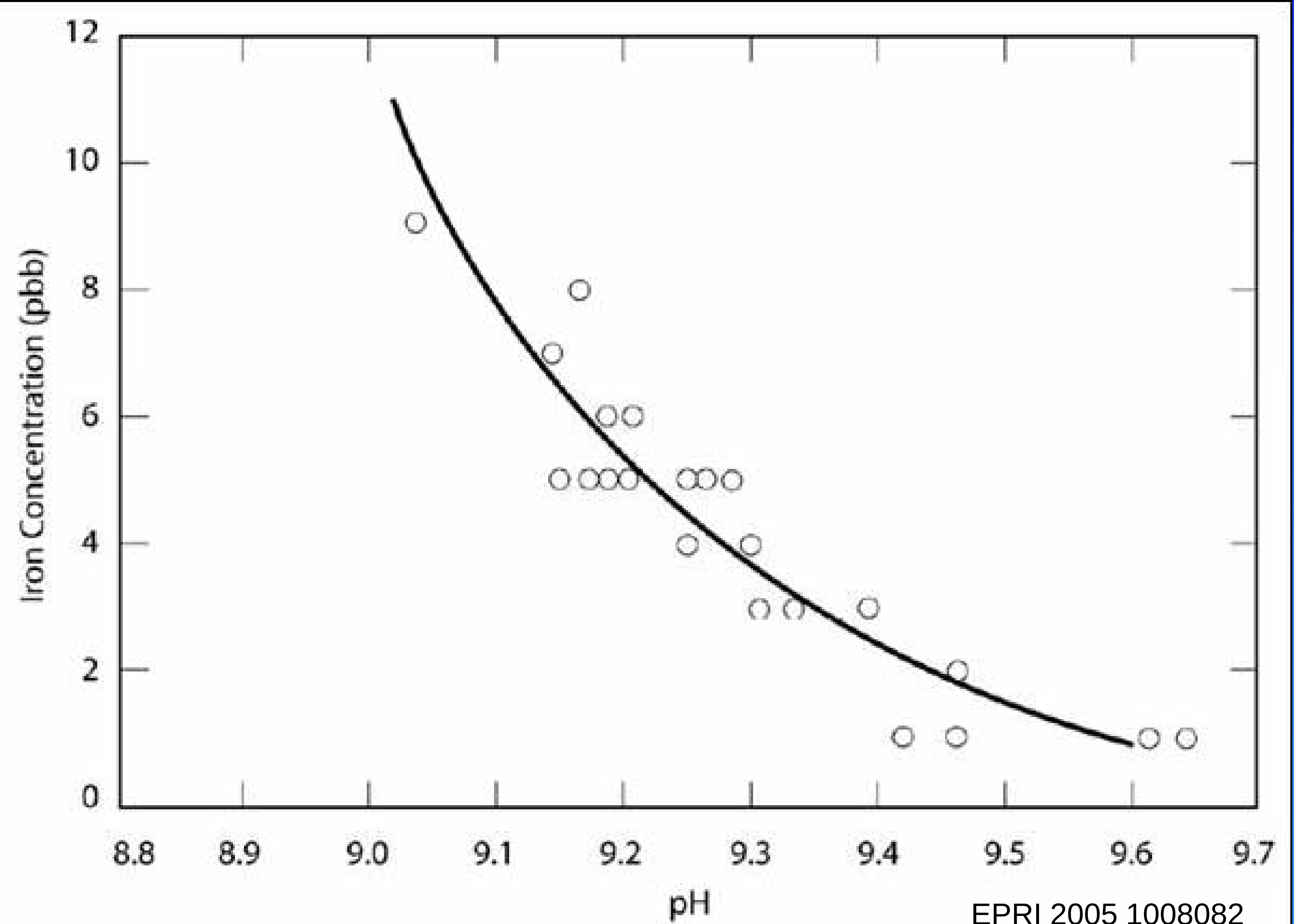
EPRI 1008082, 2005

* heat recovery steam generator

FAC Critical Parameters

- **Water chemistry**
  - ♦ **pH (<9.3)**
  - ♦ **Dissolved oxygen (<40 ppb)**
  - ♦ **Temperature (maximum at 135 °C [275 °F] water and 177 °C [350 °F] steam)**
- **Material chemistry**
  - ♦ **Cr, Cu or Mo (<0.5%)**
- **Hydrodynamics**
  - ♦ **Velocity (>4.6 m/s [>15 ft/s] water, >27 m/s [>90 ft/s] steam)**
  - ♦ **Geometry (turbulence in elbows, tees, etc.)**
  - ♦ **Steam Quality (0.1 to 0.9)**

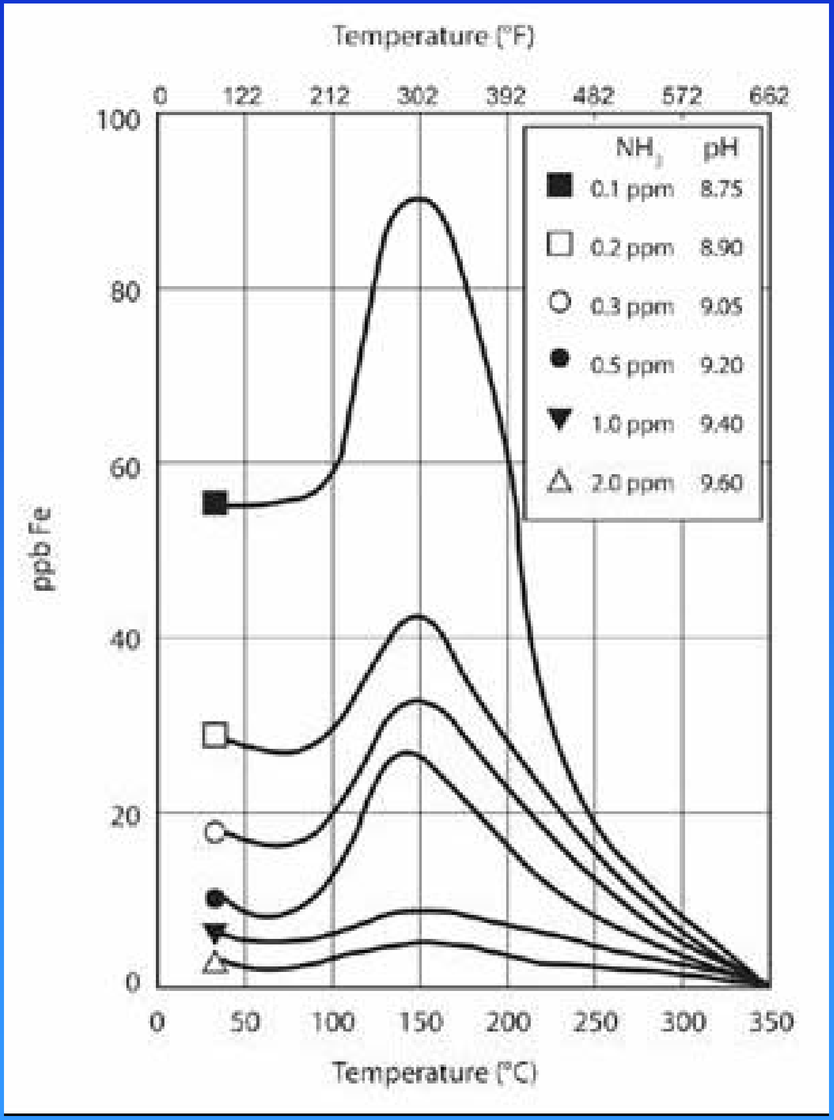
Corrosion Product Release from Carbon Steel as a Function of pH



EPRI 2005 1008082

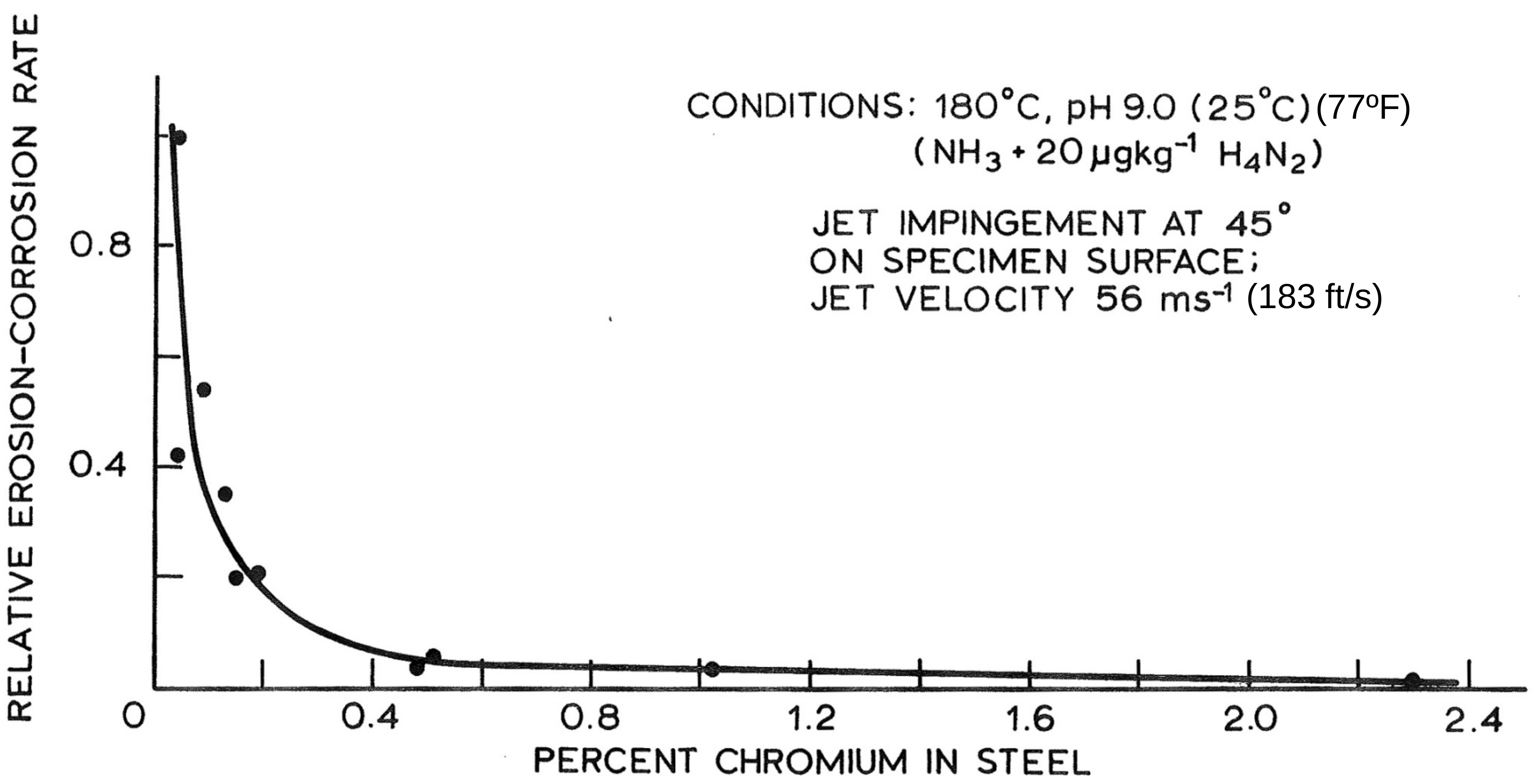
Solubility of Fe_3O_4 vs. T and NH_3

FAC is controlled by the solubility of Fe_3O_4



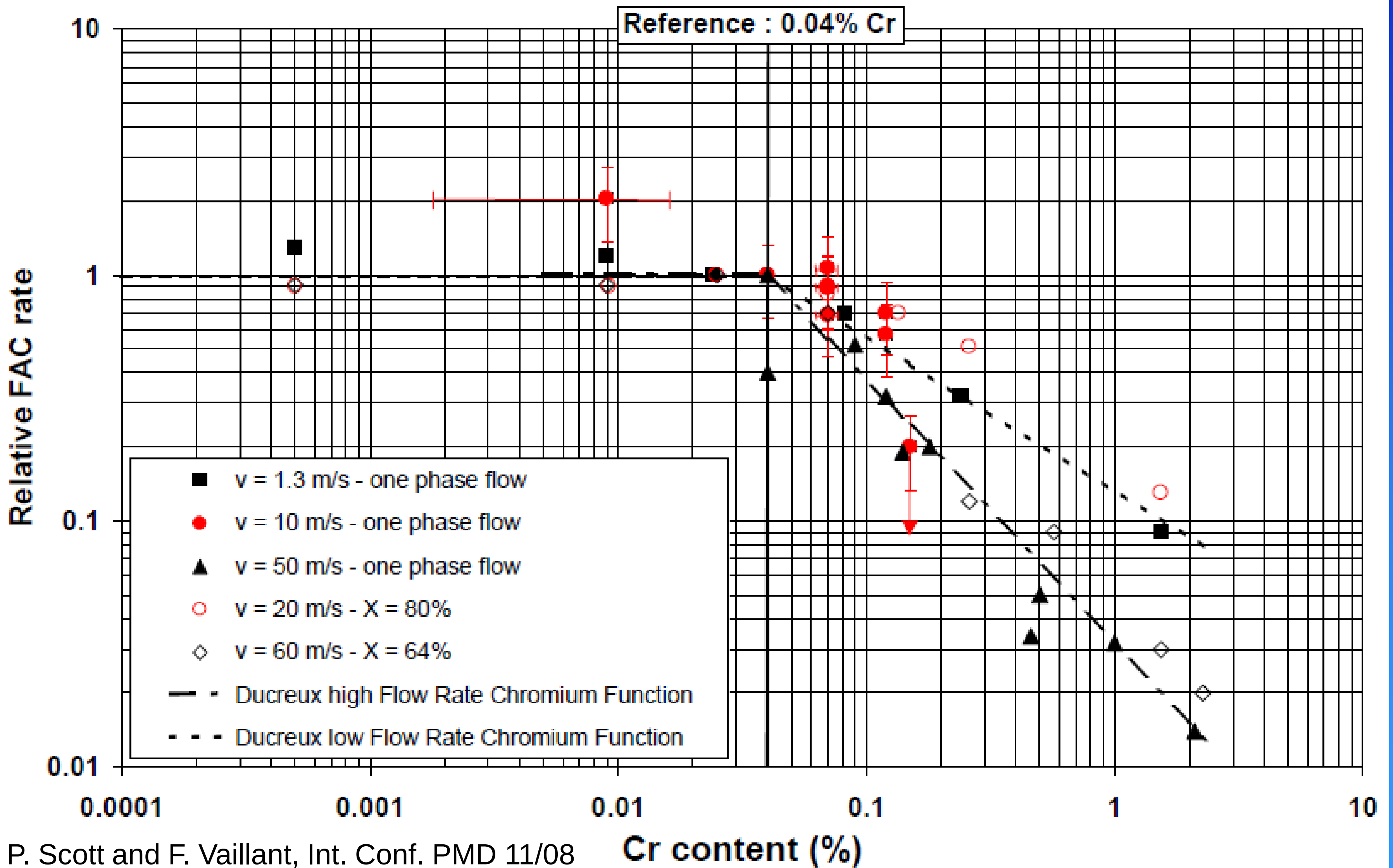
P. Sturla, 5th Nat. Feedwater Conf., 1973

Effect of Cr on Single-Phase FAC



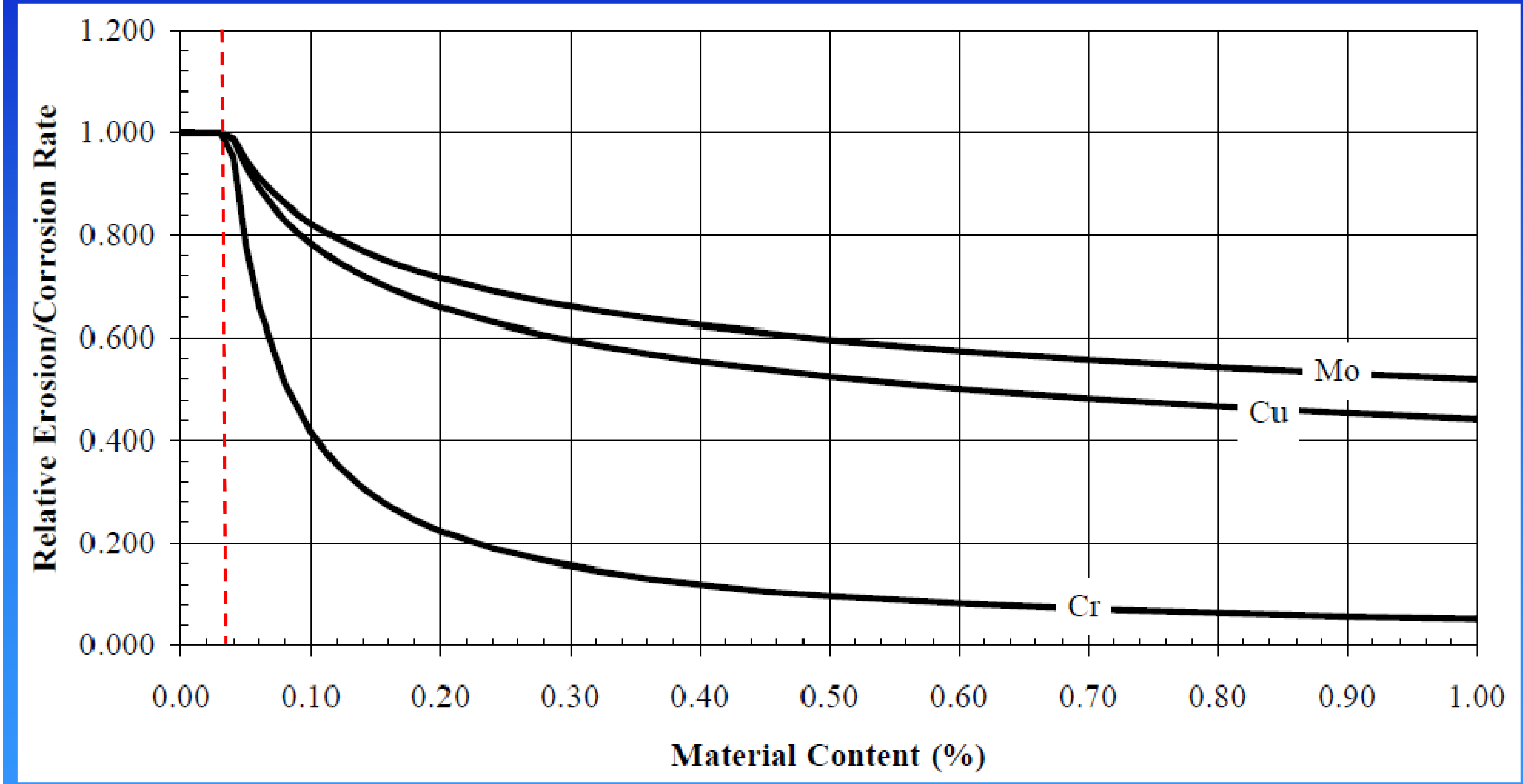
J. Ducreux, EdF, 1982

Effect of Cr on Single-Phase and Two-Phase FAC

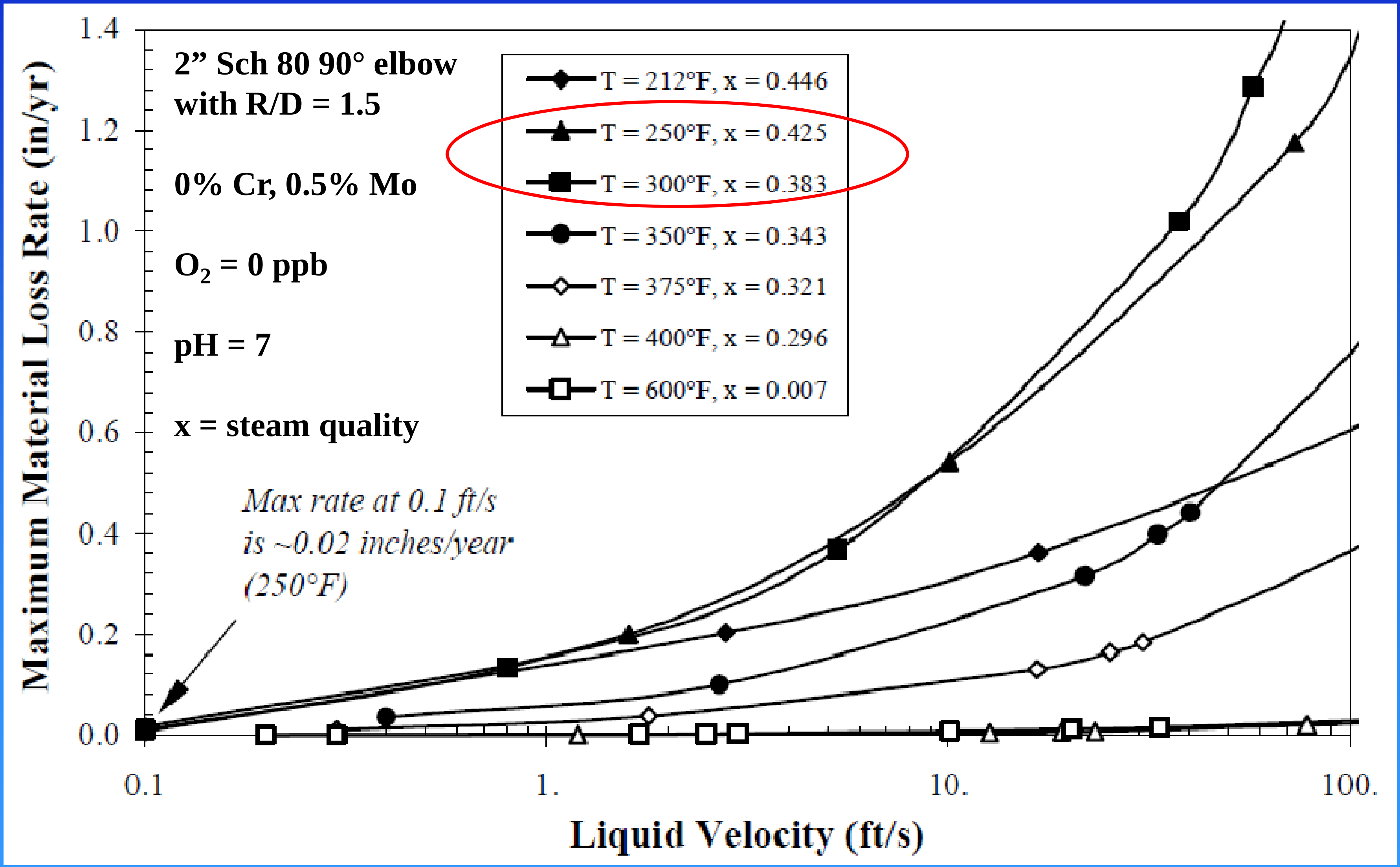


P. Scott and F. Vaillant, Int. Conf. PMD 11/08

Relative Effect of Cr, Cu and Mo on FAC



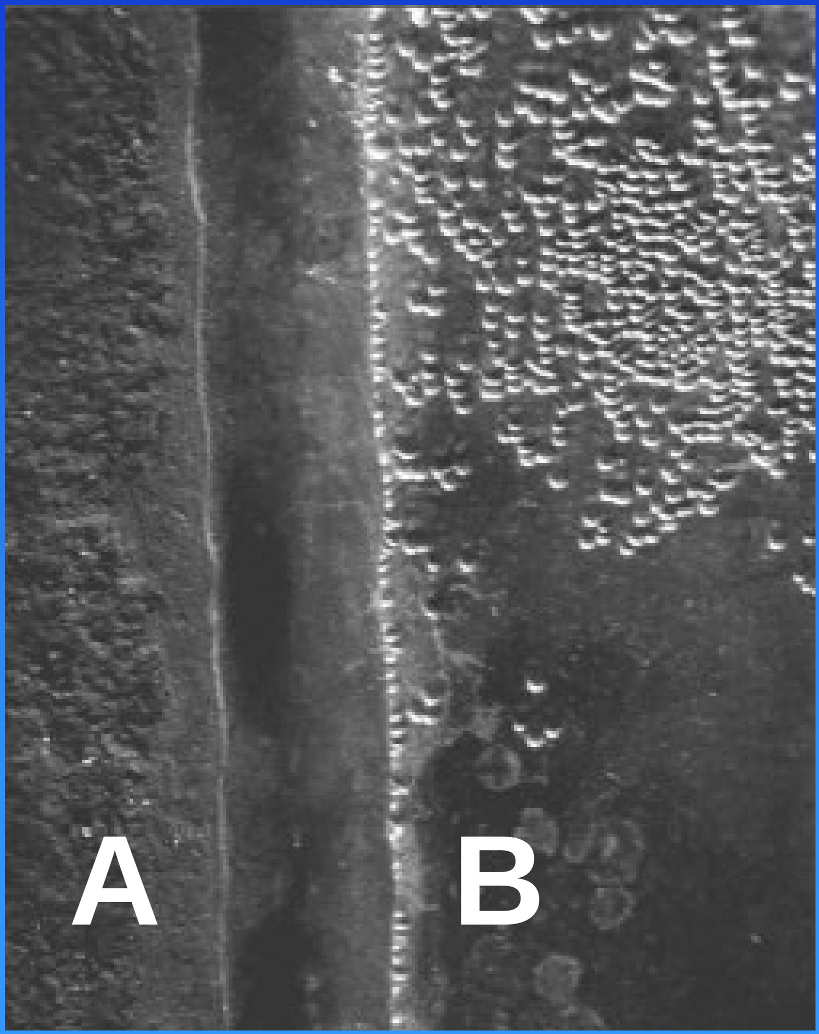
CHECWORKS™ Predictions for Saturated Two Phase Water



G. White, et al., NRC Davis-Besse Degradation, 5/22/02

Cr Equivalent on FAC

Cr-equivalent = Cr +1.4 Cu + 0.3 Mo - 0.3 C >0.09



By comparing the Cr equivalence of steels from failures and non-failures it appears that steels from FAC failures generally have a Cr-equivalence <0.09

Steel	Cr	Cu	Mo	C	Cr-eq
A	0.1	0.21	0.02	0.12	0.364
B	0.01	0.006	0.01	0.12	-0.0146

Single-Phase FAC Susceptible Carbon Steel Systems

- Condensate and feedwater
- Auxiliary feedwater
- Heater drains
- Moisture separator drains
- SG blow-down
- Reheater drains
- Lower head drain lines
- Other drains

Two-Phase FAC Susceptible Carbon Steel Systems

- **High and low pressure extraction steam lines**
- **Flashing lines to the condenser (miscellaneous drains)**
- **Feedwater heater vents**
- **Moisture separator drains**
- **Lines with leaking valves**
- **Main steam lines**
- **Reheat steam lines**

FAC Models

- EPRI – CHEC™ (Chexal Horowitz Erosion Corrosion), CHECMATE™, CHECWORKS™
- Keller
- Berge
- Électricité de France (EdF) – BRT-Cicero™
- Areva – WATHEC™ (Wall Thinning due to Erosion Corrosion)
- Atomic Energy of Canada Limited (AECL)
- Penn State University
- Central Electricity Generating Board (CEGB)
- MIT

EPRI CHECWORKS™ FAC Model Background

- Predicts the FAC rate in single or two phase flow
- Ranks components for any system in prioritized order for potential FAC
- Compares predictions with actual ISI data for statistical analysis
- Calculates time to minimum Code allowable wall thickness
- Performs mass balance dissolved oxygen content and pH calculations

EPRI CHECWORKS™ FAC Model Equation

$CR = f(T) * f(AC) * f(MT) * f(O_2) * f(pH) * f(G) * f(\alpha)$

CR = FAC rate

f(T) = temperature function

f(AC) = alloy content (Cr, Cu, Mo) function

f(MT) = mass transfer function

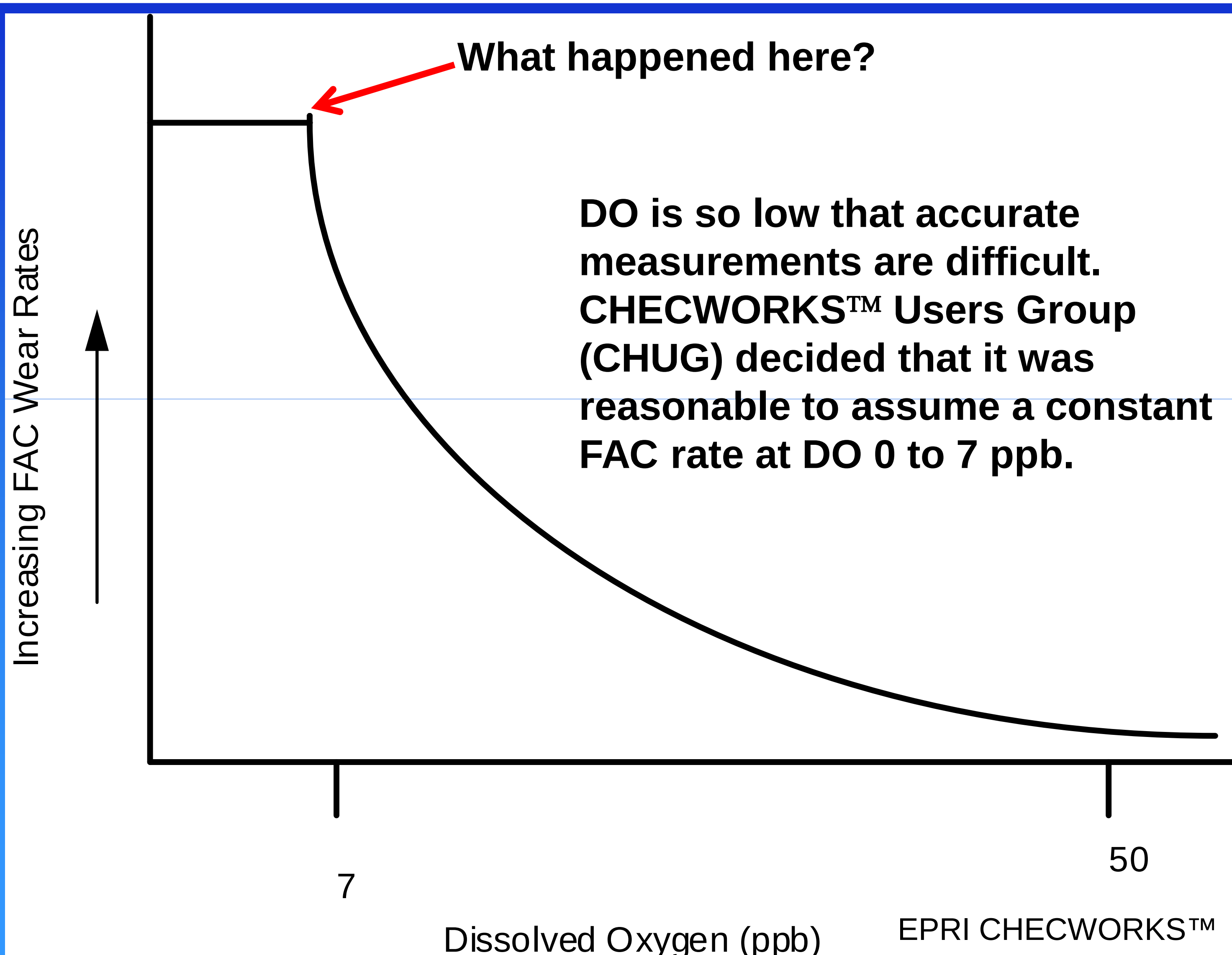
$f(O_2)$ = oxygen function

f(pH) = pH function

f(G) = geometry function

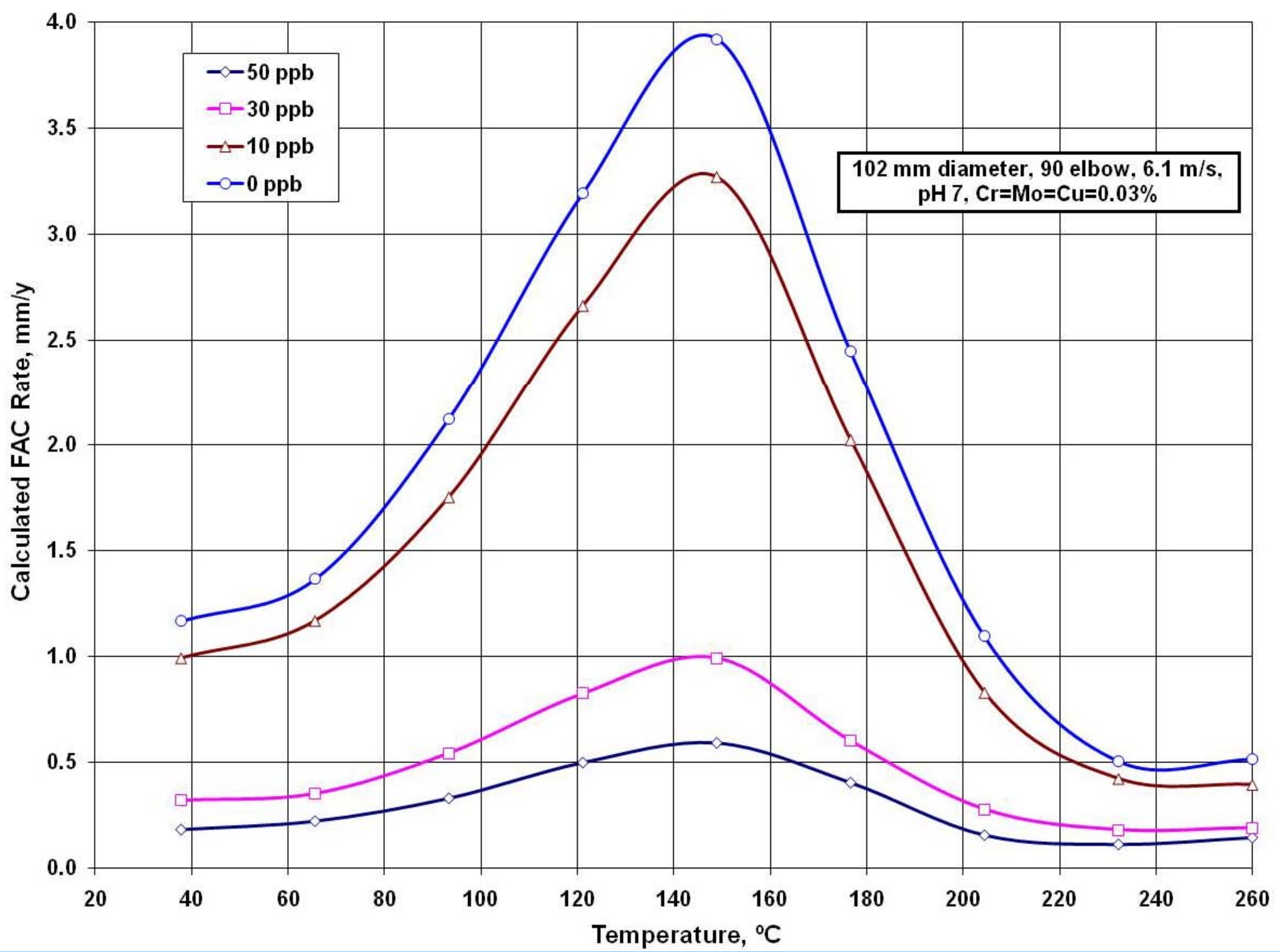
$f(\alpha)$ = void fraction function

Effect of Dissolved Oxygen on FAC

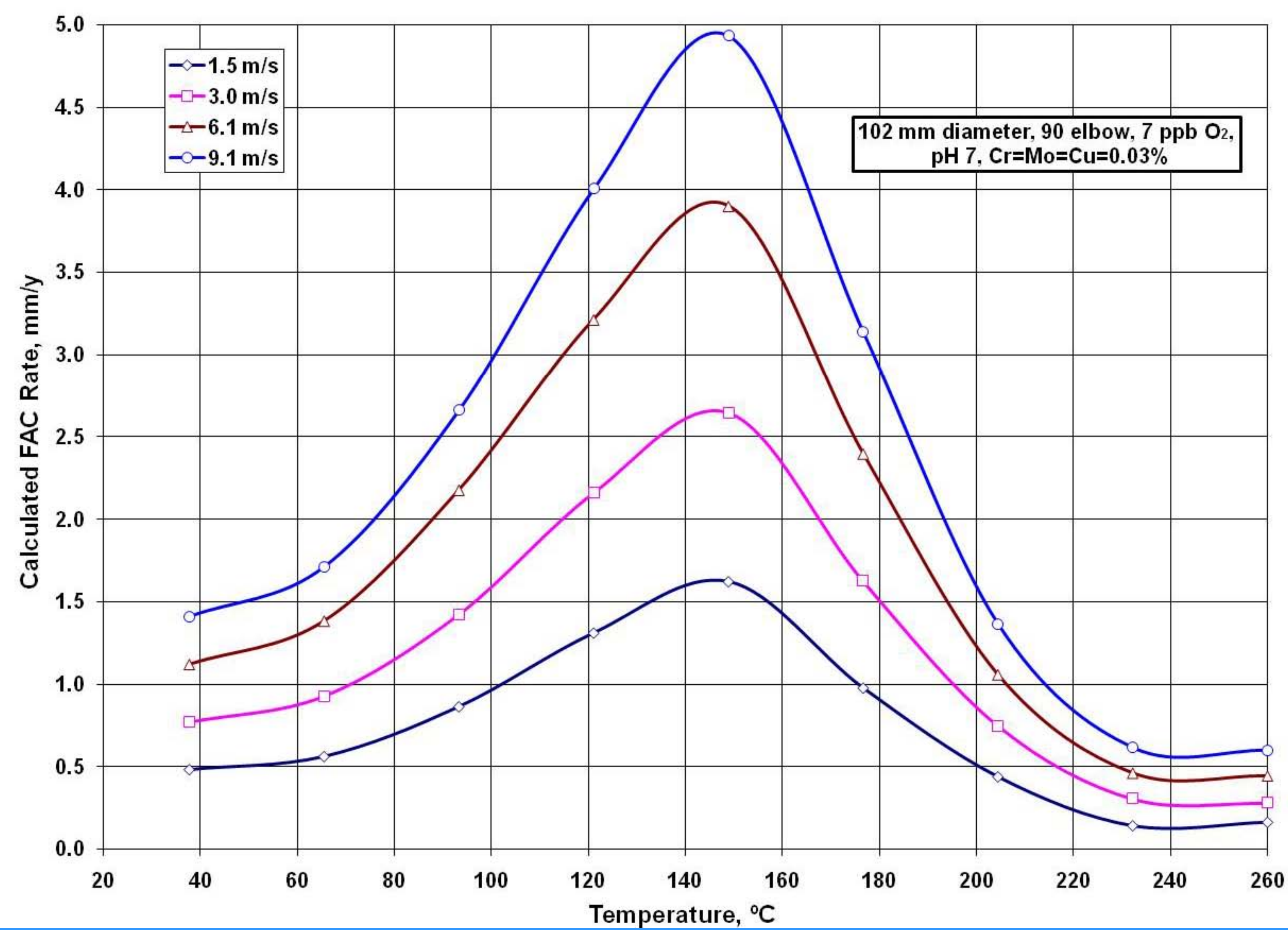


DO is so low that accurate measurements are difficult. CHECWORKS™ Users Group (CHUG) decided that it was reasonable to assume a constant FAC rate at DO 0 to 7 ppb.

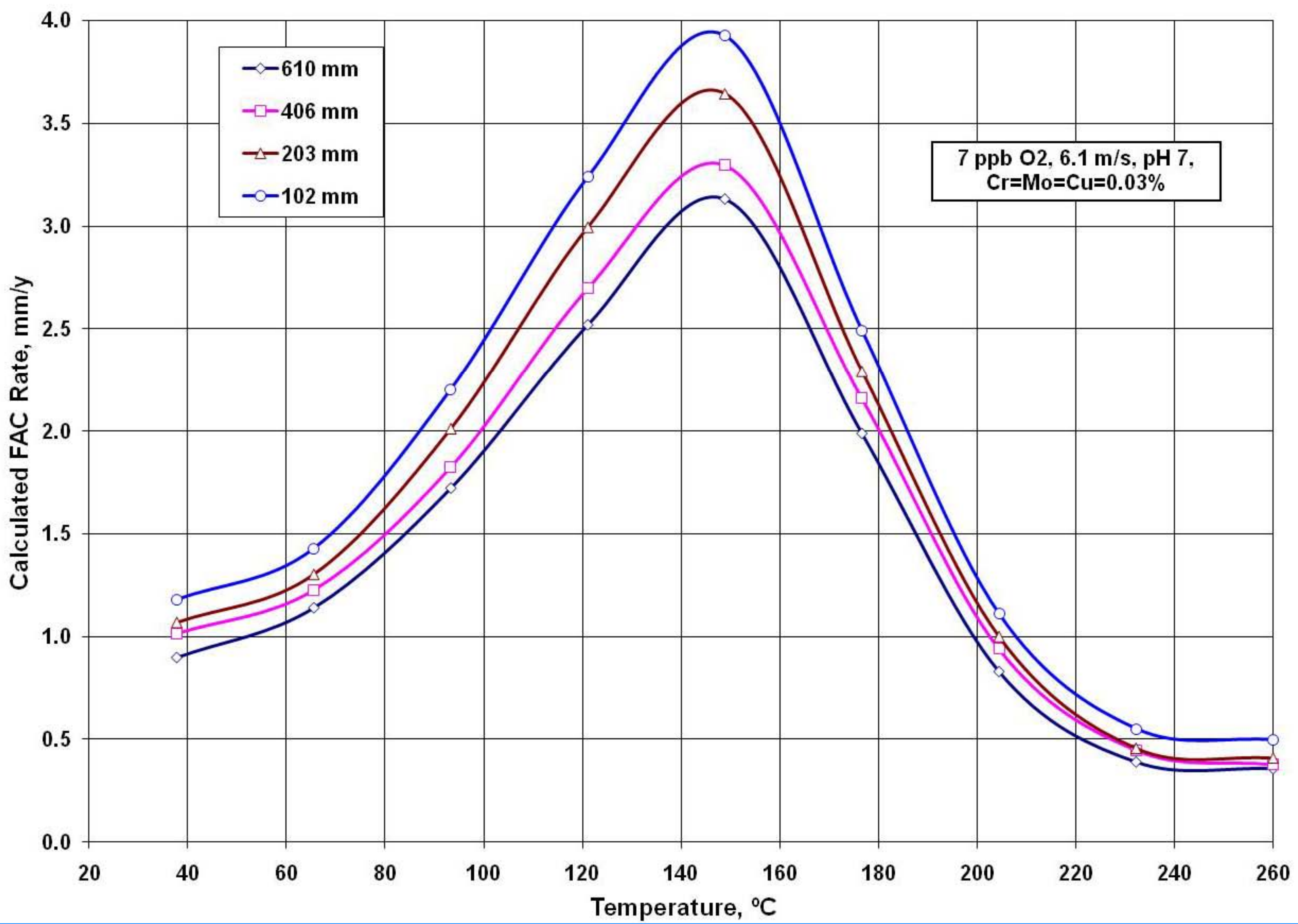
Effect of O_2 and T on Calculated Carbon Steel Two-Phase FAC Rates



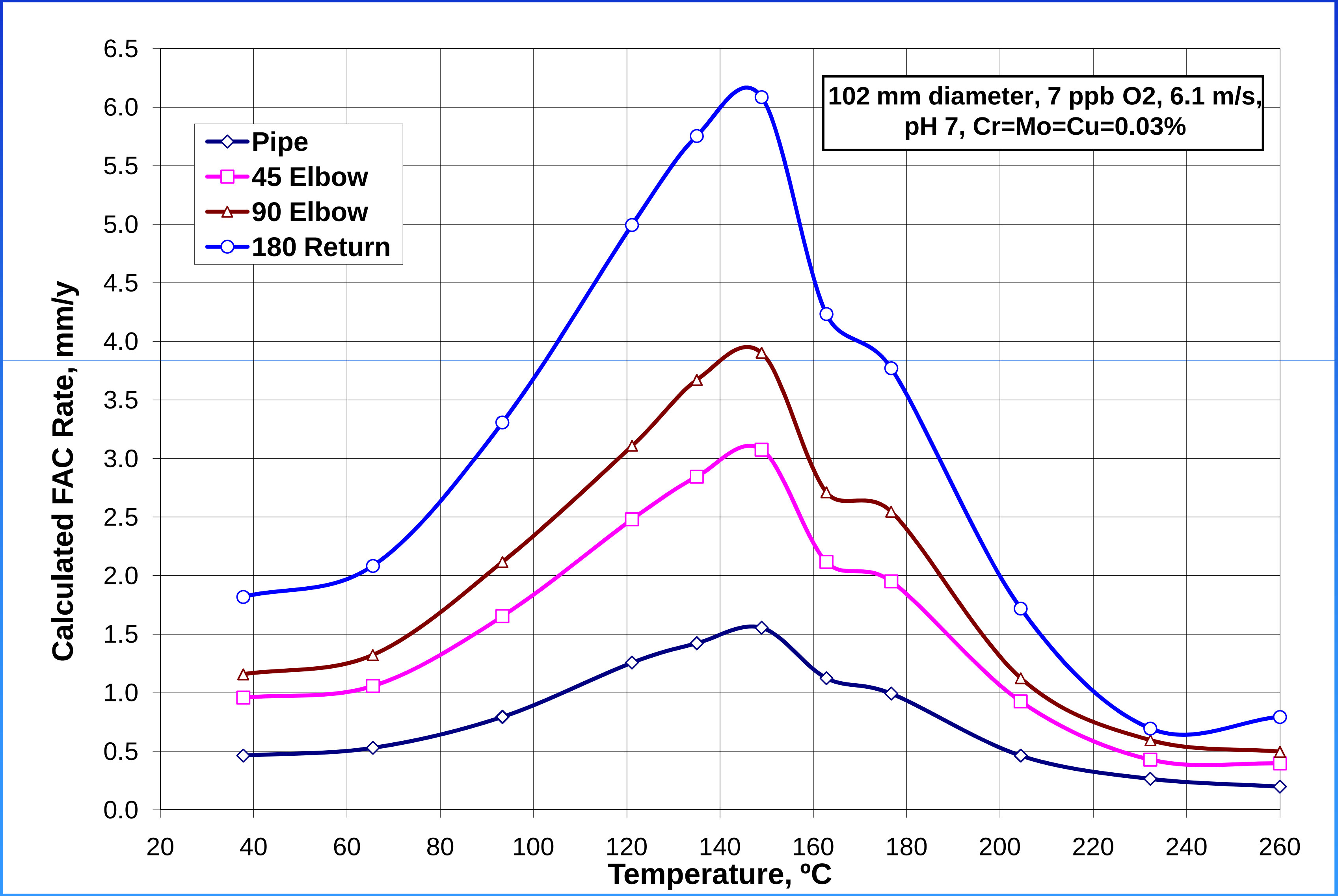
Effect of Flow Rate and T on Calculated Carbon Steel Two-Phase FAC Rates



Effect of Diameter and T on Calculated Carbon Steel Two-Phase FAC Rates

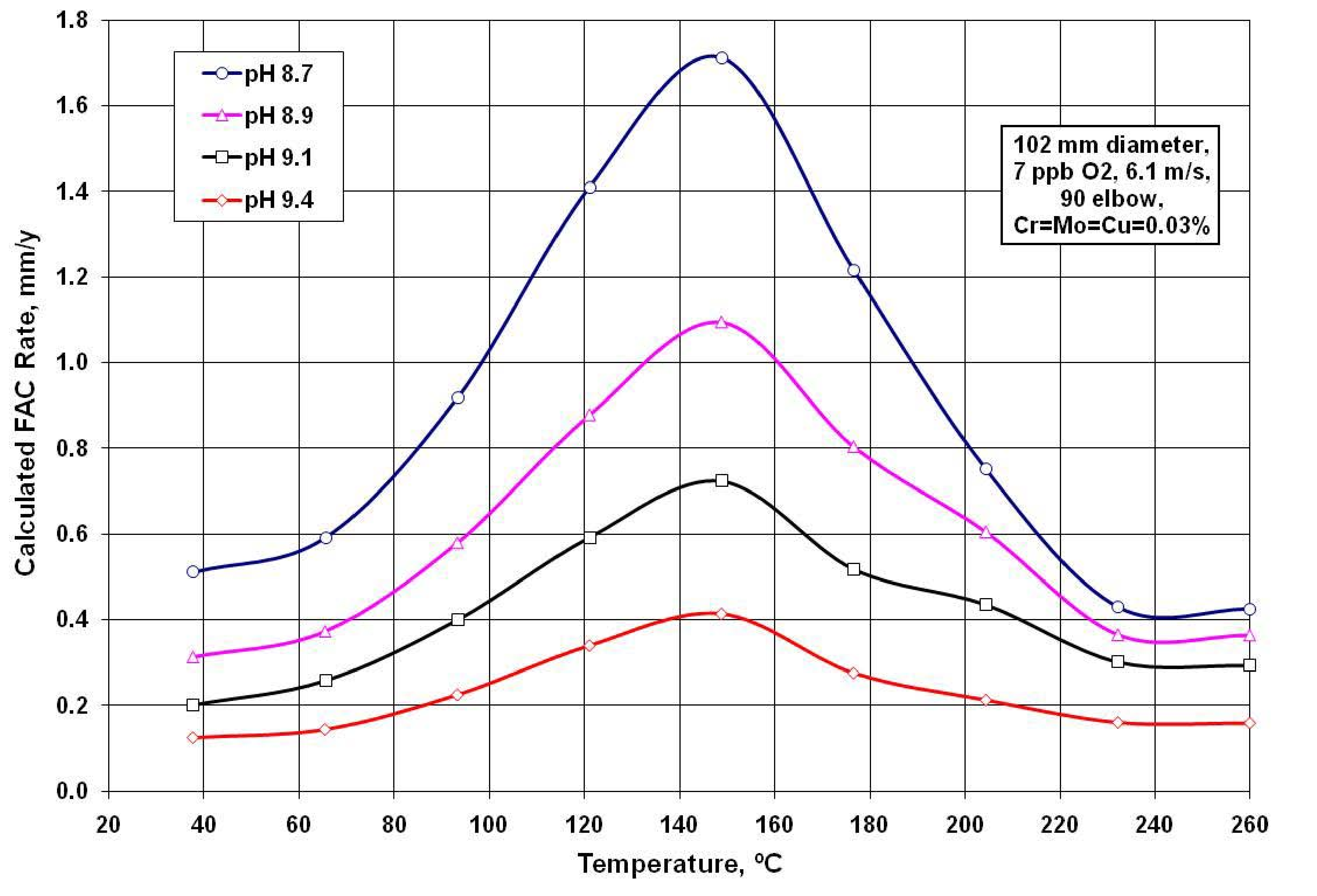


Effect of Pipe Geometry and T on Calculated Carbon Steel Two-Phase FAC Rates

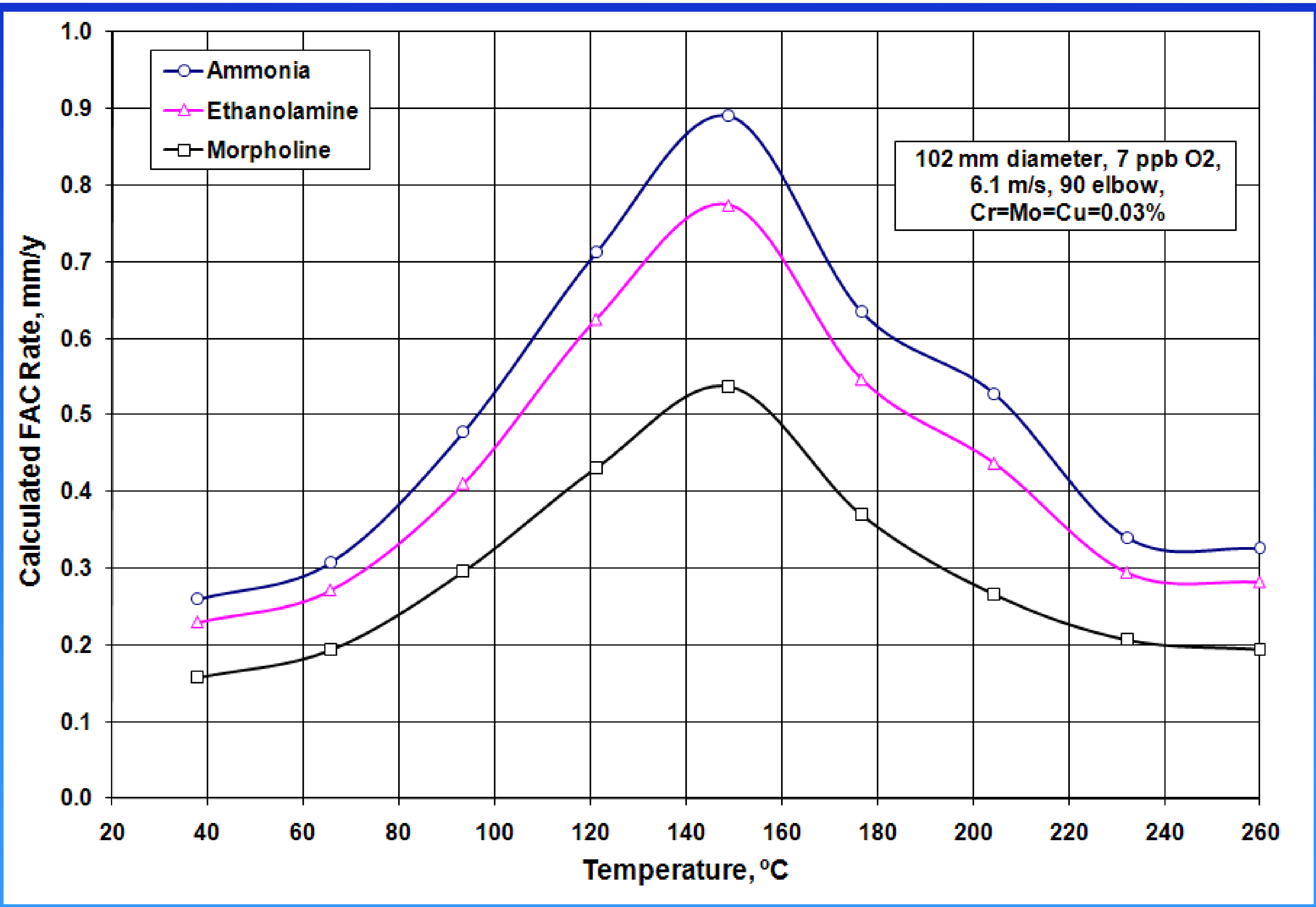


Structural Integrity Associates

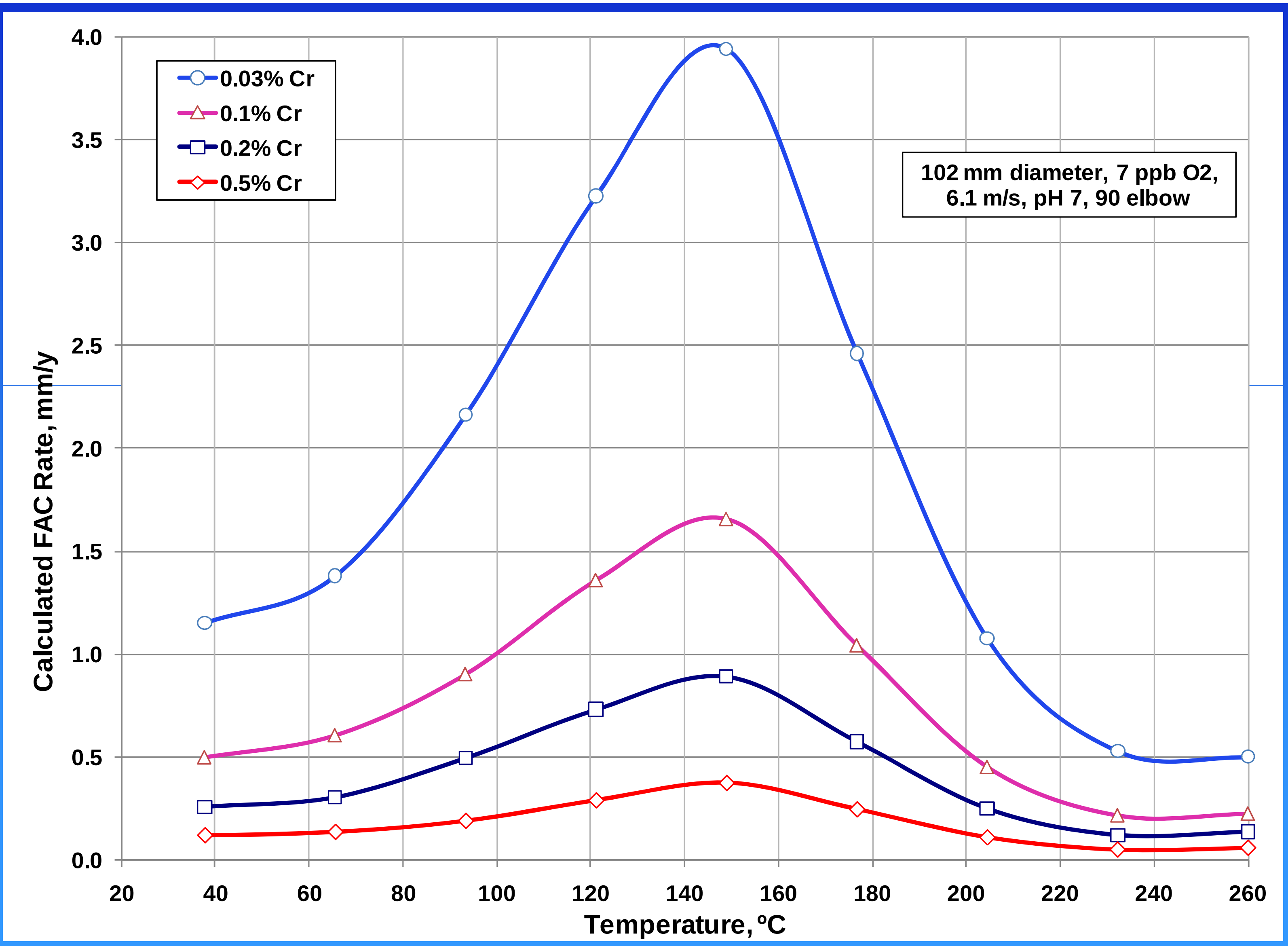
Effect of pH and T on Calculated Carbon Steel Two-Phase FAC Rates



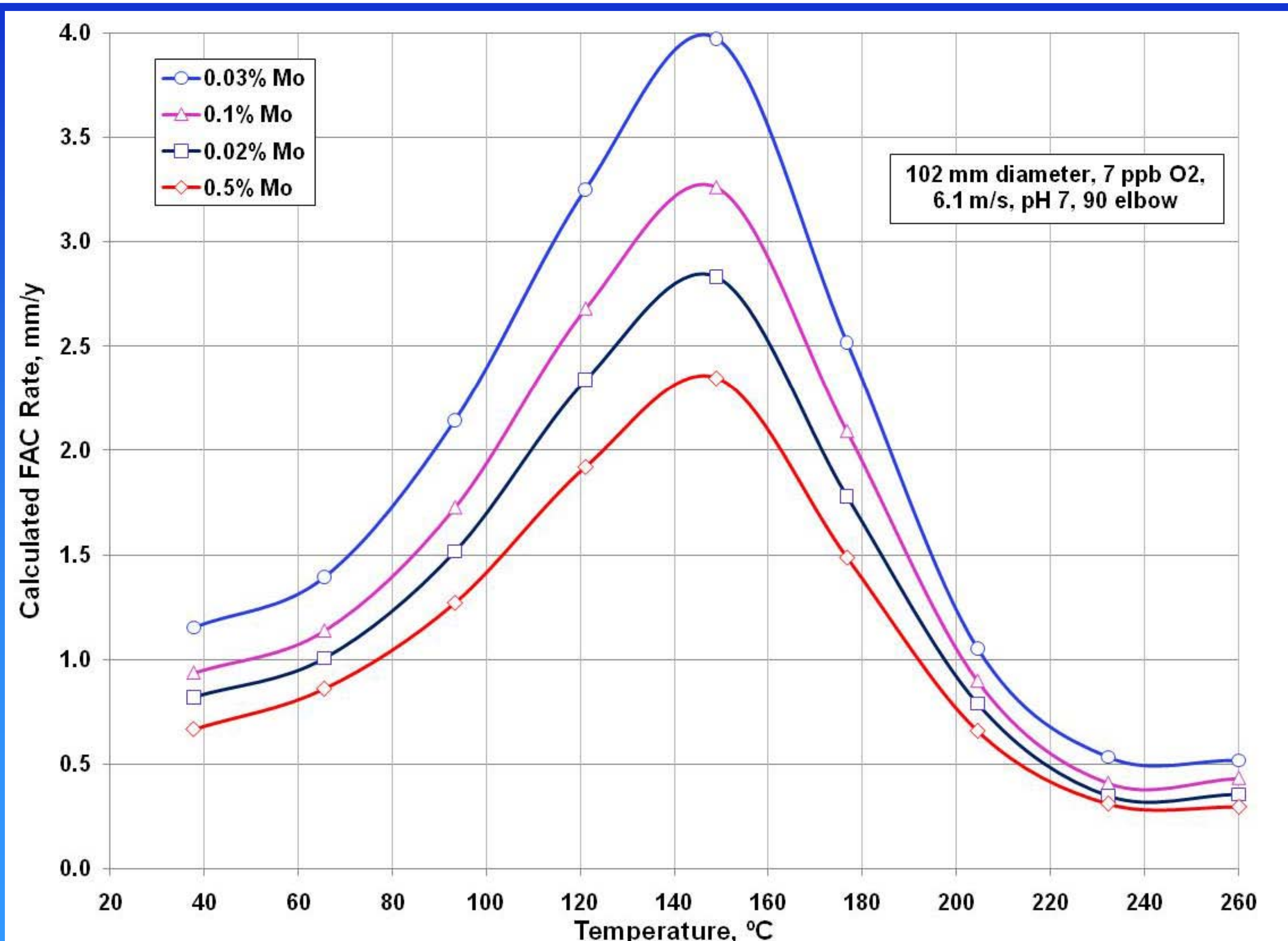
Effect of Amine and T on Calculated Carbon Steel Two-Phase FAC Rates



Effect of Cr and T on Calculated Carbon Steel Two-Phase FAC Rates



Effect of Mo and T on Calculated Carbon Steel Two-Phase FAC Rates



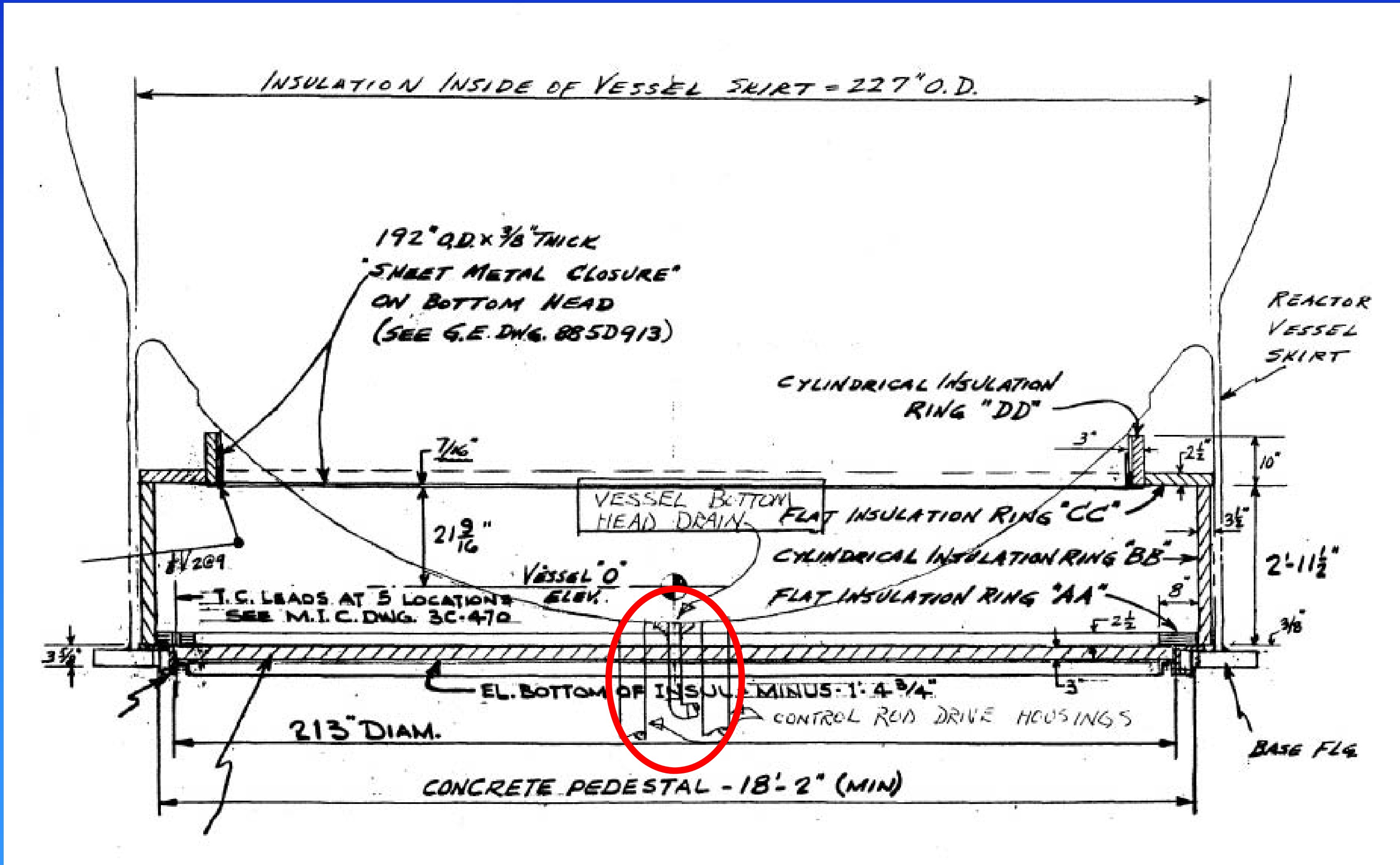
Structural Integrity Associates

BWR Bottom Head Drain Line FAC

- BWR BHDL is susceptible to FAC
- Difficult to inspect due to obstructions and high radiation dose rates
- Leak or rupture in the piping under the vessel could not be isolated and would result in a small break LOCA
- Although the BHDL has been included in many utility FAC inspection programs, a condition report written by one BWR licensee who encountered inspection difficulties led to increased utility and NRC attention to this issue

CHUG to NRC 7/22/05

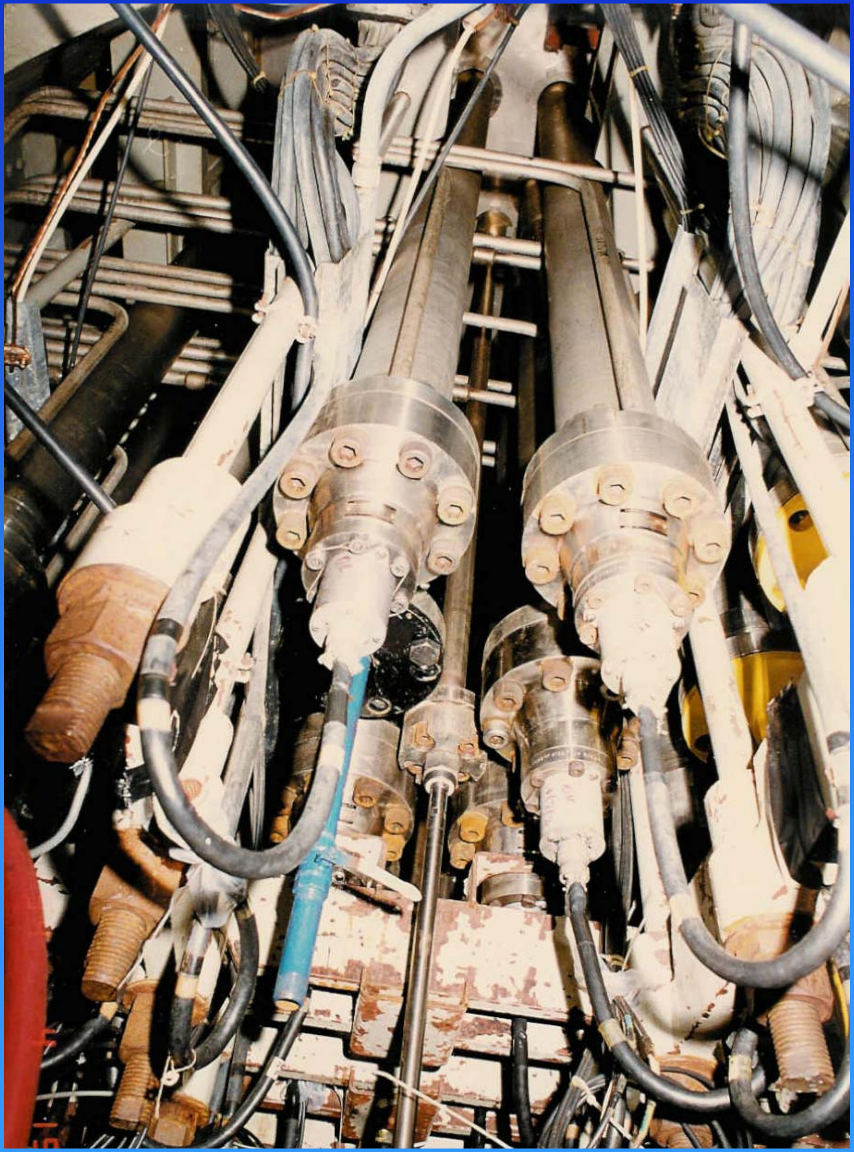
Typical Lower Vessel Drain Line Design



CHUG to NRC 7/22/05

Structural Integrity Associates

Lower Vessel Drain Line Access?



BWR Lower Head Drain Line Survey

- General configuration of BWR drain lines are similar
  - Vertical drop underneath vessel (0-100 cm [0-40" drop]), 5 cm (2") Schedule 160 CS pipe
  - 1st elbow is CS (~2/3 socket welded, ~1/3 butt-welded)
  - Horizontal run until it exits CRD area
  - After several changes in direction, ultimately connects to RWCU
  - Some lines are all CS, others change to SS
  - Some lines all 5 cm (2") diameter, others change to larger diameter
- Flow rates vary from blocked to 15 l/s (240 gpm) (most 2-4.4 l/s [30-70 gpm)
- Operating temperatures: 220 to 294ºC (430 to 562ºF)
- DO varies widely depending on water chemistry
- 11 BWRs had performed some inspections (7/05)

CHUG to NRC 7/22/05

BWR Lower Head Drain Line Parametric Analysis

- **Parametric analysis was performed using the CHECWORKS™ Steam/Feedwater Application (SFA) using a range of conditions from BWR survey**
  - **Temperature, flow rate, water chemistry**
- **CHECWORKS™ SFA used to predict FAC as well as manage inspection data**
- **Additional chemistry data for each plant was obtained from plants and BWRVIP**
  - **Water treatments (NWC, HWC-M, NMCA), exposure period on each water chemistry, etc.**
  - **Some plants were analyzed using CHECWORKS™ BWR Vessel & Internals Application (BWRVIA) to determine oxidant in lower plenum**

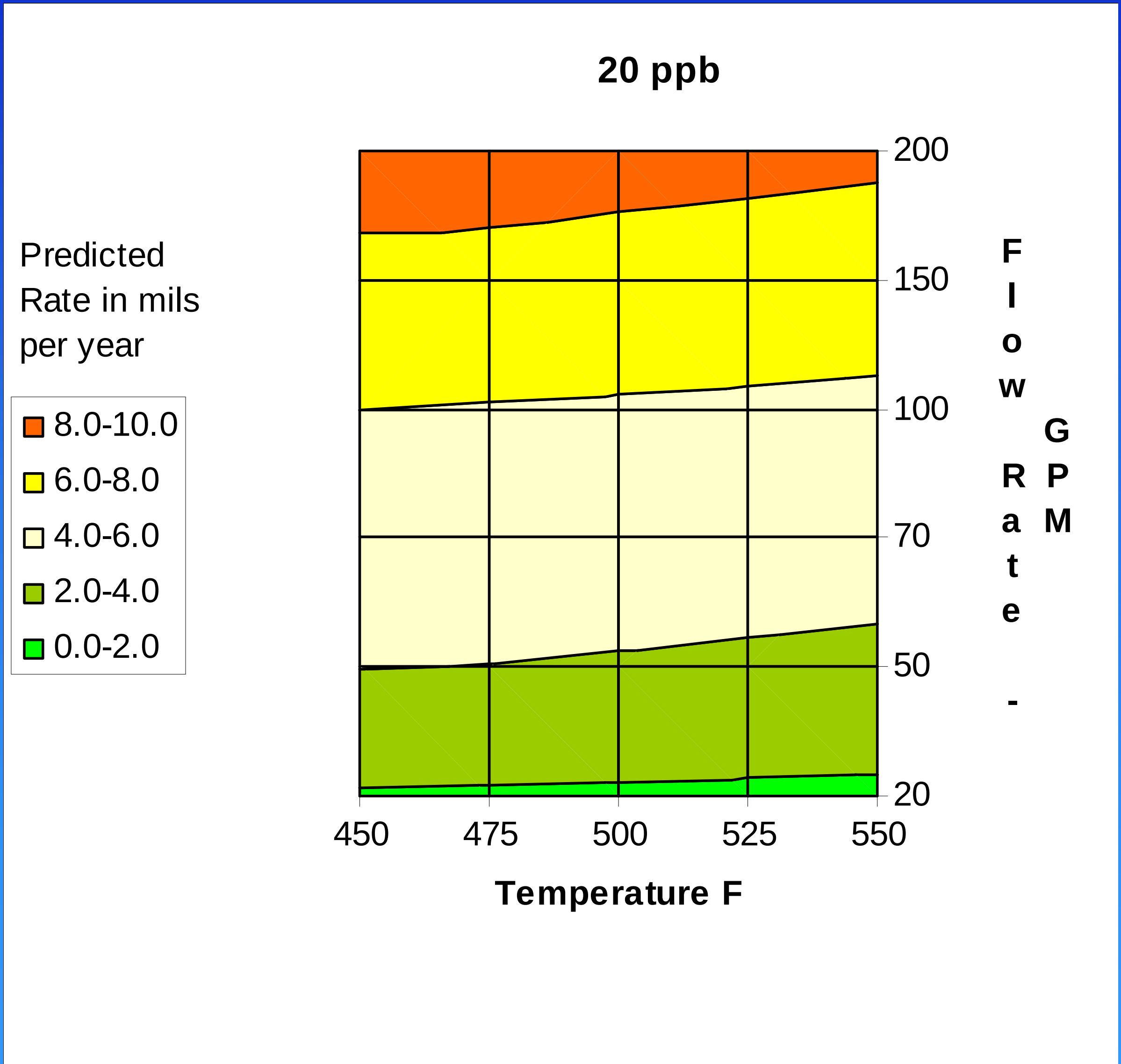
CHUG to NRC 7/22/05

BWR Lower Head Drain Line Water Chemistries

- BWRs operate with 3 types of water chemistries
  - NWC (very few), HWC and HWC + NMCA
- Different water chemistries affect the DO and hydrogen peroxide in the lower plenum
- FAC is directly related to oxidant
  - Oxidant = oxygen + 0.47 peroxide
- Typical values:
  - NWC: Oxidant = 250 ppb
  - NMCA: Oxidant = 125 ppb
  - HWC-M: Oxidant = 0 to 52 ppb, depending on level of H_2 injection

CHUG to NRC 7/22/05

BWR Lower Head Drain Line Sample Result



- **Predictions made at several oxidant levels**
- **Values plotted are FAC rates in butt-welded elbows**
- **Conditions covered the range of parameters from the survey**

CHUG to NRC 7/22/05

Results of Parametric Study

- The parametric analyses found that oxidant is the most important variable
  - NWC: 0.025 mm/y (<1 mpy)
  - HWC + NMCA: 0.05 mm/y (<2 mpy)
  - HWC: up to 0.7 mm/y (28 mpy)
- Flow rate is also important
- Temperature variations among units was relatively unimportant

CHUG to NRC 7/22/05

Case Studies and Plant Specific Analyses

- Case studies were performed to cover common plant conditions
  - Four chemistries (NWC, HWC [2 levels of H_2], and HWC + NMCA) were run at two flow rates
- Results showed that only BWRs on HWC with high levels of hydrogen (HWC-M) would have significant FAC rates (0.05 mm/y [>2 mpy])
- Based on the case studies, plant specific analyses were conducted of plants that had low oxidant for several years and moderate to high flow rates

CHUG to NRC 7/22/05

Categorization of BWRs

Based on these results, the 35 US BWRs were placed in one of three categories:

- Category A (18 units) – never on HWC-M – minimal susceptibility
  - Based on screening, total predicted FAC to date <0.9 mm (< 0.035”)
- Category B (4 units) – limited time on HWC-M – nominal susceptibility
  - Plant conditions indicate total predicted FAC to date 1.3 mm (<0.050”)
- Category C (13 units) – longer time on HWC-M – higher susceptibility

CHUG to NRC 7/22/05

Predictions for 12 Category C Units

Results of CHECWORKS™ predictions for FAC to date

Unit	Flow rate, gpm	HWC-M, yrs	Oxidant, ppb	Predicted FAC, mils (1)
Brunswick 1	20-30	11.1	0	56 – 113[2]
Dresden 2	80	12.8	0	130 – 259[2]
Fermi	63	7.5	1	98 – 196[2]
Hatch 1 & 2	55	5.2	26	61 – 122[2]
Hope Creek	195	12	52	44
Monticello	92	13.1	3	210 – 421[2]
Pilgrim	20-30	9.7	15	43 – 86[2]
Quad Cities 1	38	8.5	0	56 – 113[2]
Quad Cities 2	38	9.2	0	62 – 123[2]
Susquehanna 1 & 2	200/240	6.1/5.5	35	25

1. **For 2" schedule 160 pipe, t_{nom} = 0.344"**
2. **Range is provided for socket-welded elbows as a geometry factor has not been determined**

CHUG to NRC 7/22/05

Conservatisms in FAC Evaluations

- Ignored benefits of Zn – may reduce FAC by factor of 3
- Many BWRs have had drain line fully or partially plugged for extended periods
  - Reduced flow → reduced FAC
- Believe geometry factor used in predictions for socket-welded elbows is conservative
  - Lower bound used was 3.7 (= butt-welded elbow)
  - Upper bound used was 7.4 (2x butt-welded elbow)
  - Highest geometry factor found to date is 6.0
- Ignored benefits of noble metals on FAC
  - Limited data shows reduces dissolution of oxide
- Assumed all components to have zero Cr
  - Cr >0.04% reduces FAC

CHUG to NRC 7/22/05

Methods to Control FAC in LWRs

- BWRs
  - Replace carbon steel with low alloy steel/SS
  - Increase dissolved oxygen content (e.g., >30 ppb)

Oxygen (ppb)	Relative FAC
10	1.00
30	0.30
50	0.18
100	0.11
200	0.003

- PWRs
  - Replace carbon steel with low alloy steel/SS
  - Increase pH

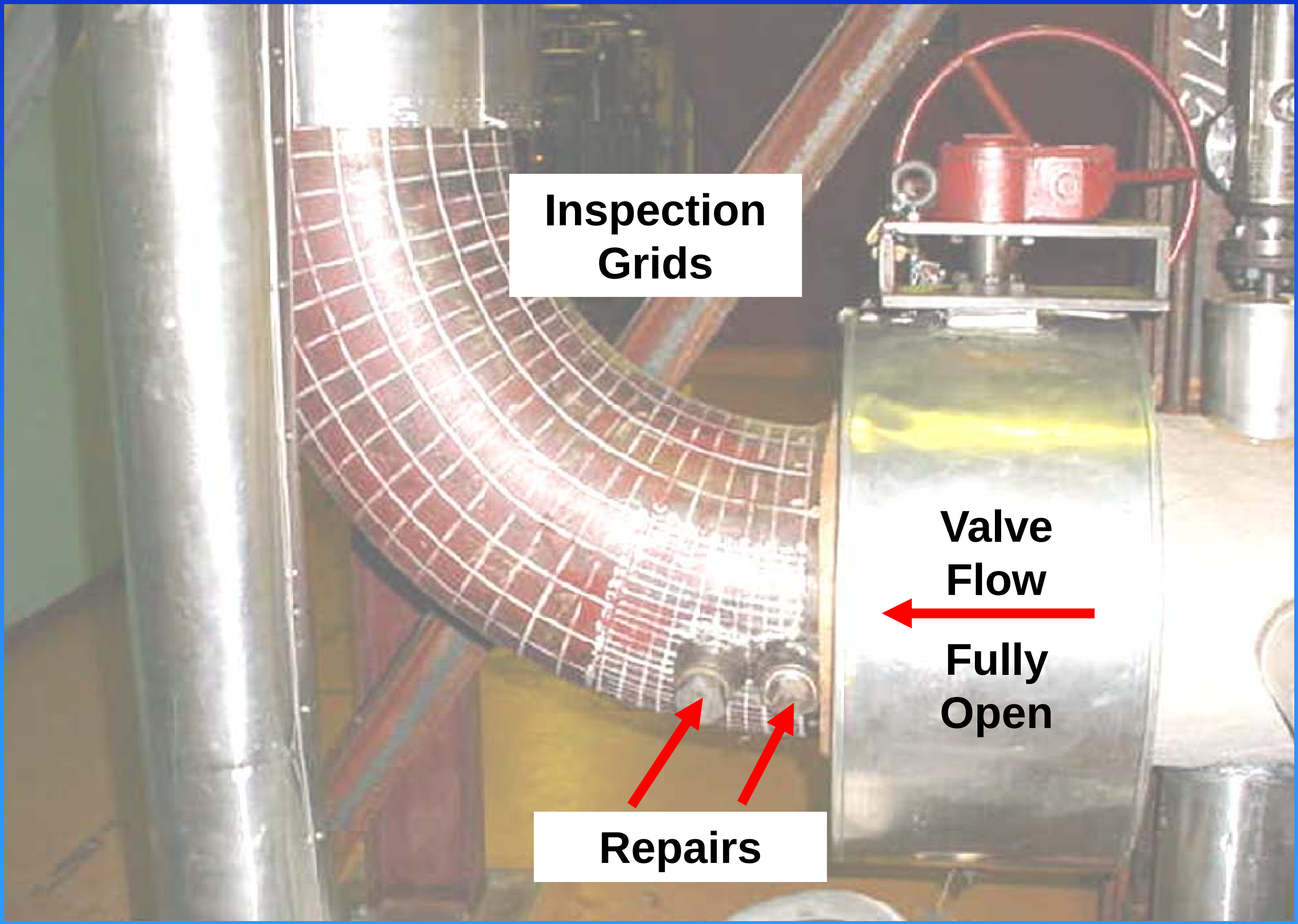
Cavitation

- Cavitation is the repeated nucleation, growth and violent collapse of cavities, or bubbles, in a liquid
- Rapidly collapsing vapor bubbles produce shock waves that produce pressures as high as 414 MPa (60 ksi)
- Cavitation can occur in any liquid in which the pressure fluctuates either because of flow patterns or vibrations in the system
- If the local pressure falls below the vapor pressure of the liquid, cavities can nucleate, grow to a stable size and be transported down-stream with the flow
- When they reach a higher-pressure region, they become unstable and violently collapse
- Cavity collapse velocity typically ranges from 100 to 150 m/s (225 to 335 mph)! – You actually hear it!

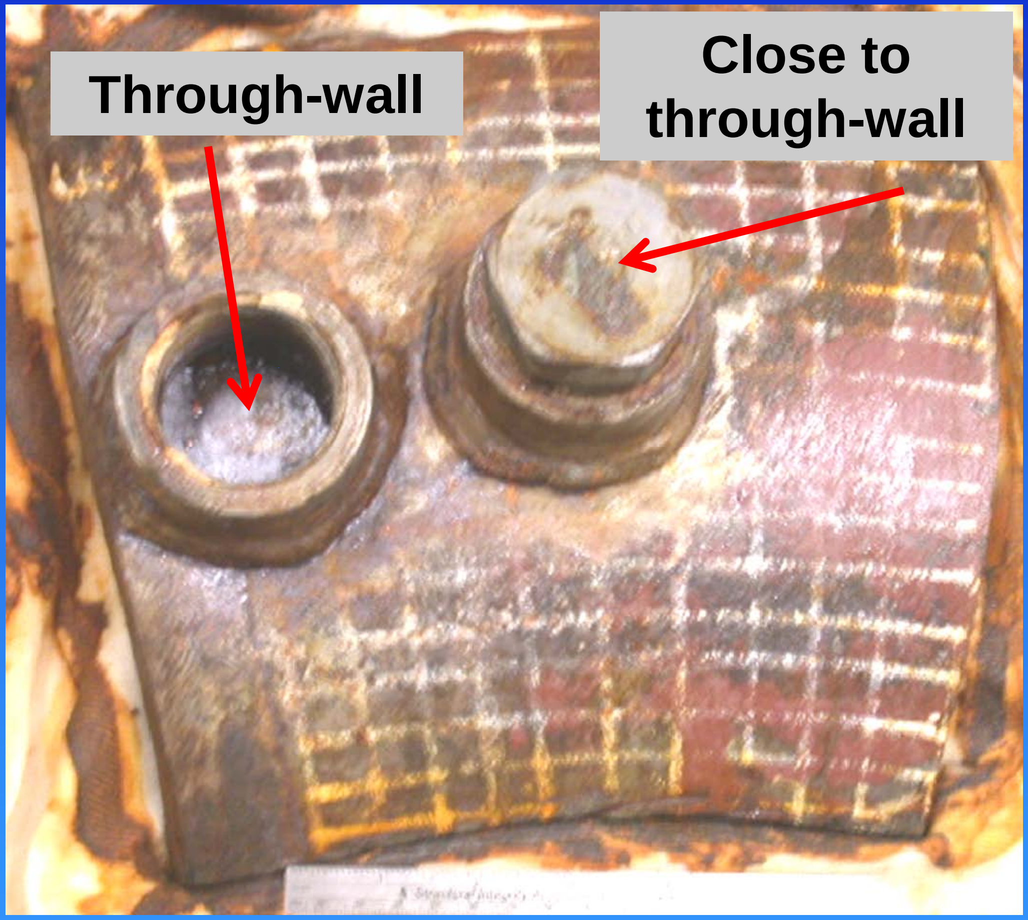
Cavitation

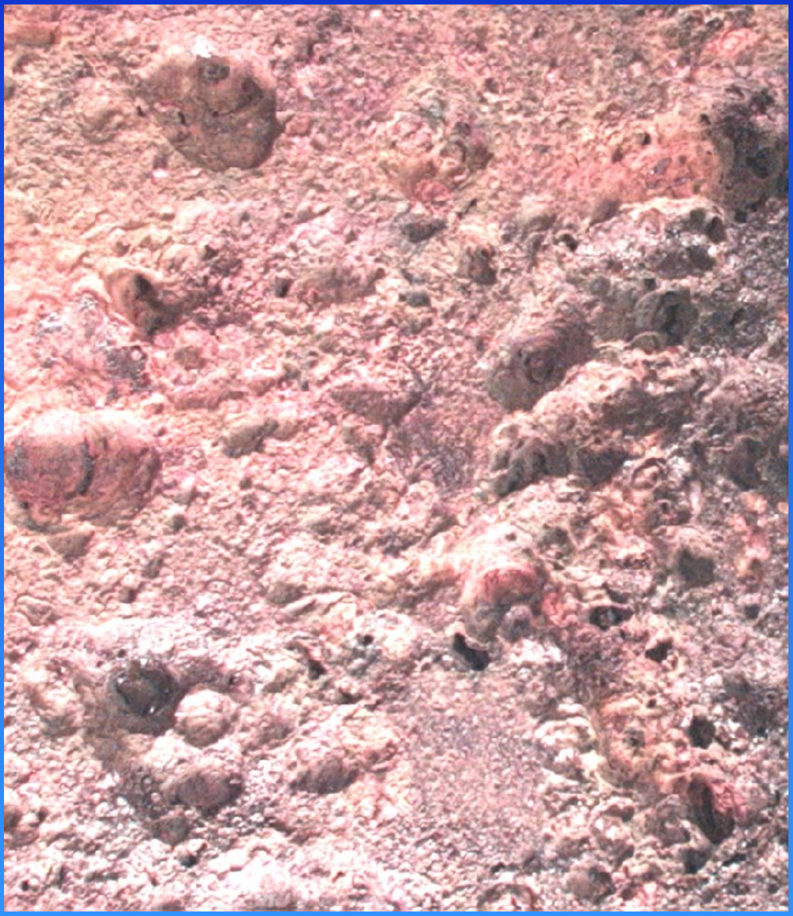
- Commonly occurs in hydrofoils, pipelines, hydraulic pumps and valves
- Pressures produced by the collapse may cause localized deformation and/or removal of material (erosion) from the surface
- Cavitation can also interact with corrosion processes as the collapsing vapor bubbles mechanically destroy the protective surface films and fresh surfaces are exposed to corrosion and the reestablishment of protective films, followed by more cavitation, etc.
- Damage occurs when the cycle is allowed to repeat over and over again

Cavitation of Perry Carbon Steel Elbow



Carbon Steel Elbow Cavitation

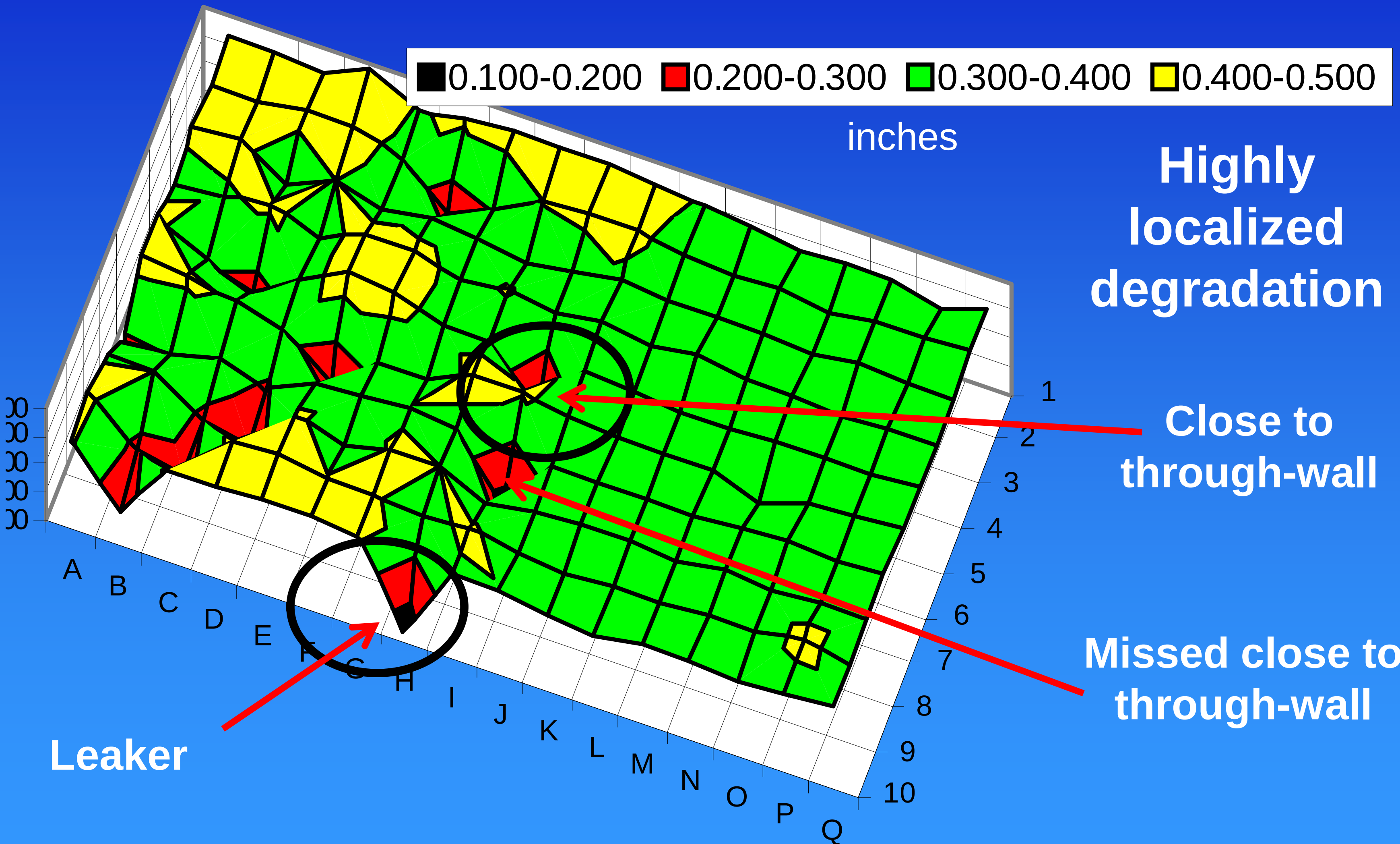




Section of Elbow with Welded Repairs Designed to Capture Two Pinhole Leaks

ID Surface Corrosion Product

Carbon Steel Elbow UT Thickness Map



Nominal thickness = 9.5 mm (0.375")

Impingement Corrosion

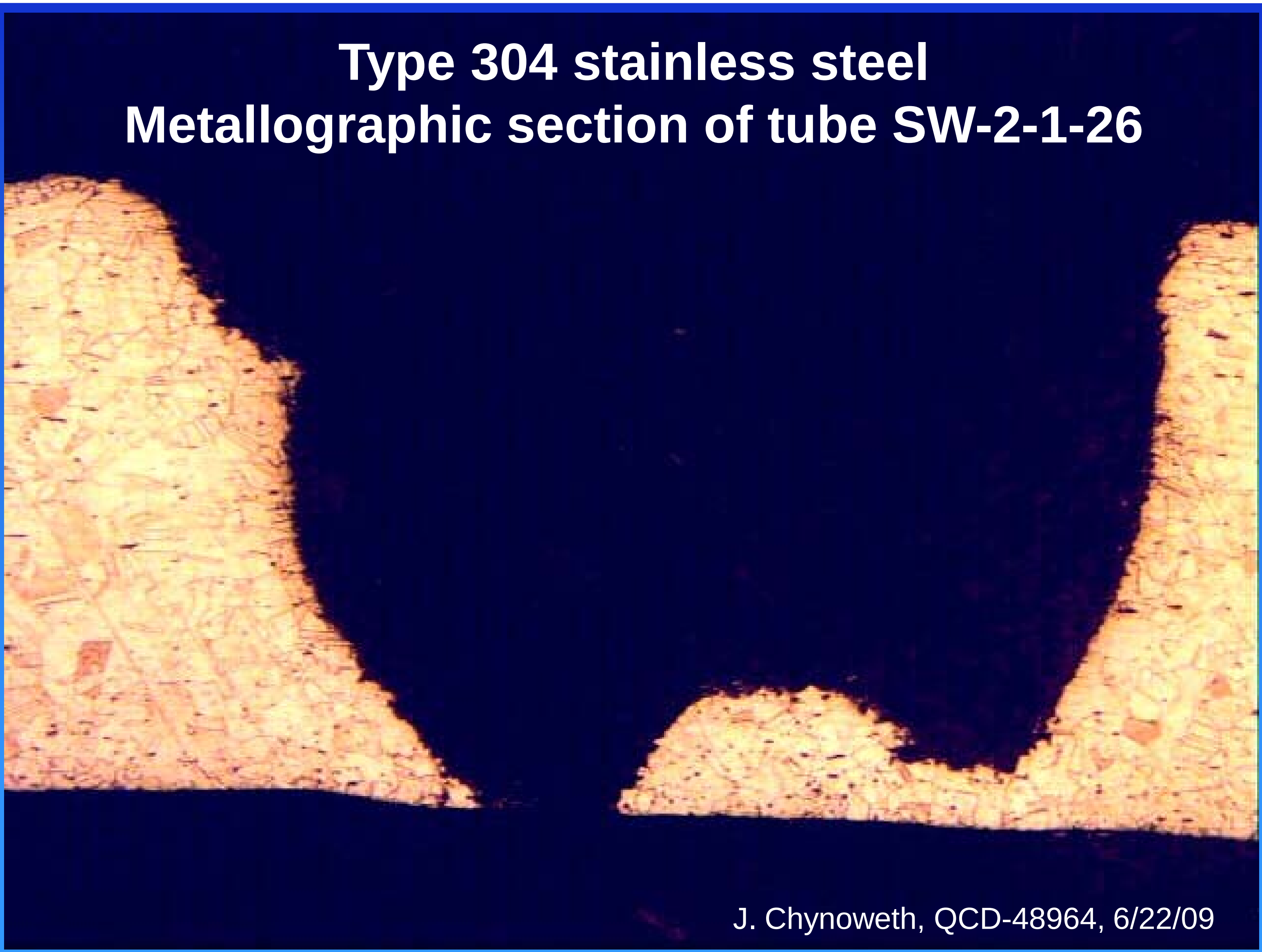
- Impingement corrosion is related to cavitation corrosion
  - ♦ Localized erosion-corrosion caused by turbulence or impinging flow
  - ♦ Accelerated by entrained air bubbles and suspended solids
  - ♦ Occurs in pumps, valves, orifices, on heat-exchanger tubes and at elbows and tees in pipelines
- Produces a pattern of localized attack with directional features
  - ♦ Pits or grooves tend to be undercut on the side away from the source of flow
- Impingement and cavitation may occur together

Impingement Corrosion of Quad Cities 1 Main Condenser

Engraved Tube support edge

J. Chynoweth, QCD-48964, 6/22/09

Impingement Corrosion of Quad Cities 1 Main Condenser



Impingement Corrosion of Ti Condenser Tubes

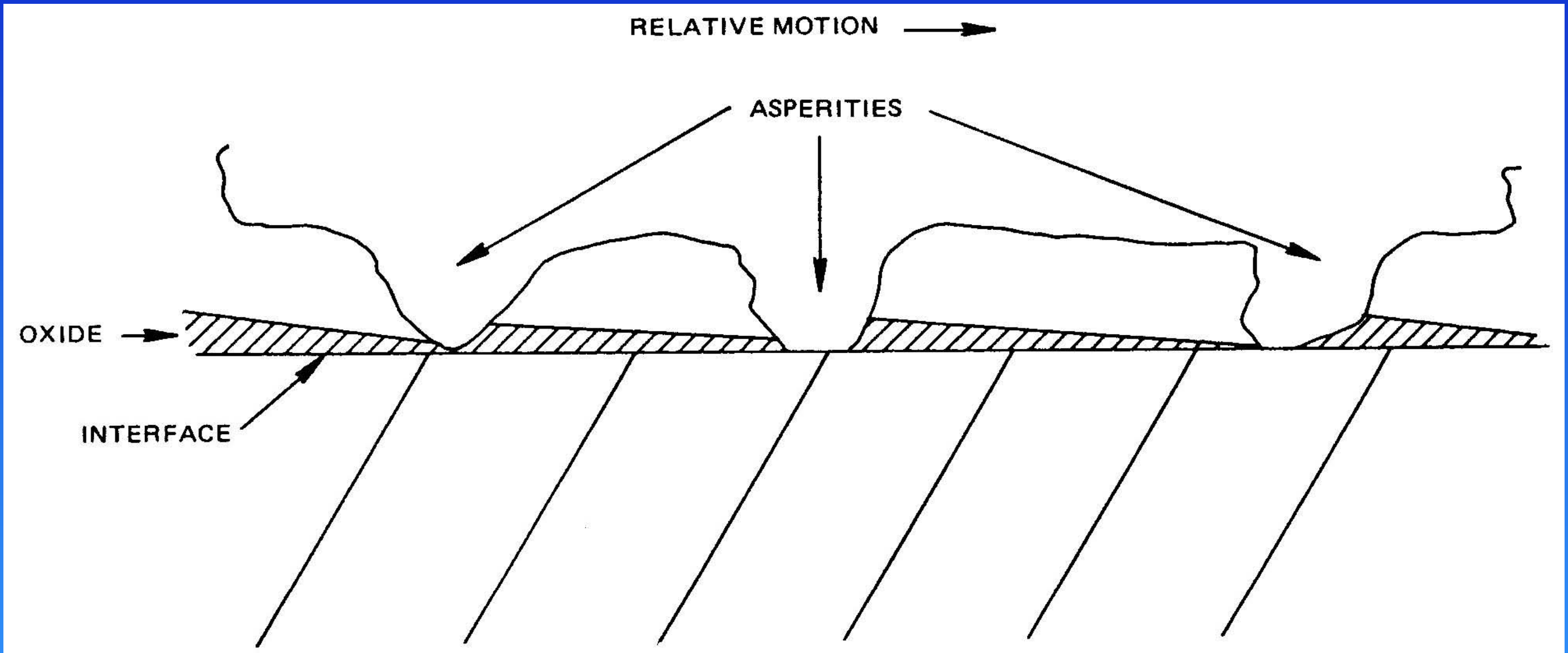
Reheater dump header caused a high-velocity water and steam to impinge on the top row of Ti tubes

D. Daniels, POWERnews, 10/10

Fretting Corrosion

- Fretting corrosion is a wear process enhanced by corrosion at the asperities of contact surfaces (while E-C is a corrosion process enhanced by wear)
- Damage is induced under load and in the presence of repeated relative surface motion, as induced for example by vibration
- Fretting results from abrasive wear of surface oxide films
- Slight motion (vibration) wears away the protective film and underlying metal
- Metallic wear particles are rapidly oxidized to hard oxides that act like abrasives

Fretting Corrosion



L. Shreir, et al., Corrosion, 1994

Fretting Factoids

- Fretting will increase linearly with increasing contact load if the fretting amplitude is not reduced
- No amplitude below which fretting does not occur. However, if the contact is only elastic, no fretting damage
- Fretting wear loss increases with amplitude
  - Amplitude effect can be linear or
  - Can be a “threshold” amplitude above which rapid increase in wear occurs
- Fretting wear incubation period is negligible

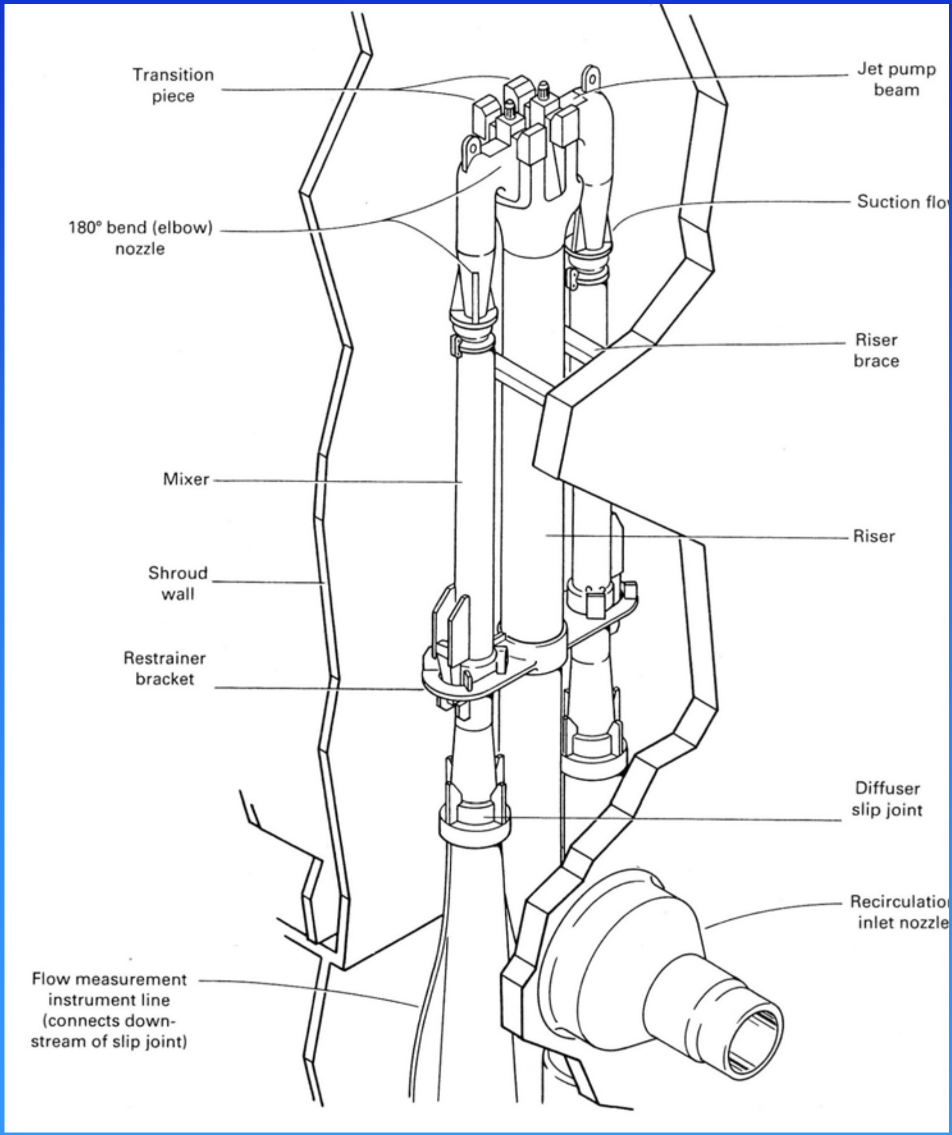
Example of Fretting Corrosion

Automobile Wheel Bearings

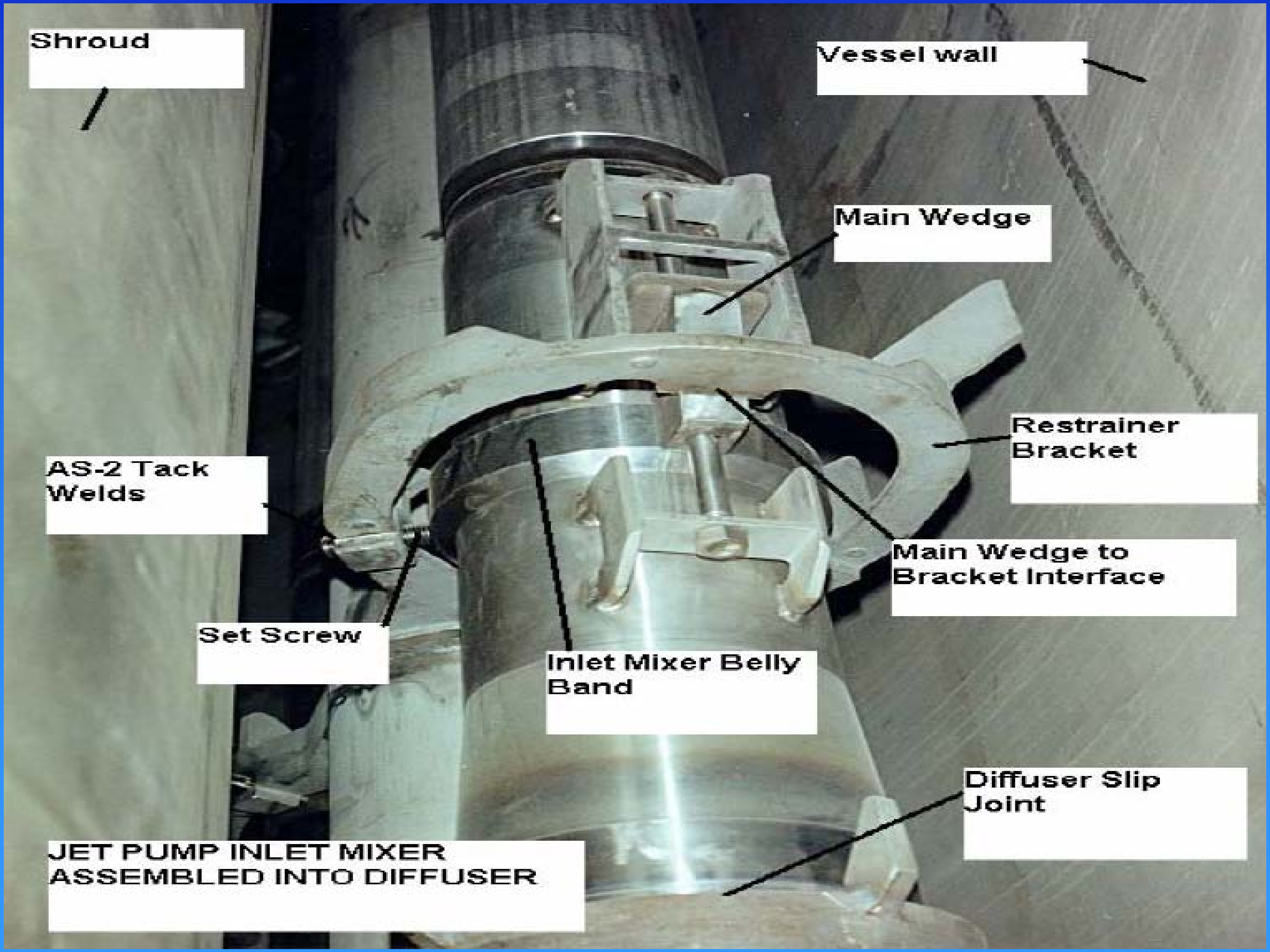
- Shipment of cars via rail or ships over long distances (e.g., Detroit to West Coast)
- Severe corrosion found between the axles and the front wheel bearings when cars were secured by chocking the wheels
  - Damage worse in winter than summer
  - Cars were not operable upon delivery to dealers!
- Mitigated by supporting the axles so the wheels hung free decreasing the load and severity of attack
  - Fretting corrosion was mitigated, but not completely eliminated

Mitigation of Automobile Wheel Bearing Fretting Corrosion

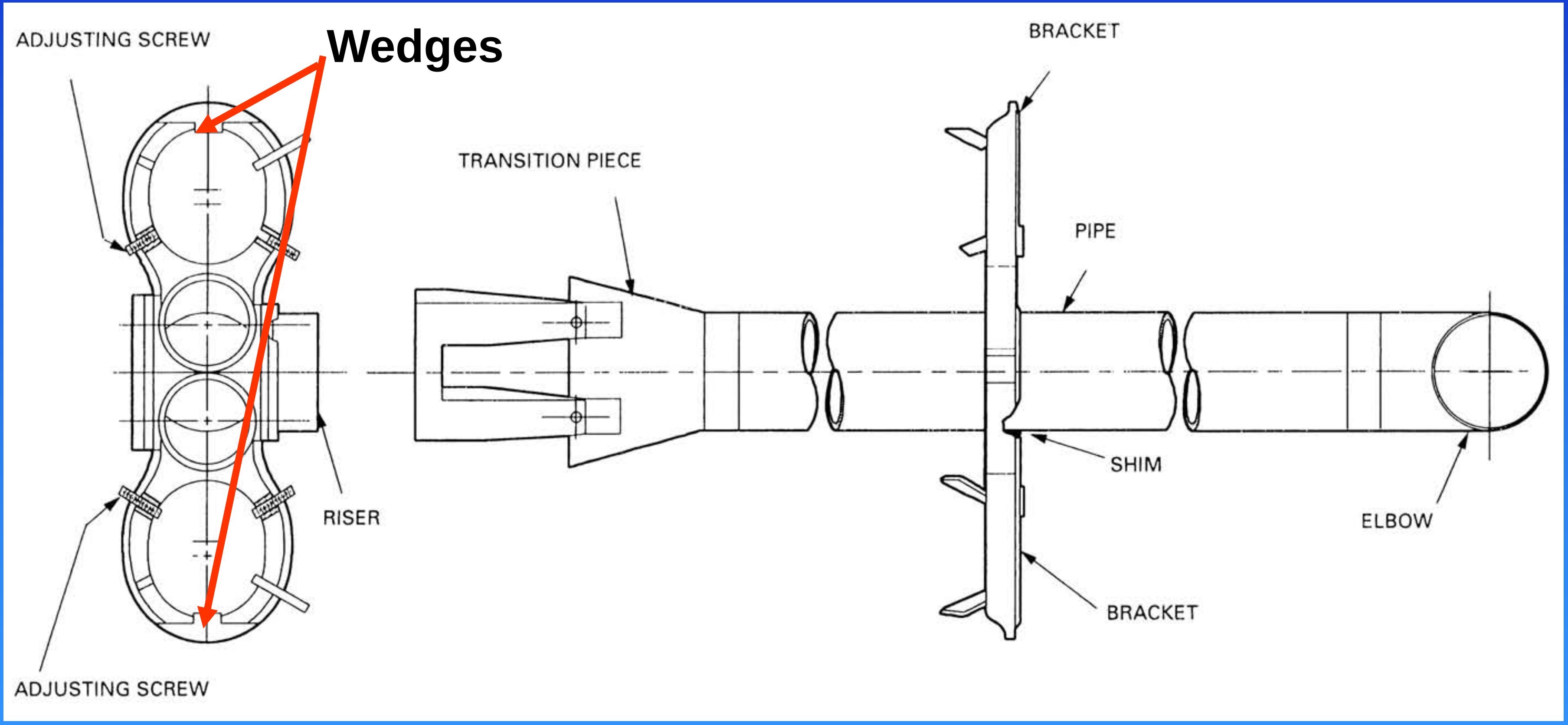
BWR Jet Pump Assembly



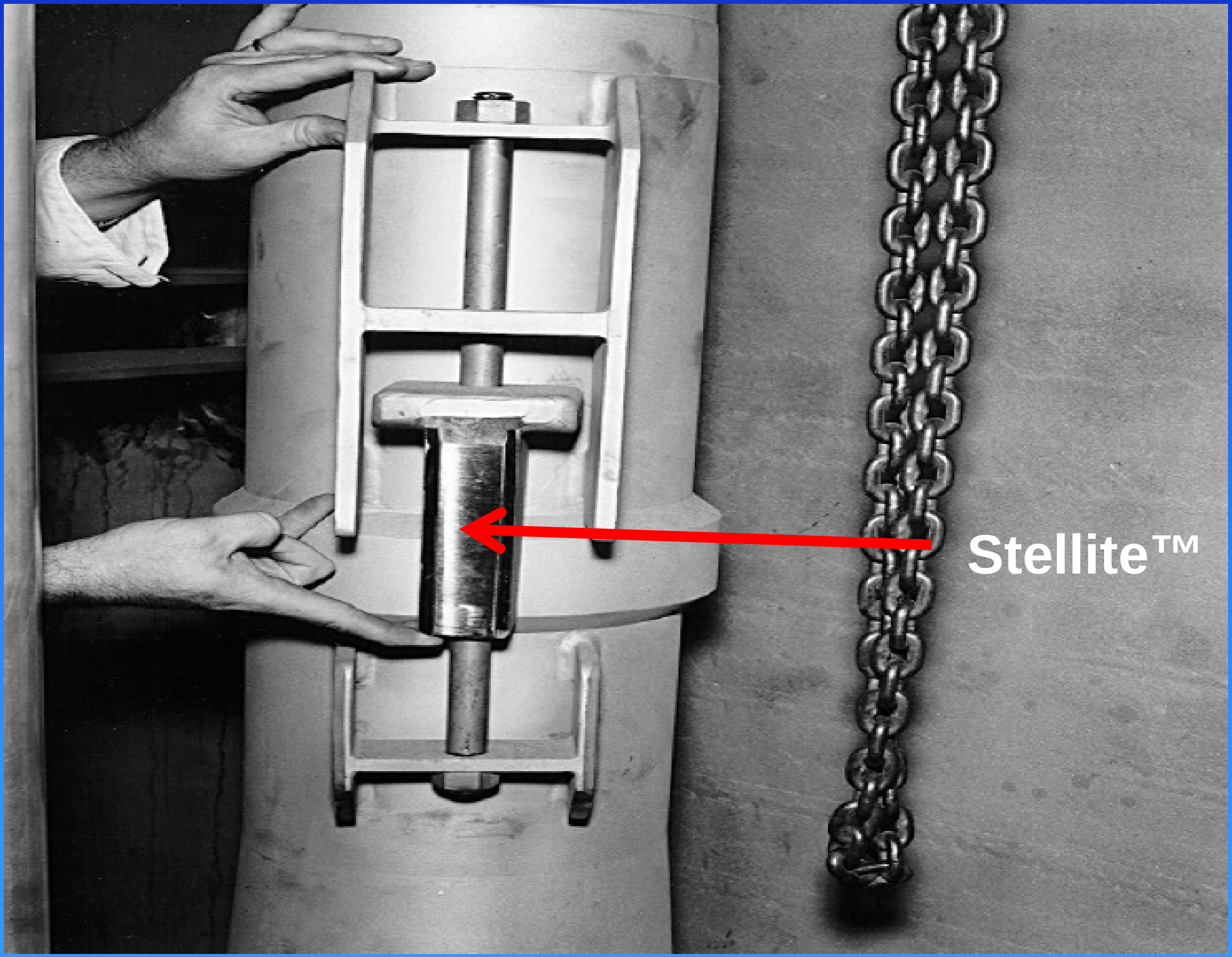
Jet Pump Close Up



BWR Jet Pump Wedges

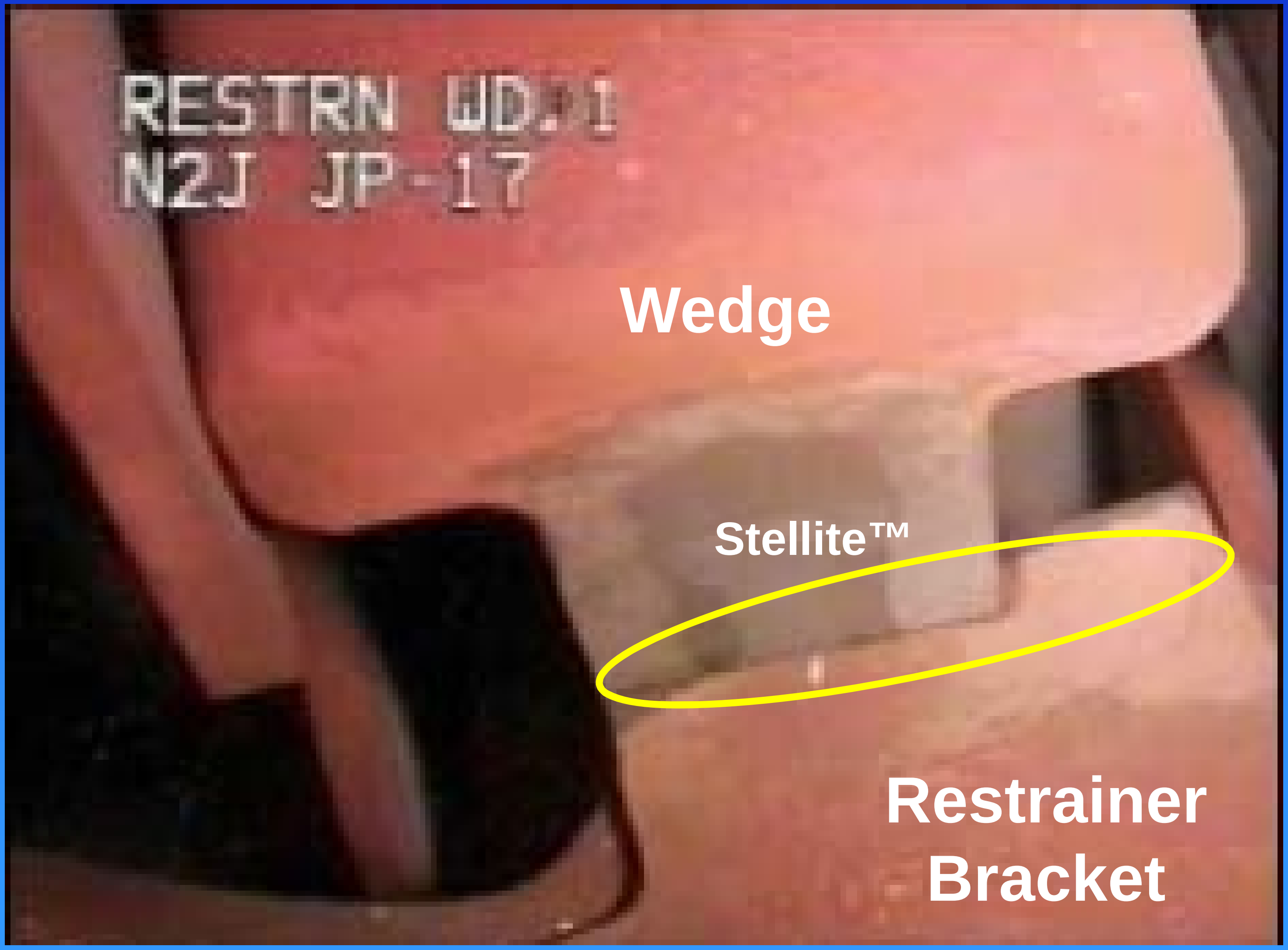


Stellite™ Wedge



Jet Pump Wedge Fretting Corrosion

Jet Pump Wedge Fretting Corrosion



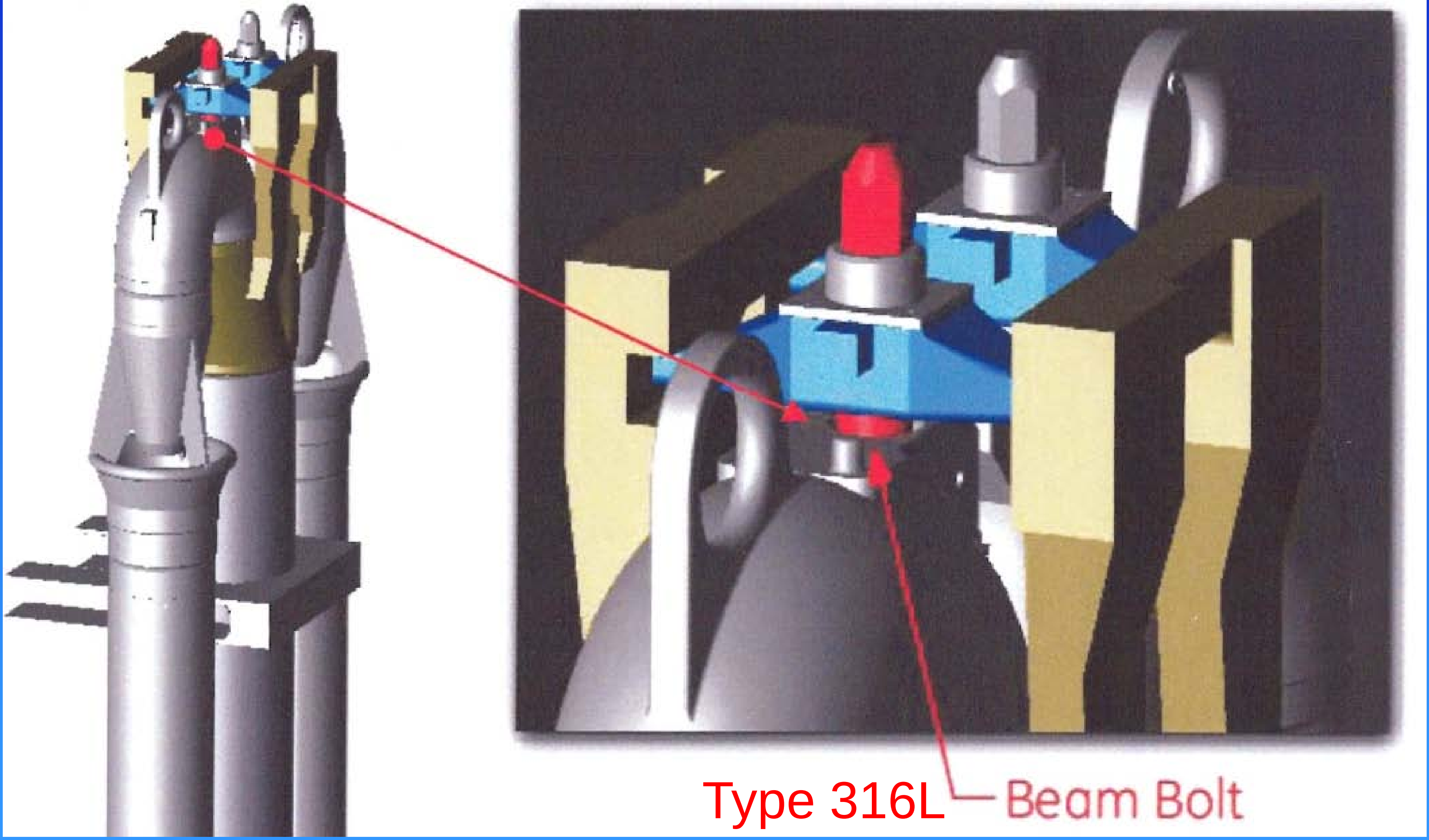
Jet Pump Bolt Fretting Corrosion

- Spring 2011 - JP retainer plate loose under one jet pump beam
- Plate used for beam alignment during installation, otherwise provides no other function
- Retainer bolt pulled out during beam replacement in 1994 and then worked its way out
- Retainer and retainer bolt were removed and upon inspection noted notching on the hold down beam bolt due to fretting corrosion

Jet Pump Beam Bolt Fretting Corrosion

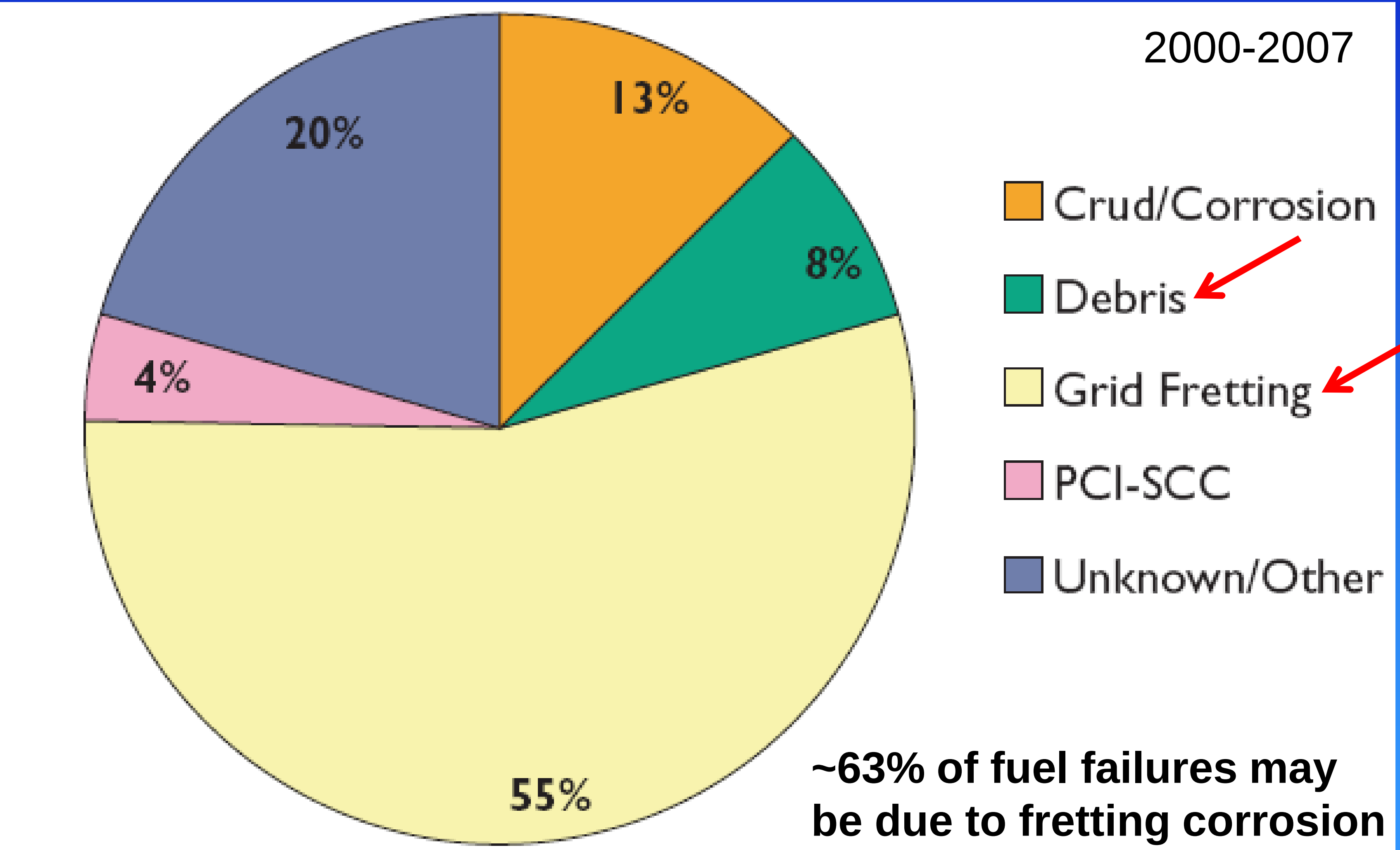
- Spring 2011 - examinations were performed on the Jet Pump 05 retaining fingers
  - JP retainer plate loose under one jet pump beam
  - Plate used for beam alignment during installation, otherwise provides no other function
  - Retaining fingers revealed the attachment bolt had backed out
- Removed retaining fingers revealed
  - Loose finger movement generated fretting corrosion of Type 316L SS beam bolt on the jet pump 5 side
  - No wear on the Jet Pump 6 side of the bolt or jet pump beam

Location of Jet Pump Beam Bolt



Jet Pump Beam Type 316L SS Bolt Fretting Corrosion

Percentage of Fuel Failures by Mechanism for PWRs and BWRs



~63% of fuel failures may be due to fretting corrosion

B. Thompson, Nuclear News, 06/08

Fretting Corrosion of Fuel Rods and Foreign Material Exclusion

- NRC requires utilities to shut down and replace leaking fuel rods, which is extremely expensive
- Fuel rod failures also negatively affect the utilities' insurance premiums and their operational licenses
  - Therefore, they expect foreign material prevention controls throughout the supply chain of their suppliers
- Utilities are highly sensitive to the issue of debris and require their suppliers to have programs for control
- Institute of Nuclear Power Organizations (INPO) has required utilities to take actions to assure no leakers by the year 2010

GNF, 1/08

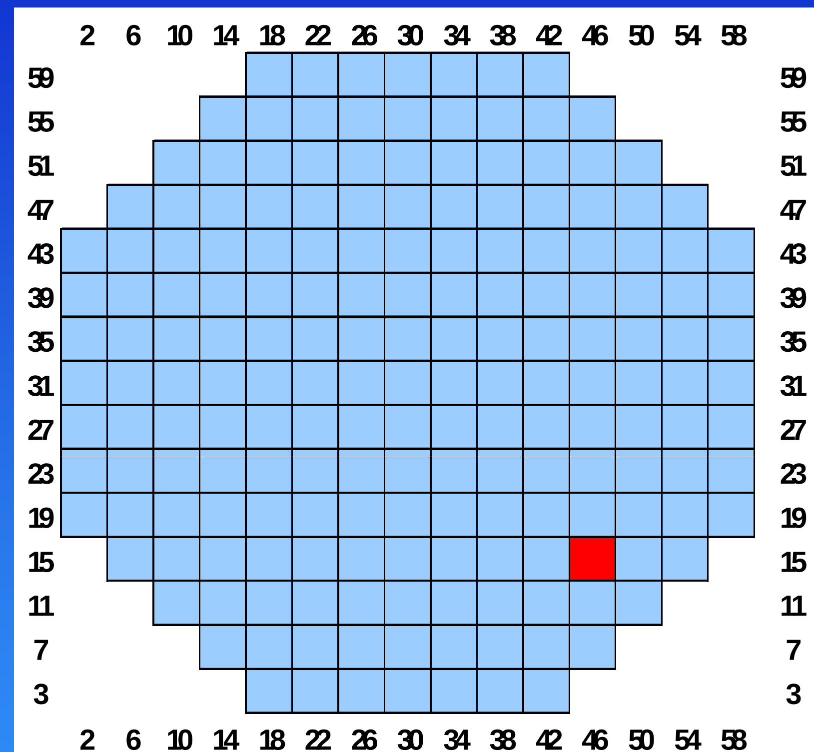
What is a "leaker"?

- Fuel rods can fail by leaking radioactive material into the reactor water through cracks or holes created in the fuel rod, i.e., "leakers"
- These cracks and holes are usually caused by either debris in the reactor water (or by hydrogen material inside the fuel rod)
- To remove the leaker, the reactor site must find the leaking bundle, suppress the reaction and replace the fuel rod
- The operators doing this work on the reactor floor are exposed to a higher radiation dose rate and the cost to the utility is $Ms in extra expense and lost revenue

GNF, 1/08

Fuel Leaker Consequences

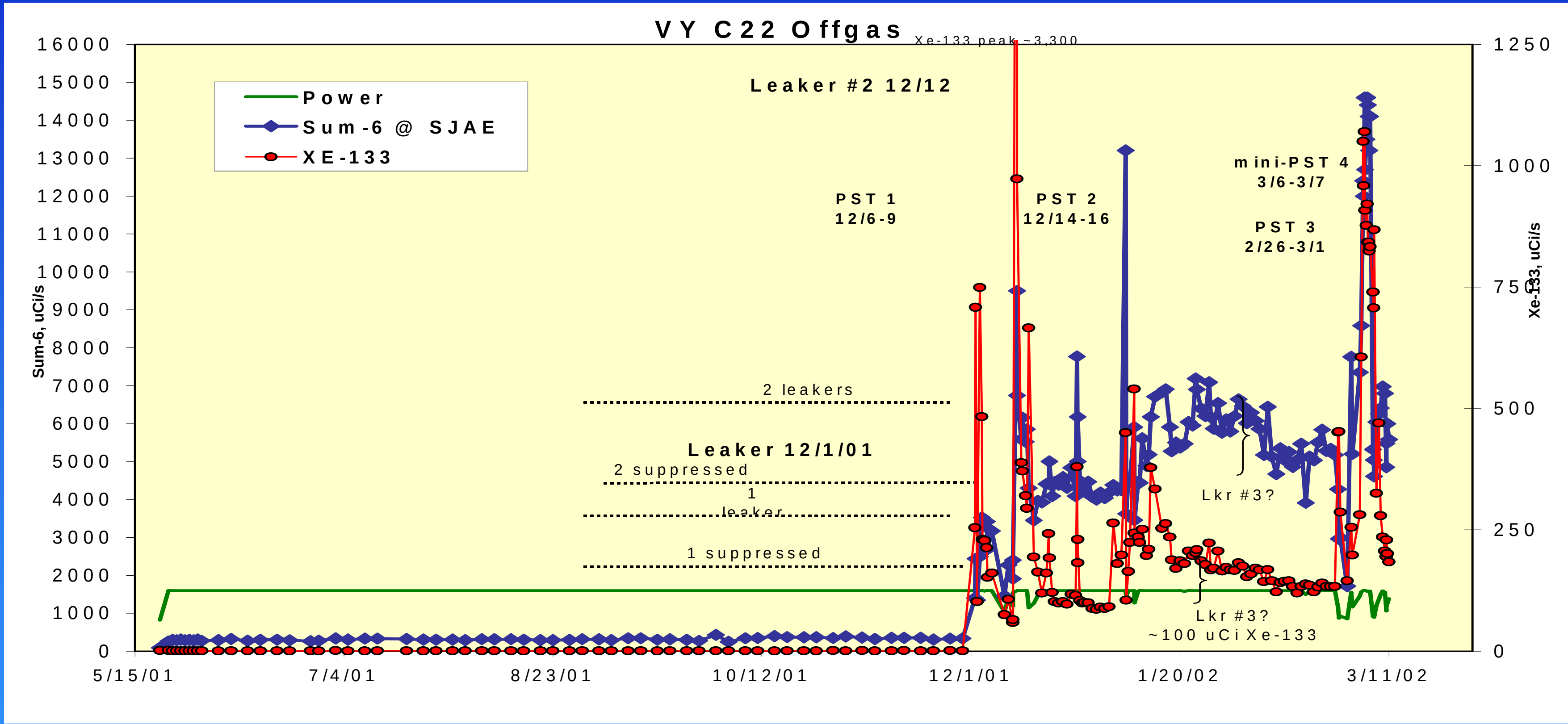
Fuel rod develops a crack or hole due fretting corrosion that allows gases to escape



Plant may spend significant time trying to identify and remove the leaker

GNF, 1/08

Fuel Leaker Consequences

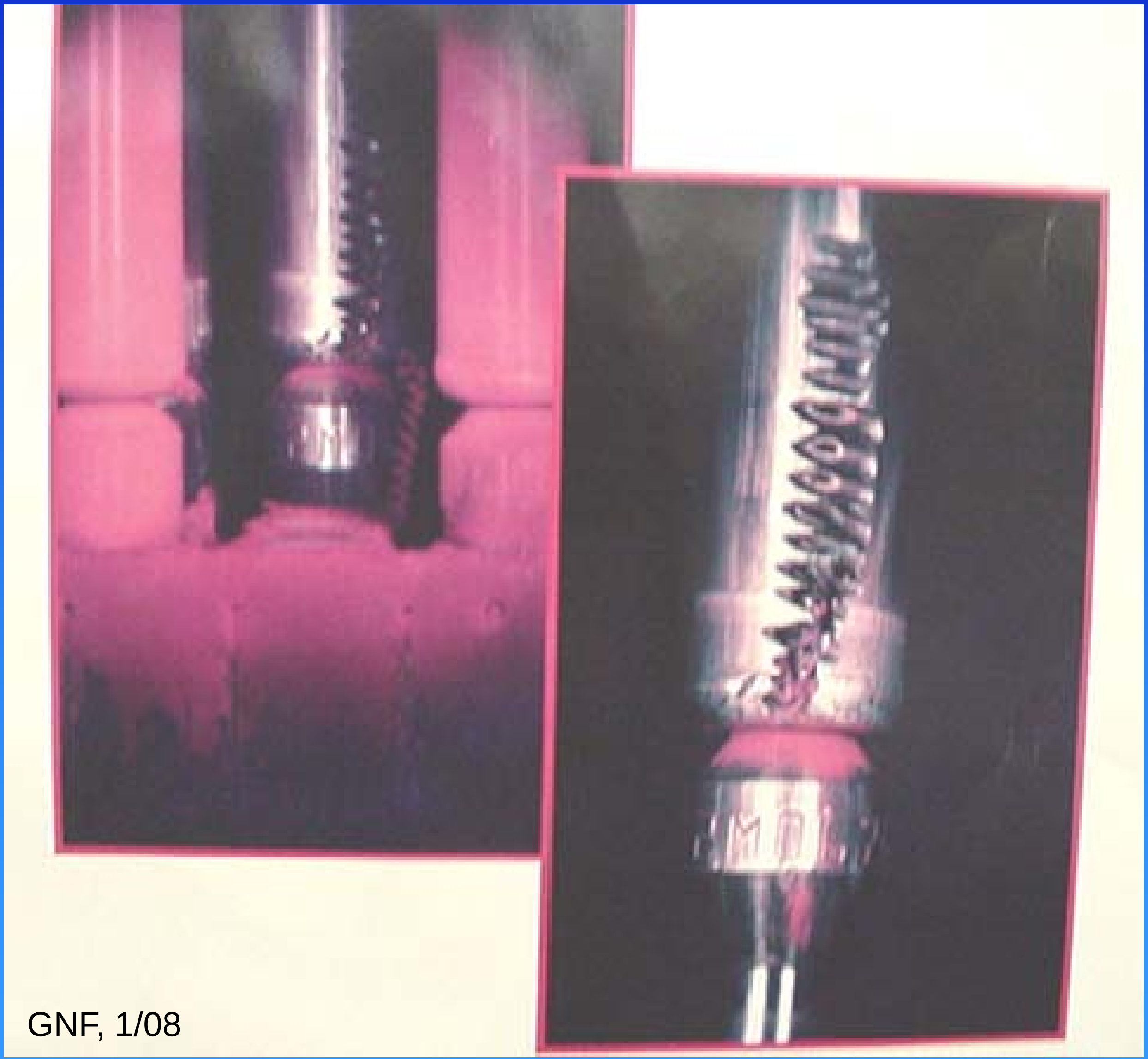


Increased steam radiation levels detected by monitors

GNF, 1/08

Debris Fretting Corrosion Failures

- Debris can get caught in a spacer or tie plate in a fuel bundle allowing the debris to rub against the rod during reactor operation
- Debris rubbing against a rod can create a hole and cause leakage of radioactive fissile material



GNF, 1/08

Debris Fretting Corrosion Failures

GNF, 1/08

What is Debris?

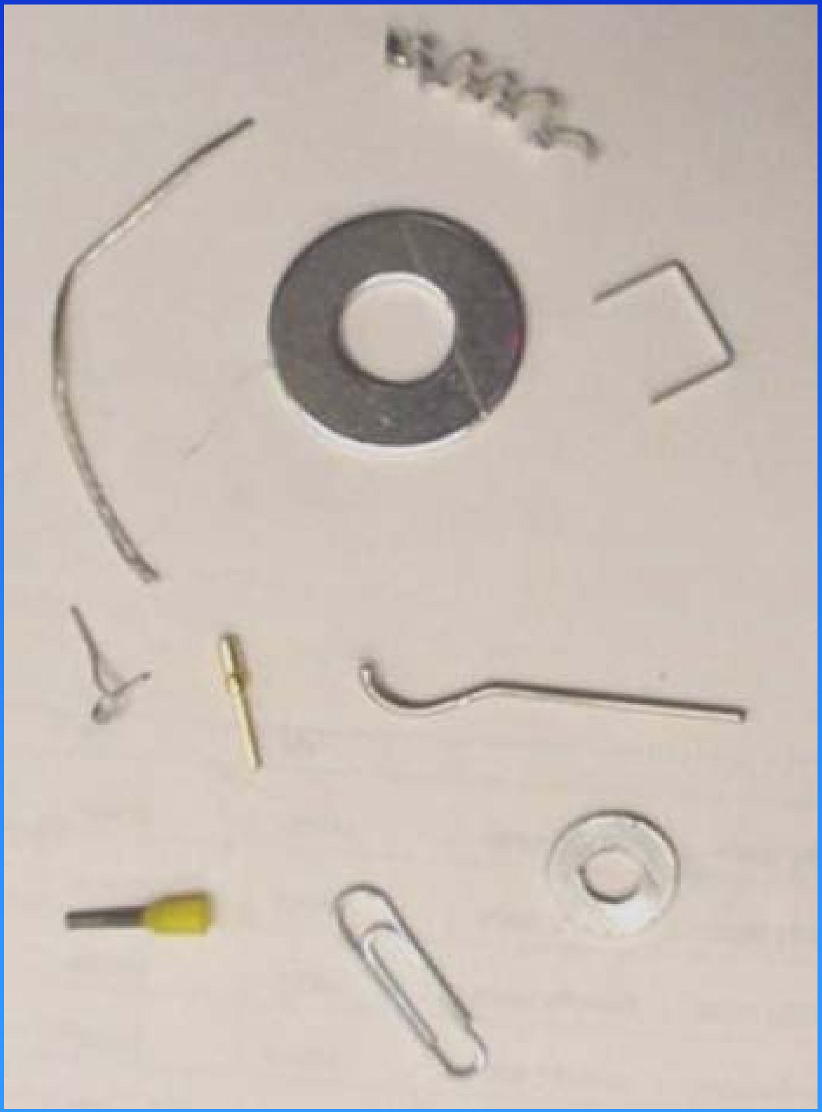
Manufacturing - Wire brushes, weld splatter, machining burrs

Broken Tools or Parts - Crane springs, extender keyways, etc.

Dropped Hardware - Nuts, washers, springs, etc.

Maintenance Activities - Clipped wires, drill turnings, etc.

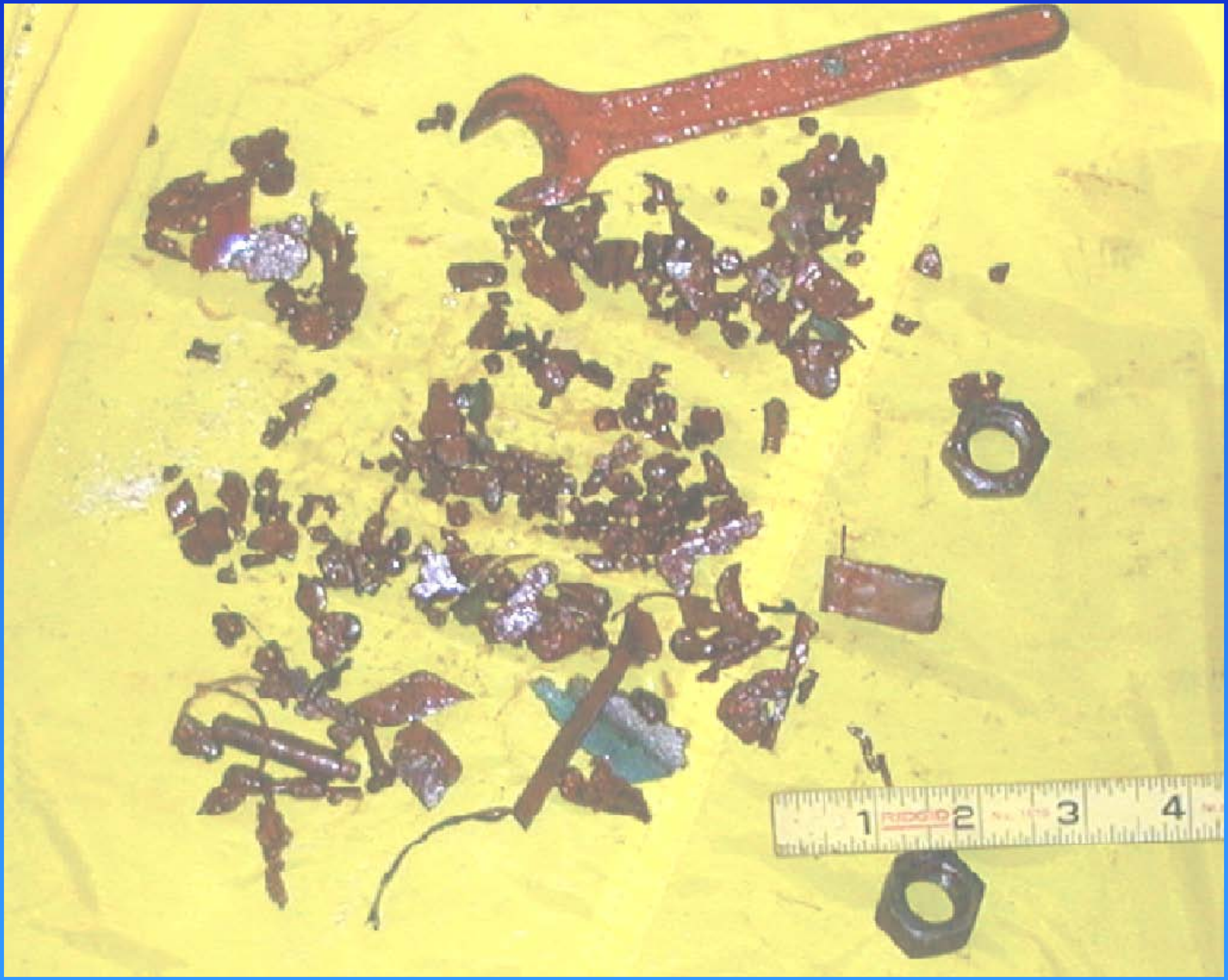
Unintentional Entry - Paper clips, earring studs, pen clips, etc.



GNF, 1/08

Feedwater Heater Debris

Debris found in a feedwater heater where a fretting fuel failure occurred



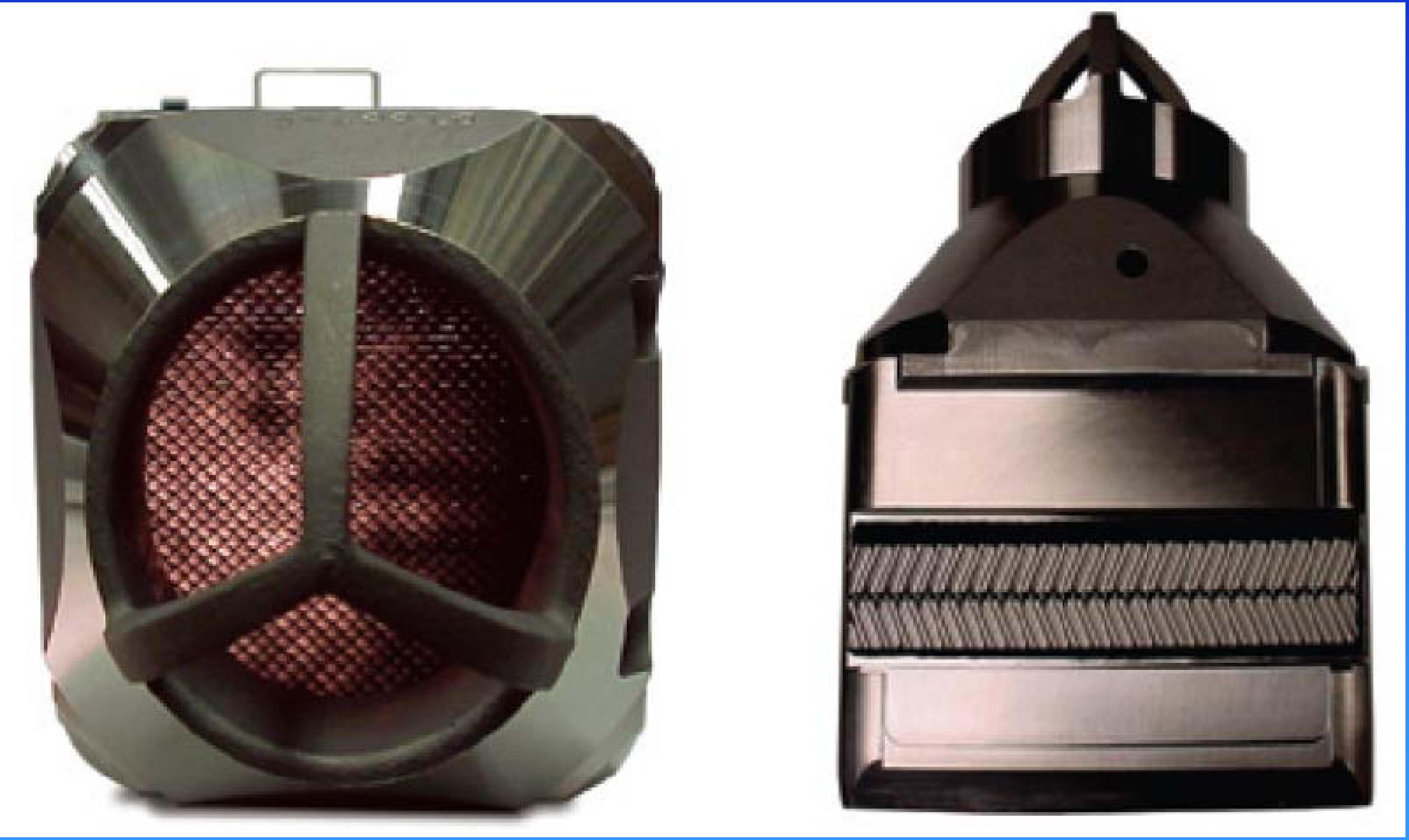
GNF, 1/08

Debris Control Guidelines

- Maintain excellent housekeeping practices
- Establish a foreign material control area
  - No open food, drink, or hand lotion
  - No smoking!
- Control all activities that may introduce foreign material, such as preventive maintenance work, relocation of equipment, use of power tools for drilling or wire brushing
  - Remove all product from the area or protected from inadvertent contamination
  - Thoroughly clean area upon completion of such activities before re-introduction of product
- Protect and cover unattended product
- Avoid use of staples, metal paper clips, pens with metal clips, etc.
- Avoid wearing of loose jewelry, such as earrings, bracelets and necklaces
- Fuel debris filters

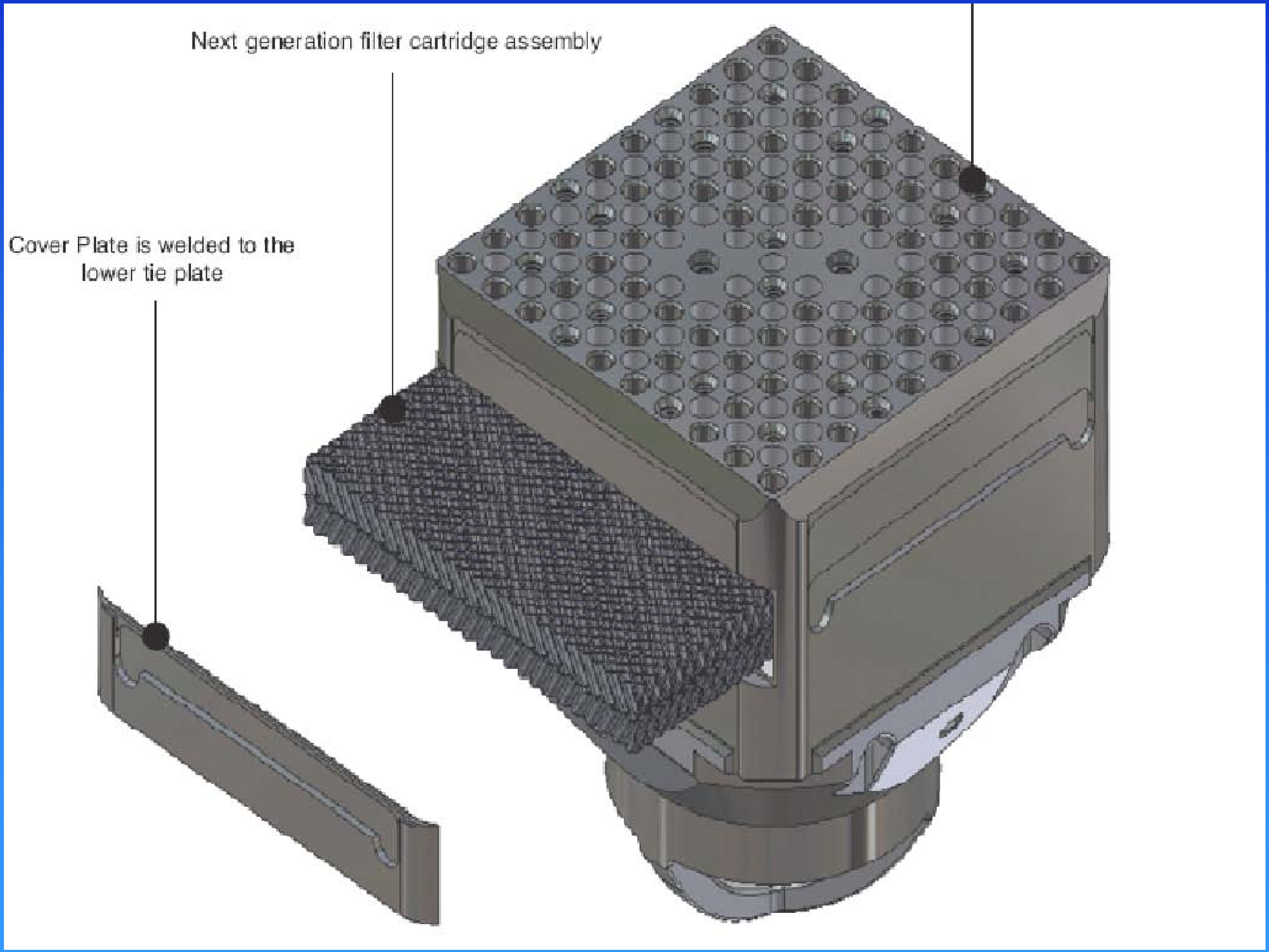
GNF, 1/08

BWR Fuel Debris Filter



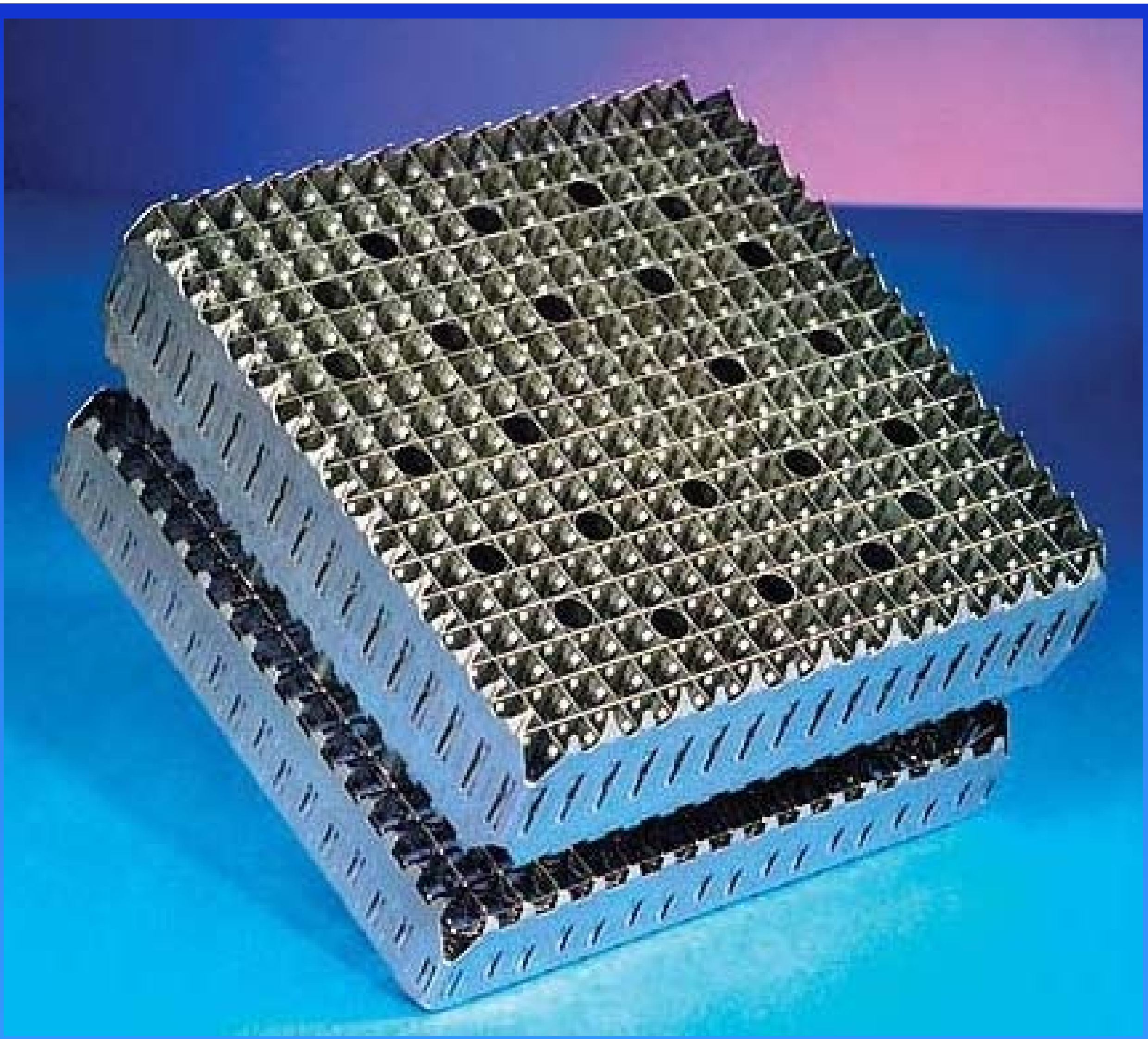
GEA-14511 09/06

BWR Fuel Debris Filter



GEA-14511 09/06

PWR Fuel Debris Filter



Westinghouse 11/04

Galvanic, Dealloying and Velocity Phenomena Summary

- Galvanic Corrosion
  - Due to the diversity of materials and environments
  - Not a concern at high temperatures in LWRs
- Dealloying Corrosion
  - Preferential dissolution of more active metal in an alloy – some Cu alloys and cast iron
- Velocity Phenomena
  - Effects of flow rate on corrosion may be unpredictable
  - FAC is main LWR velocity related corrosion concern