U.S.NRC
United States Nuclear Regulatory Commission
Protecting People and the Environment

Crevice Corrosion
Pitting Corrosion
IGA

HRTD
Human Resources
Training & Development

Note: While this course does not contain proprietary BWRVIP or MRP information, per se, it does contain open literature information that was used in the creation of BWRVIP or MRP documents or BWRVIP or MRP information that was subsequently made non-proprietary via publication, etc.

Crevice Corrosion, Pitting Corrosion and IGA Learning Objectives

- Understand the mechanism of crevice corrosion
  - ♦ How are crevice corrosion in BWRs and PWRs different?
    - There is a BWR crevice corrosion diagram, but no PWR crevice diagram. Why?
  - ♦ Steam generators crevice corrosion and mitigation
- Understand the mechanism of pitting corrosion
- Understand the mechanism of IGA

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

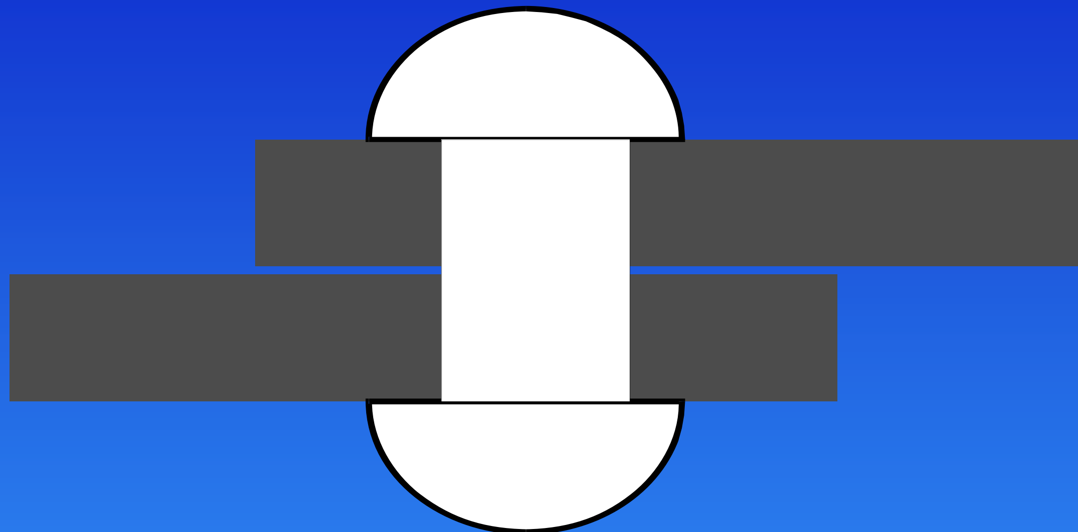
Items 2–5: Macro Localized Corrosion

Items 6–9: Micro Localized Corrosion

Microbiological activity can affect all of the above

Crevice Corrosion

Crevice Corrosion



- Mechanism
- LWR Case Study Examples
  - BWR Safe Ends
  - SG Tubes/Tubesheet/Support Plates

Introduction to Crevice Corrosion

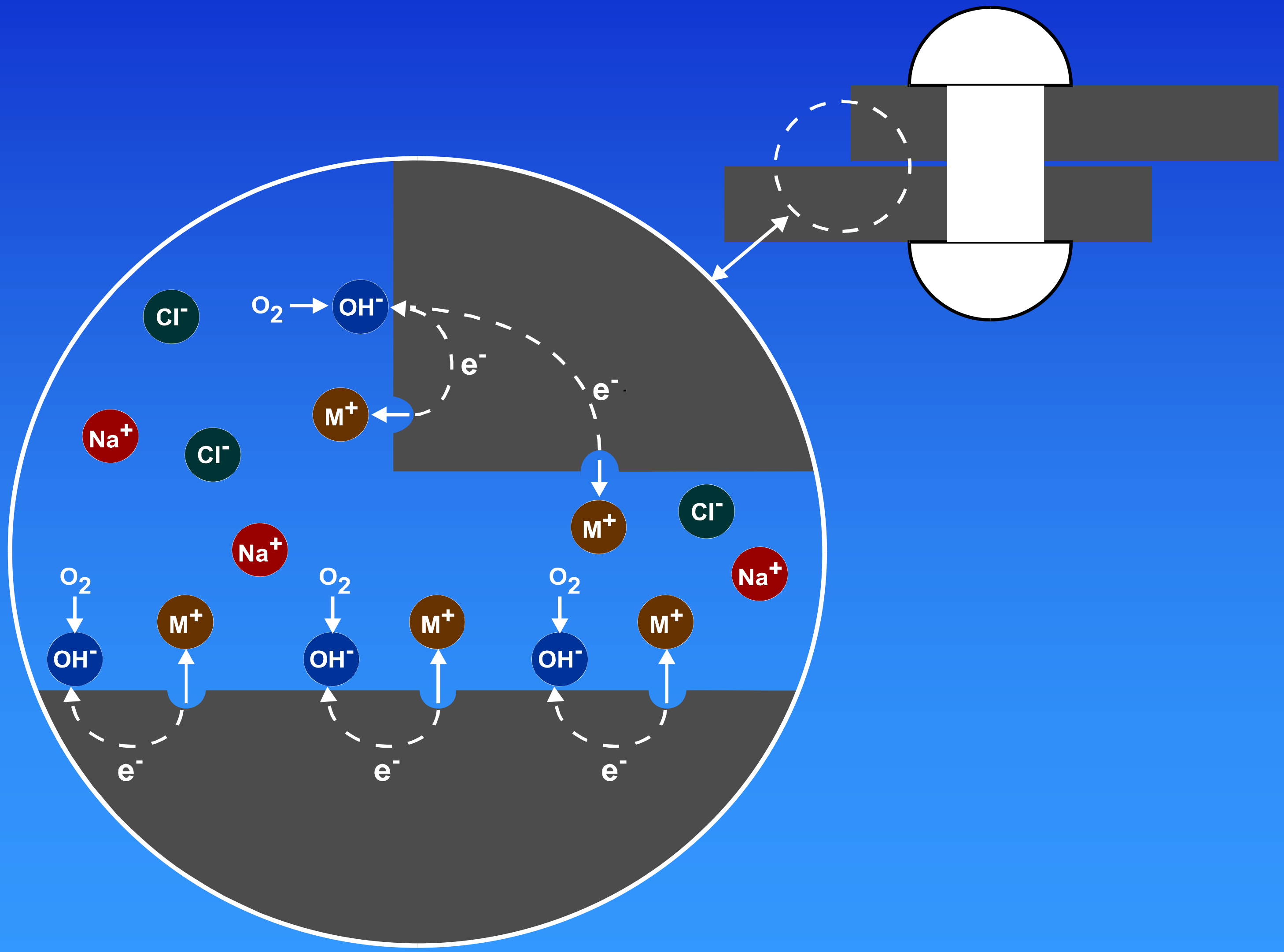
- Associated with geometries with a relatively stagnant solution and where there is a mechanism to make the crevice solution more aggressive (e.g., increased acidity and increased anionic impurity concentration)
- Crevices are typically inherent in the component design:
  - Gaskets, lap joints, bolt heads and threads
  - Under corrosion deposits and sludge piles
- Critical factors in controlling this form of attack are:
  - Geometry of the crevice
  - Conditions that affect the thermal hydraulics within the crevice
  - Mechanisms that change the cationic and anionic concentrations within the crevice

NUREG-6923, 2/07

Crevice Corrosion

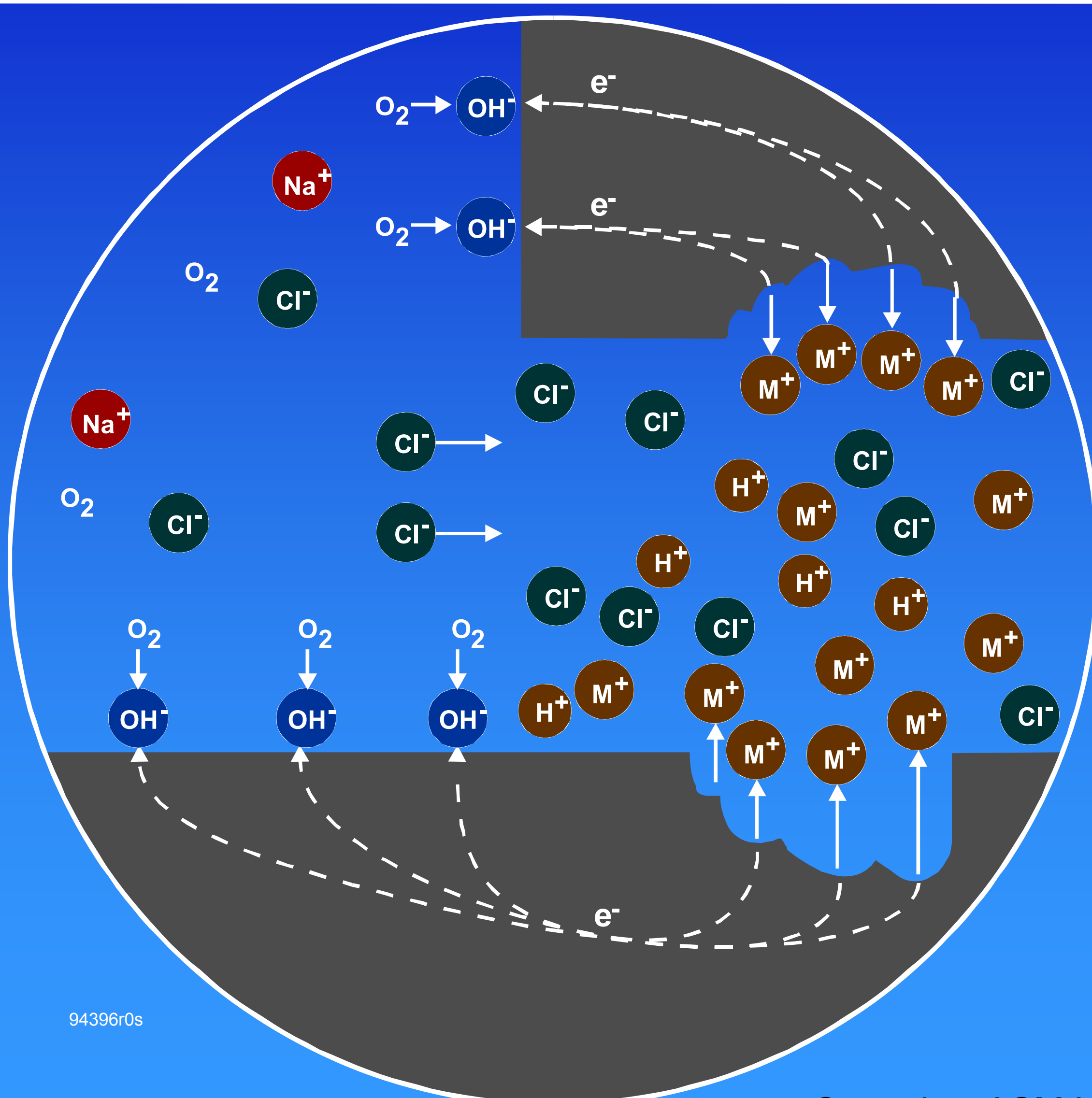
- Two type of crevice corrosion in LWRs:
  - ♦ Due to dissolved oxidants – most common form of crevice corrosion including BWRs
  - ♦ Due to heat transfer in deaerated environments - PWRs
- Stationary electrodes
- Access to stagnant solution within crevice is far more difficult and can be achieved only by diffusion
- Occluded cell - shielded from view and can remain completely undetected until failure

Crevice Corrosion - Initial Stages



Corrosion, ASM Handbook, Vol. 13, 1987

Crevice Corrosion - Later Stages



Corrosion, ASM Handbook, Vol. 13, 1987

Four Stages of Crevice Corrosion in Oxygenated Environments

1. Depletion of oxygen in the crevice solution

2. Increase in acidity (lower pH) and anion content (e.g., Cl^-, SO_4^{-2}) of the crevice solution

3. Permanent breakdown of the passive film and the initiation of rapid corrosion

4. Autocatalytic propagation of crevice corrosion

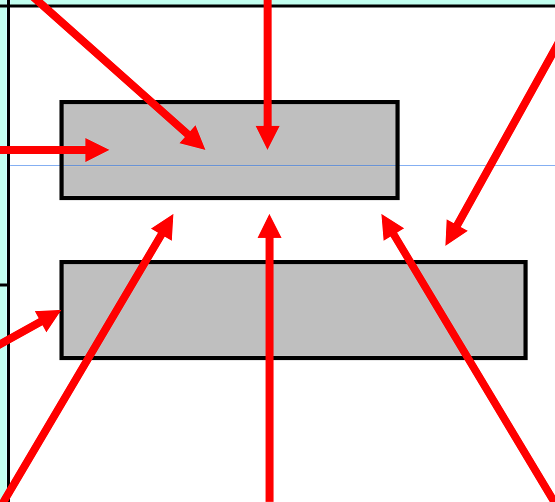
Factors Affecting Crevice Corrosion

Crevice Type
- Metal/metal
- Metal/non-metal
- Metal/marine growth
- Galvanically protected

Crevice Geometry
- Gap
- Depth

Total Geometry
- Exterior to interior crevice area ratio
- Number of crevices

Alloy Composition
- Major alloying elements
- Minor constituents
- Impurities



Bulk Solution Composition
- Cl^- content
- O_2 content
- pH
- Pollutants

Passive Film Characteristics
- Passive Current
- Film stability

Bulk Solution Environment
- Temperature
- Agitation
- Volume

Electrochemical Reactions
- Metal dissolution
- O_2 reduction
- H_2 evolution

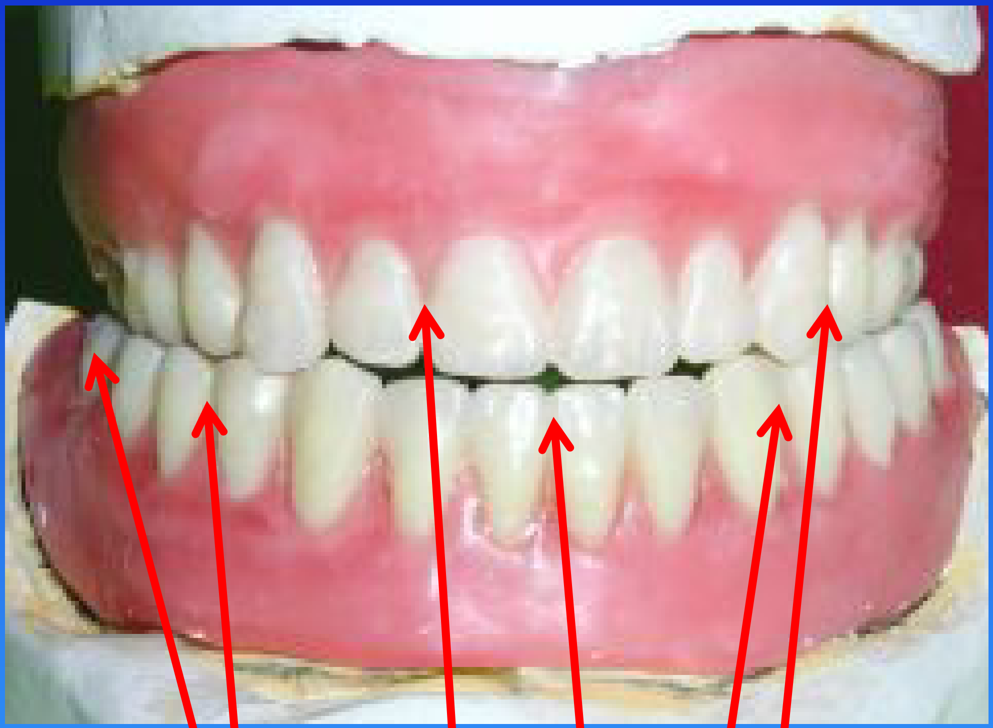
Crevice Solution
- Hydrolysis equilibria

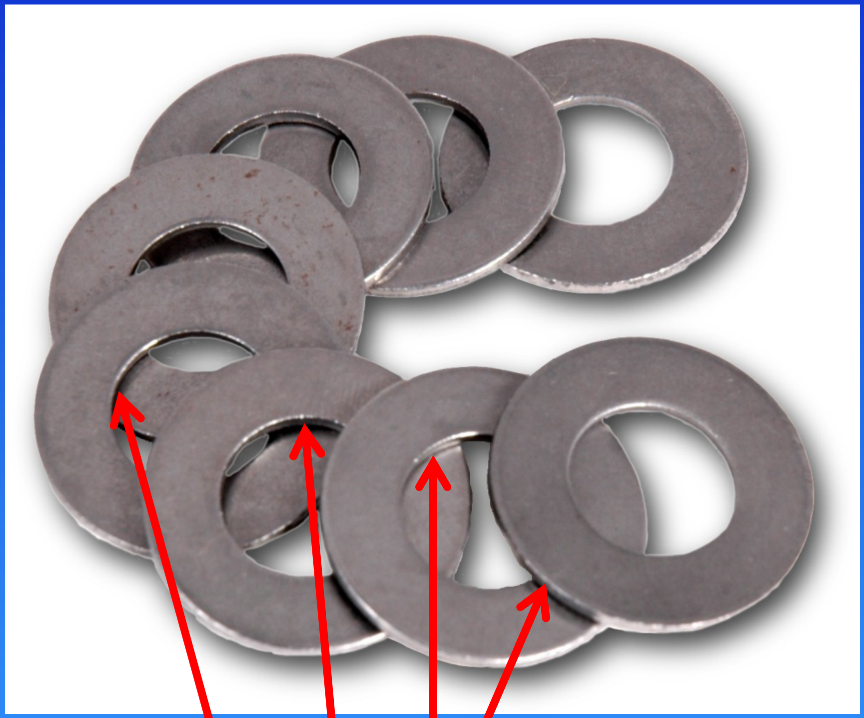
Mass Transport In and Out of Crevice
- Migration
- Diffusion
- Convection

J. Oldfield and W. Sutton, Br. Corros. J. Vol. 13, No. 1, 1978

Examples of Crevice Corrosion

Non-metallic and Metallic Crevices





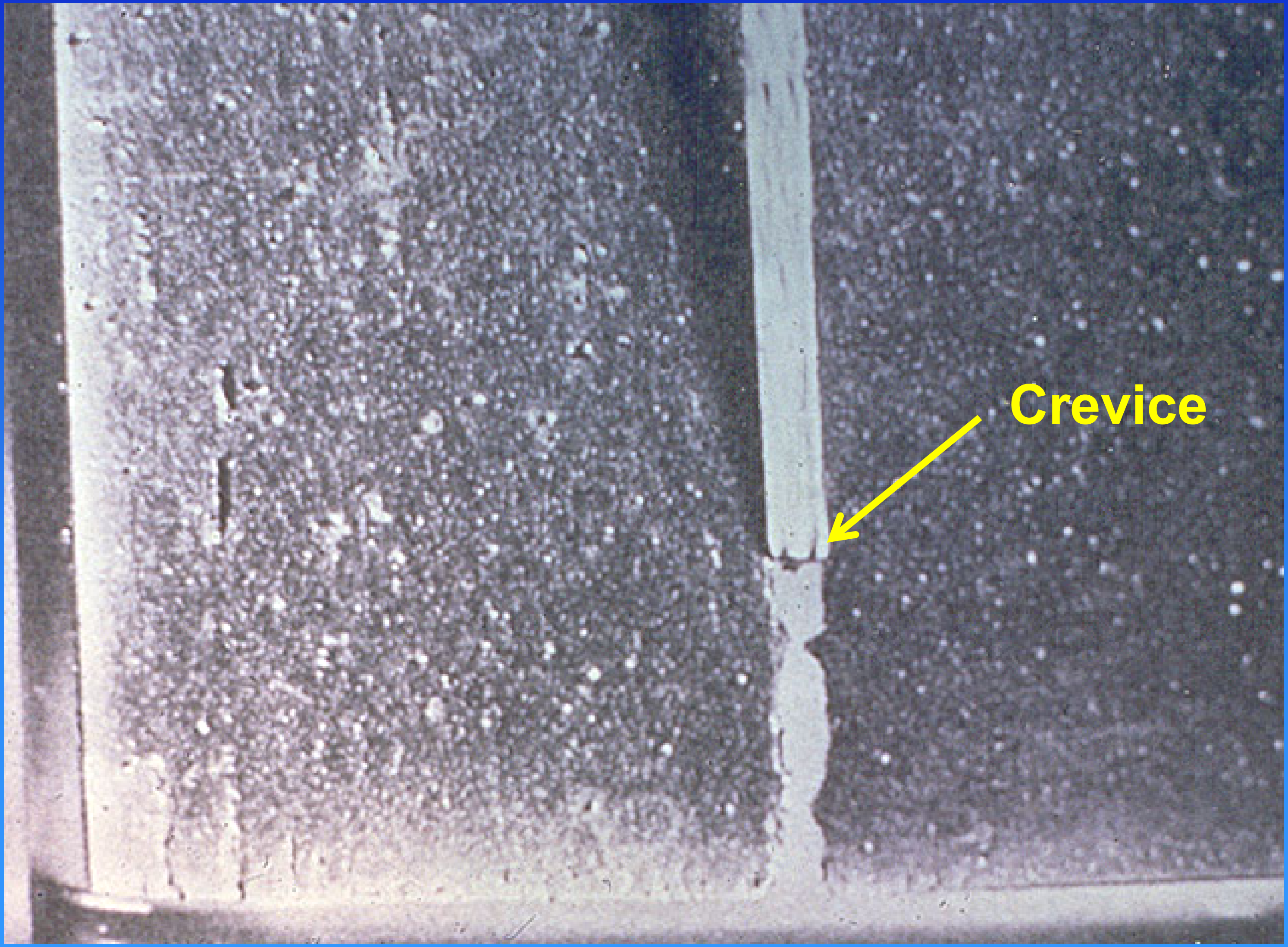
Crevices: Most tooth decay occurs here

Crevices: Most corrosion occurs here

Mitigation: Flossing and Sufficient Flow

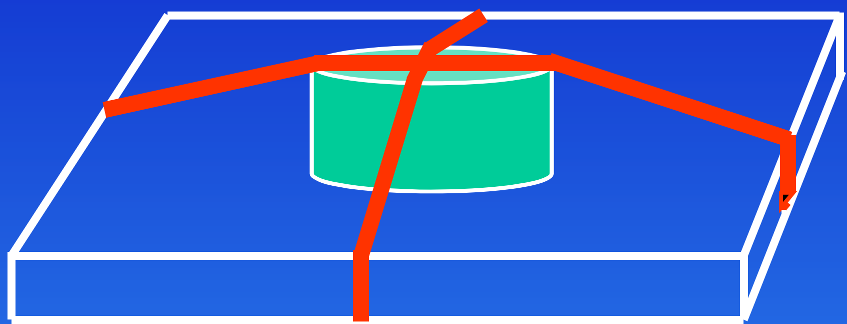
Household Crevice Corrosion

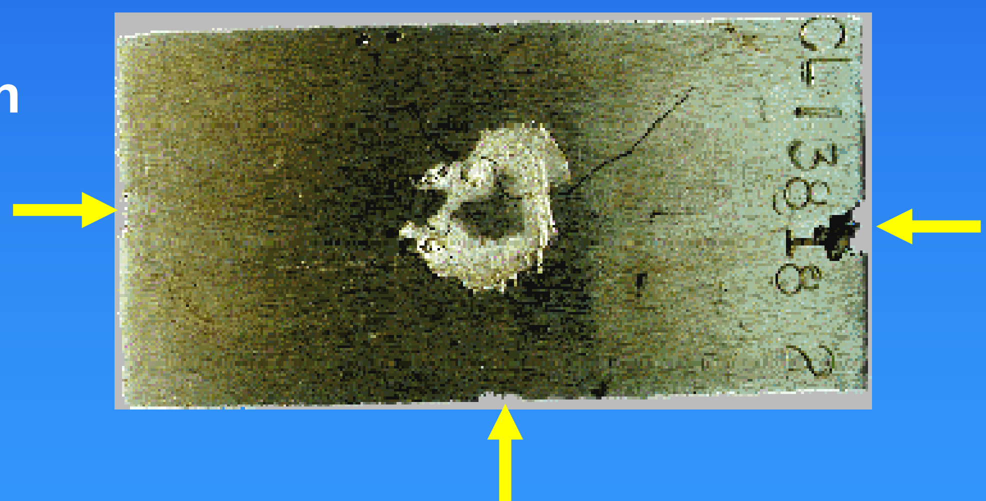
Headline: "Rubber Band Cuts Through Steel!"



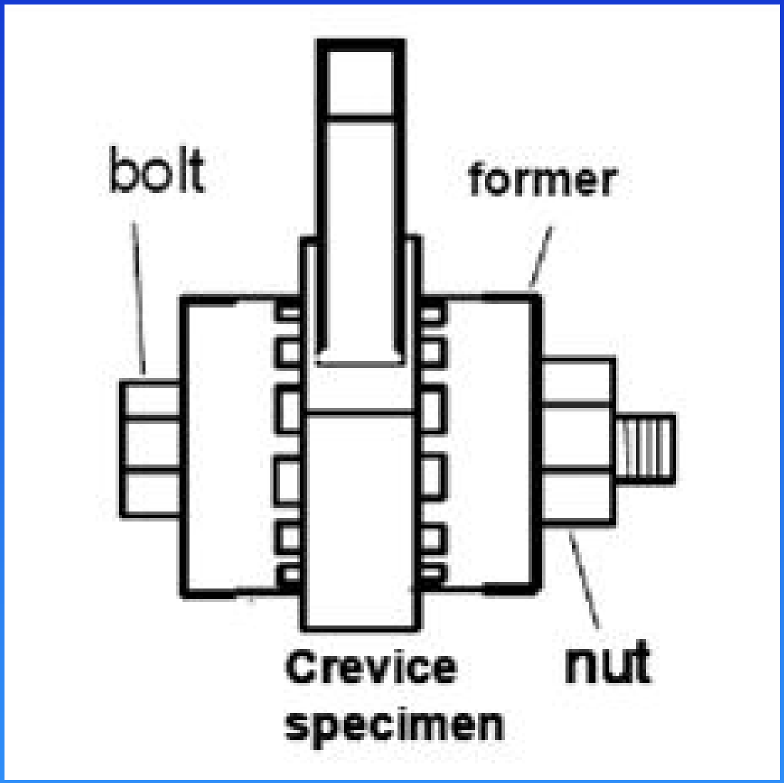
Crevice Corrosion of Stainless Steel

- Stainless steel
- ASTM G48 Method B ferric chloride ($FeCl_3$) test
- Crevice created with a non-metallic block
- Test coupon is not attacked except in the middle of the coupon where it was in contact with the block and on the edges where a rubber band/O-ring are used to hold the block in





Multiple Crevice Assembly (MCA) Crevice Corrosion Specimen



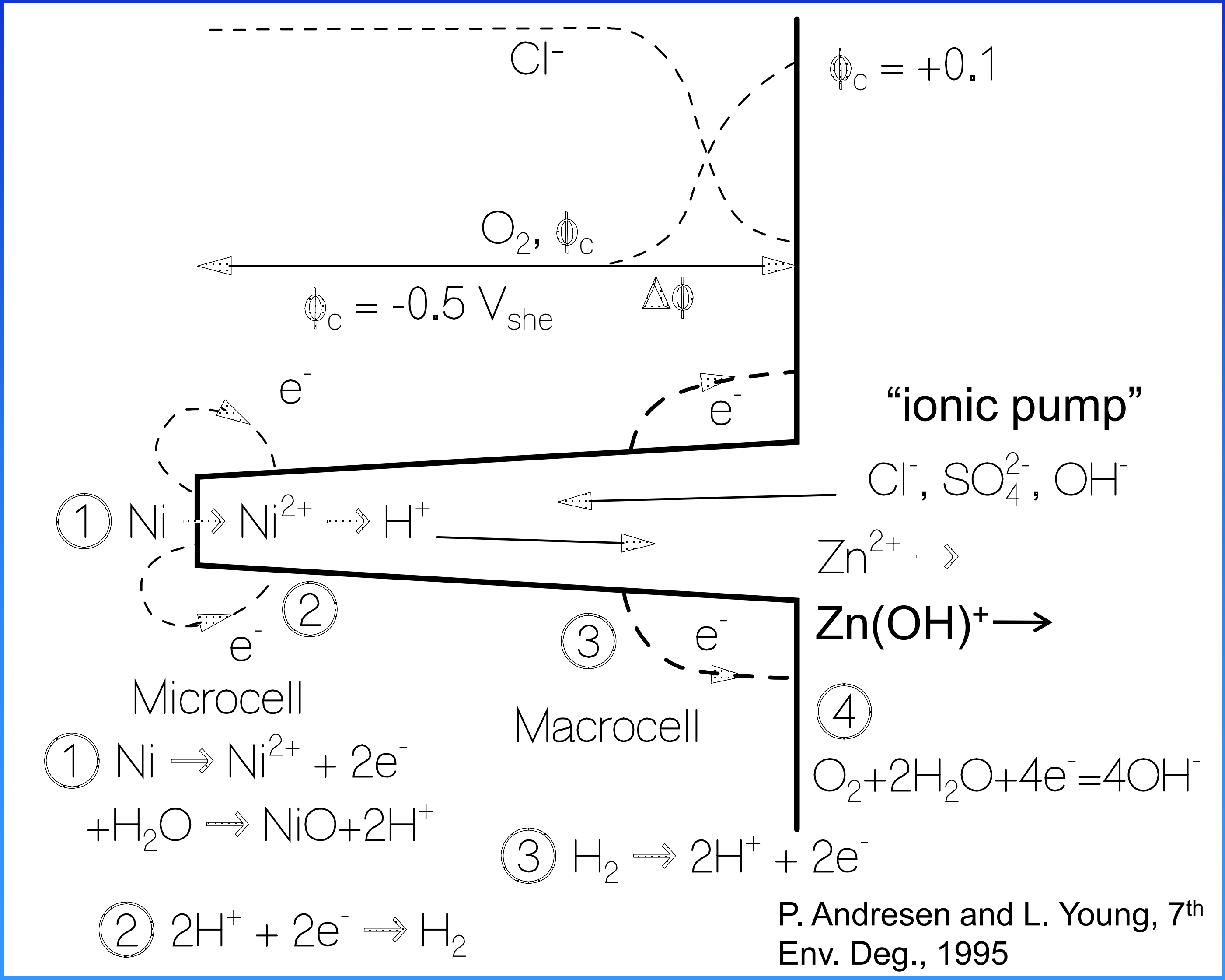
ASTM G78

Example of MCA Results

X. He, paper 1663, Corrosion 2008

Crevice Corrosion in LWRs

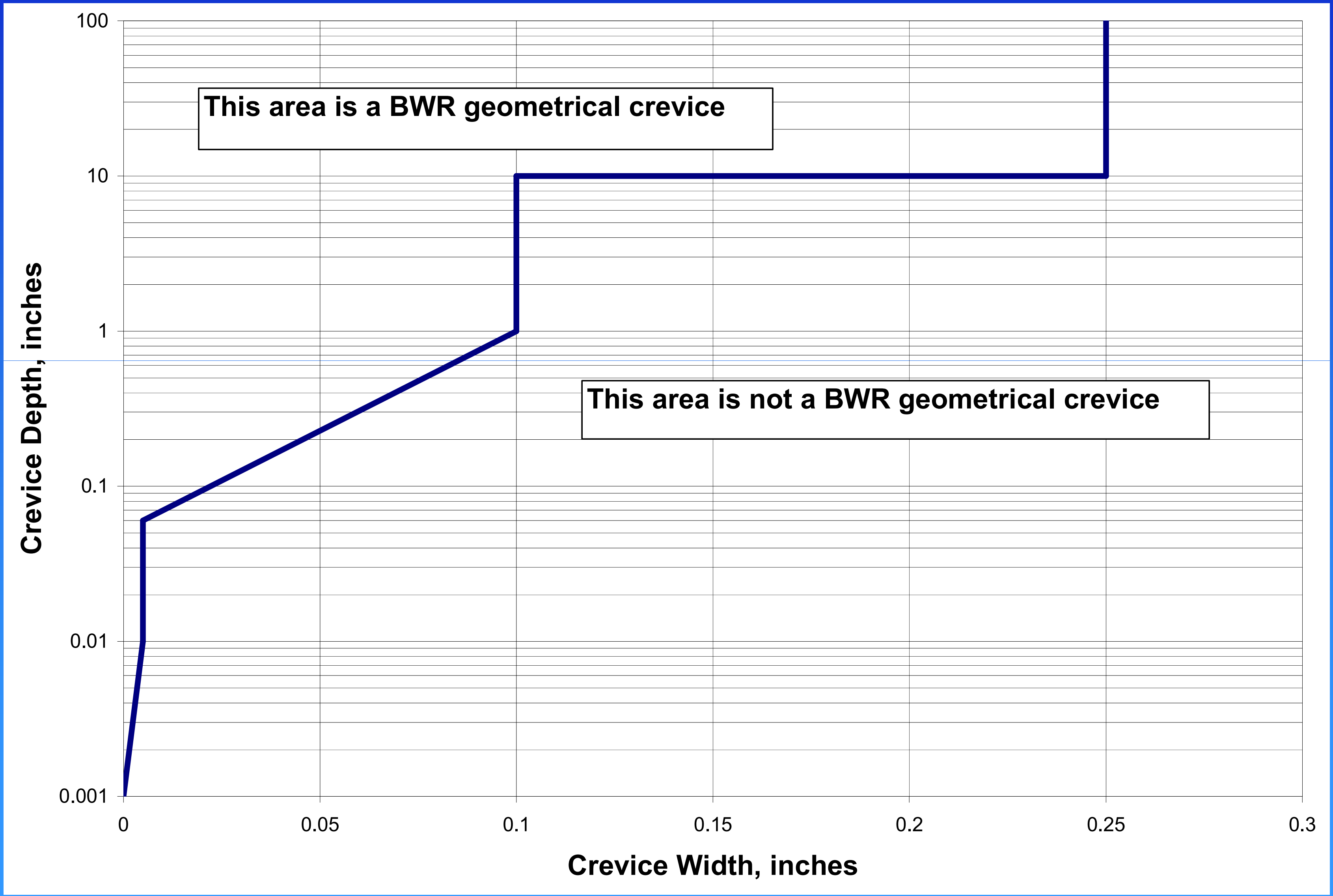
Crevice Microcells and Macrocells in an Aerated Environment



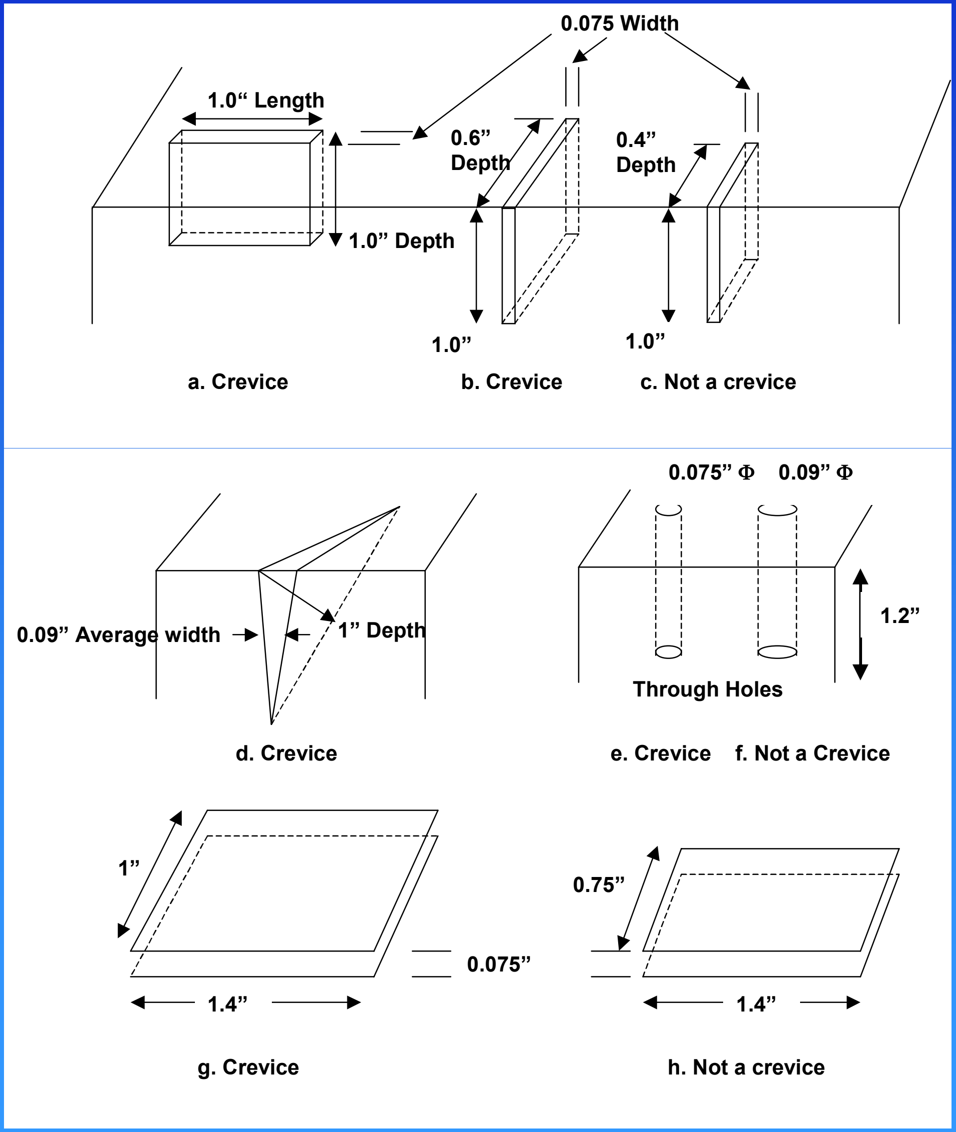
Crevices in Aerated Environments

- ~30x concentration in anion activity (above the bulk) will occur in a crevice
- Mass transport of deleterious ions into the crevice is greater than their egress from the crevice, i.e., achieve high concentrations
- Difference in corrosion potential acts to "pump" anions into the crack
- Precipitation (e.g., of metal sulfides) is an even larger problem, because it limits the activity of S in the crevice, which further aids its ingress and dramatically slows its egress

BWR Crevice Definition Diagram



Application of BWR Crevice Definition



Structural Integrity Associates

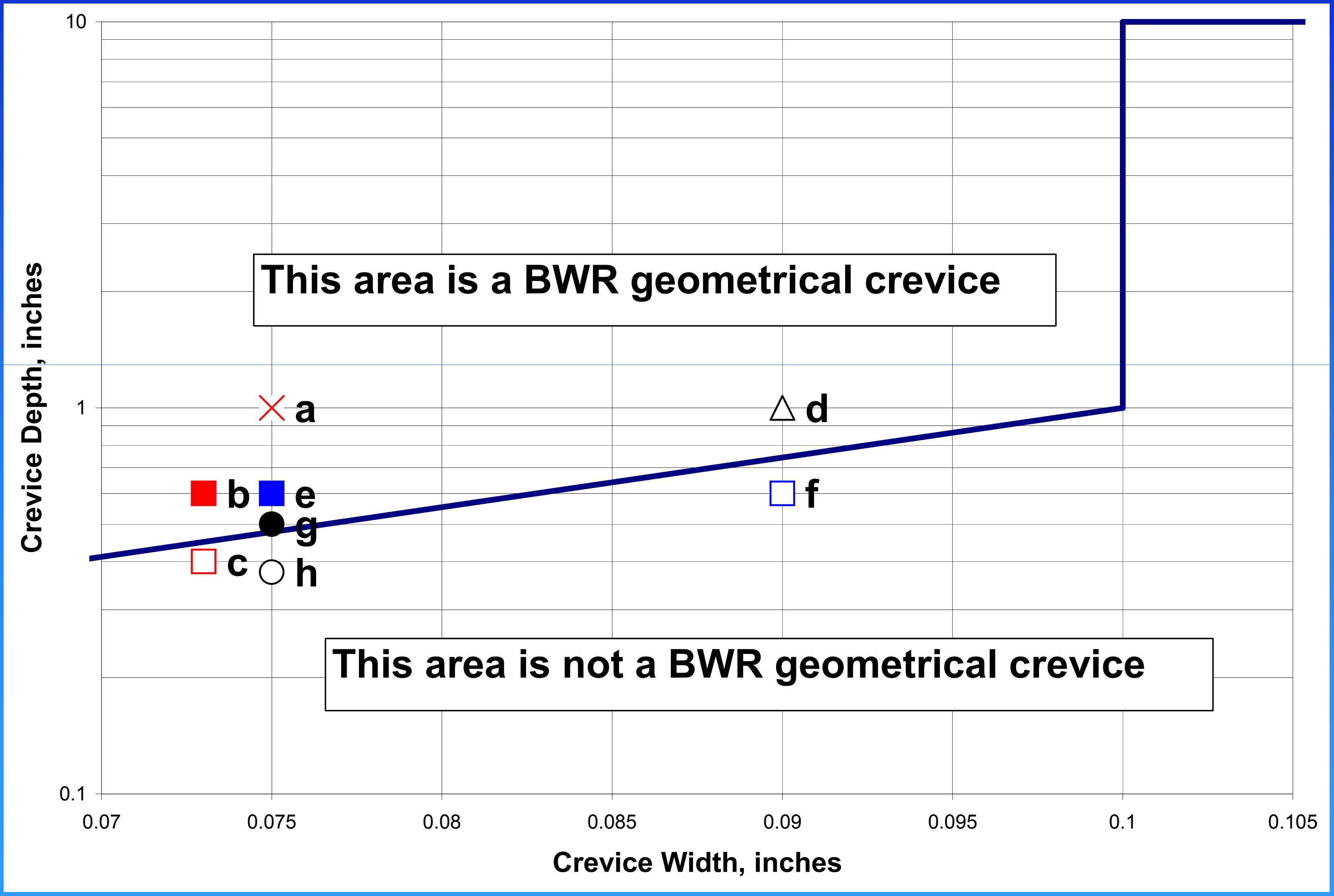
Application of BWR Crevice Diagram

- A crevice must be wide enough to permit entry of the solution (line contact), but sufficiently narrow to maintain a stagnant zone of solution. Typical crevice widths are 25 to 100 μm (1 to 4 mils).
- Drawing (a) shows that, for a closed bottom configuration with one surface exposed to the bulk solution, the length is to be ignored. Thus, for a given width and depth, any length is a crevice.
- Drawings (b) and © illustrate cases where two surfaces are exposed to the bulk solution. To be considered a crevice for a given width, both other dimensions must fall above the line in BWR crevice diagram. This is because, for any point in the gap, a line can be drawn to the bulk solution that is less than or equal to the shortest edge dimension.

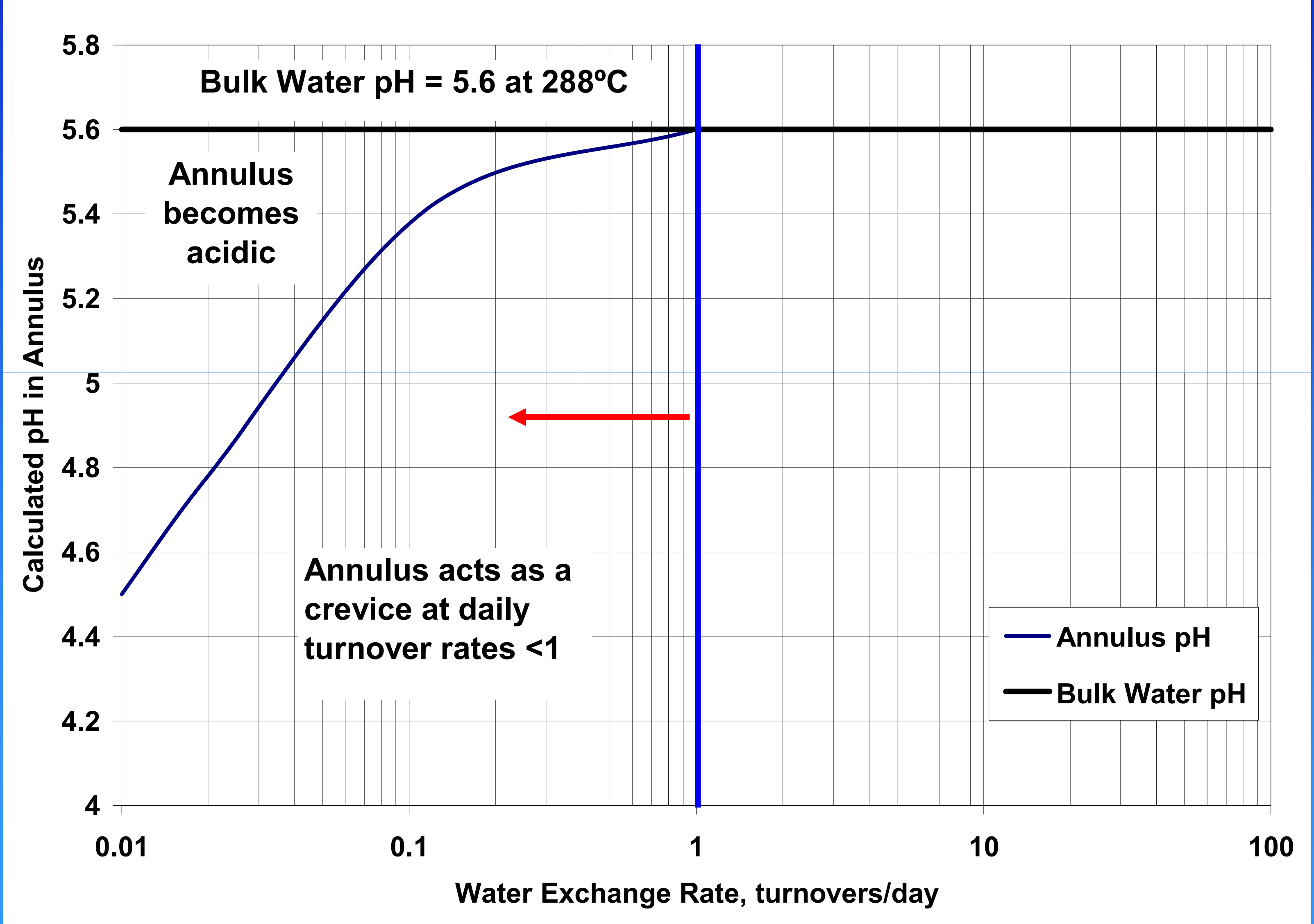
Application of BWR Crevice Diagram

- Drawing d. Non-orthogonal configurations similar to © presents a different concern. In this figure, the width or depth is not constant. In this instance, the depth should equal the distance to the point furthest from the bulk solution and the width should be the average width.
- Drawings e. & f. For through-drilled holes, the depth defined for crevice definition is one half the through-drilled length. Again, this is the longest distance from the bulk solution.
- Drawings g. & h. For parallel plates, exposed to the bulk solution on its entire perimeter, the depth is half of the shortest edge dimension or the shortest dimension to the bulk measured from the point furthest from the bulk.

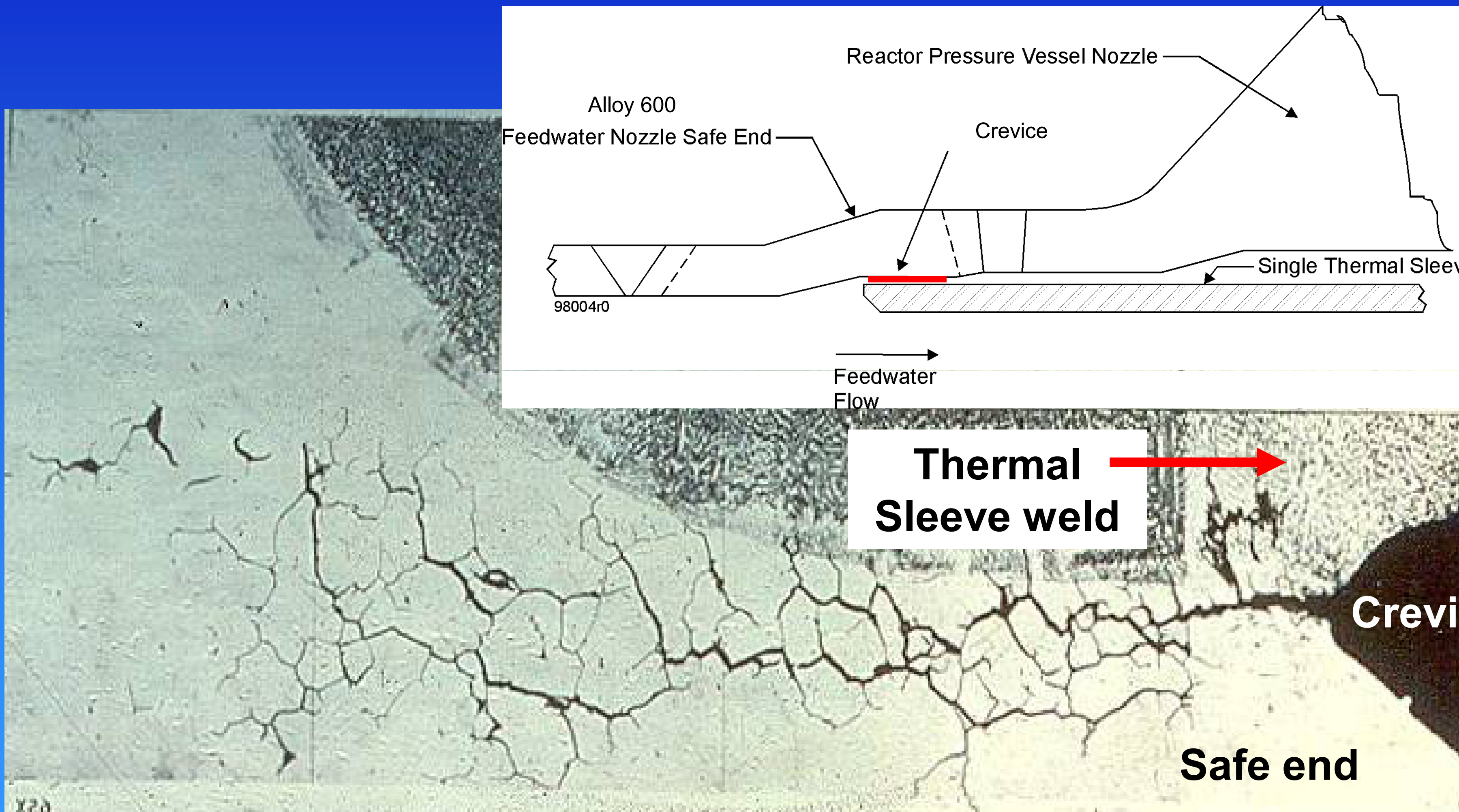
Application of BWR Crevice Diagram



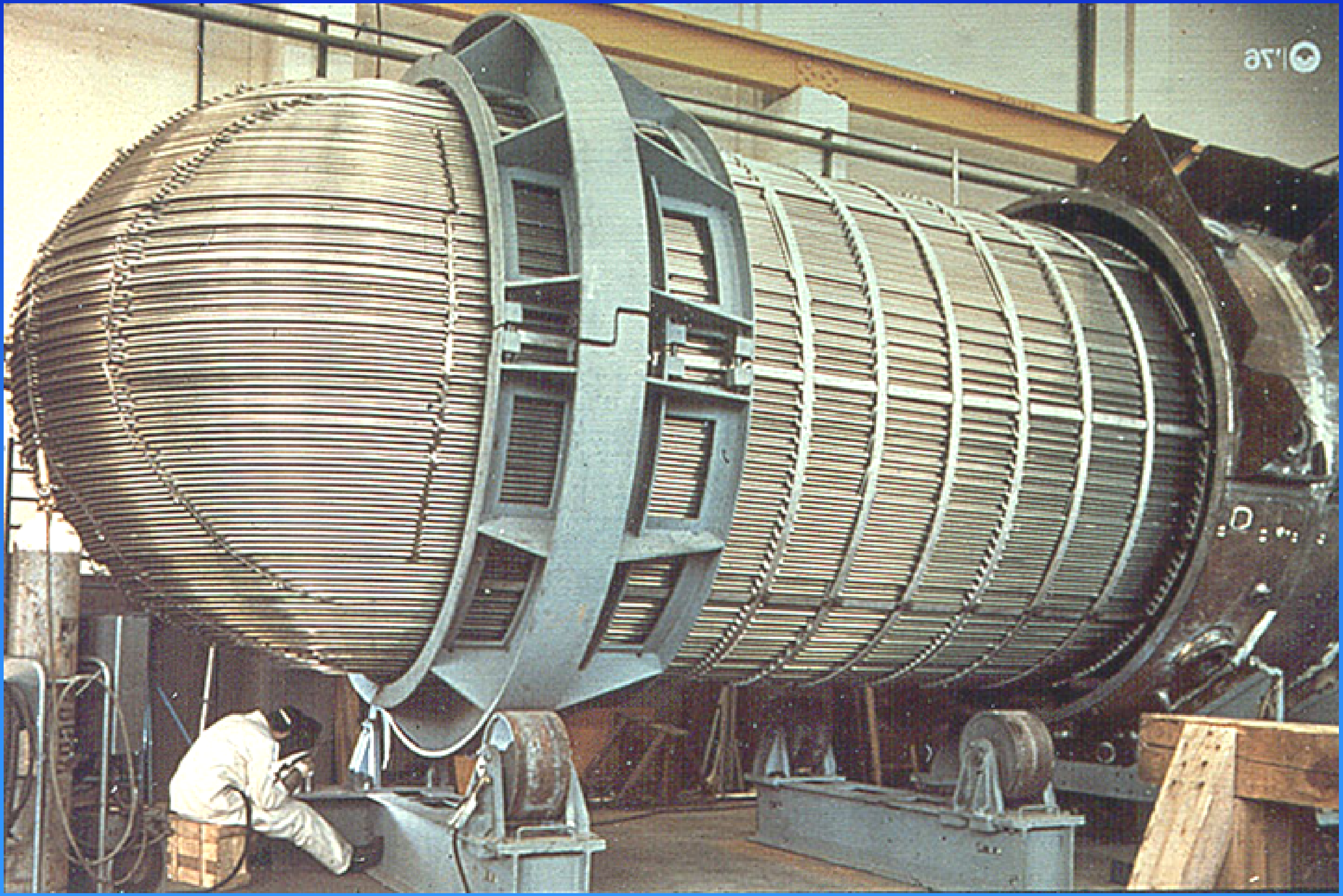
Effect of Water Exchange Rate on Crevice Formation



Duane Arnold Recirculation Inlet Alloy 600 Safe End Crevice



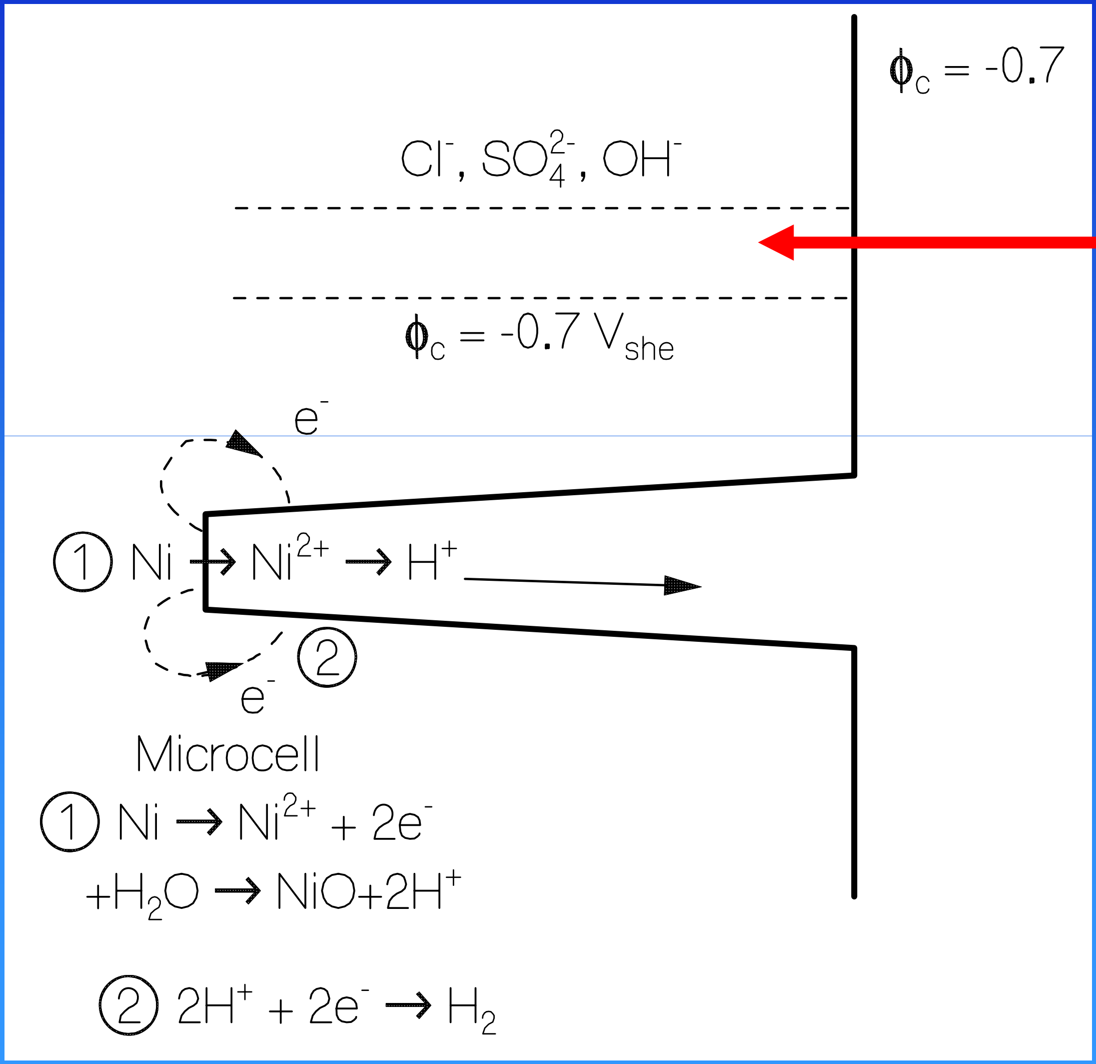
PWR Steam Generators



PWR Steam Generator Crevices

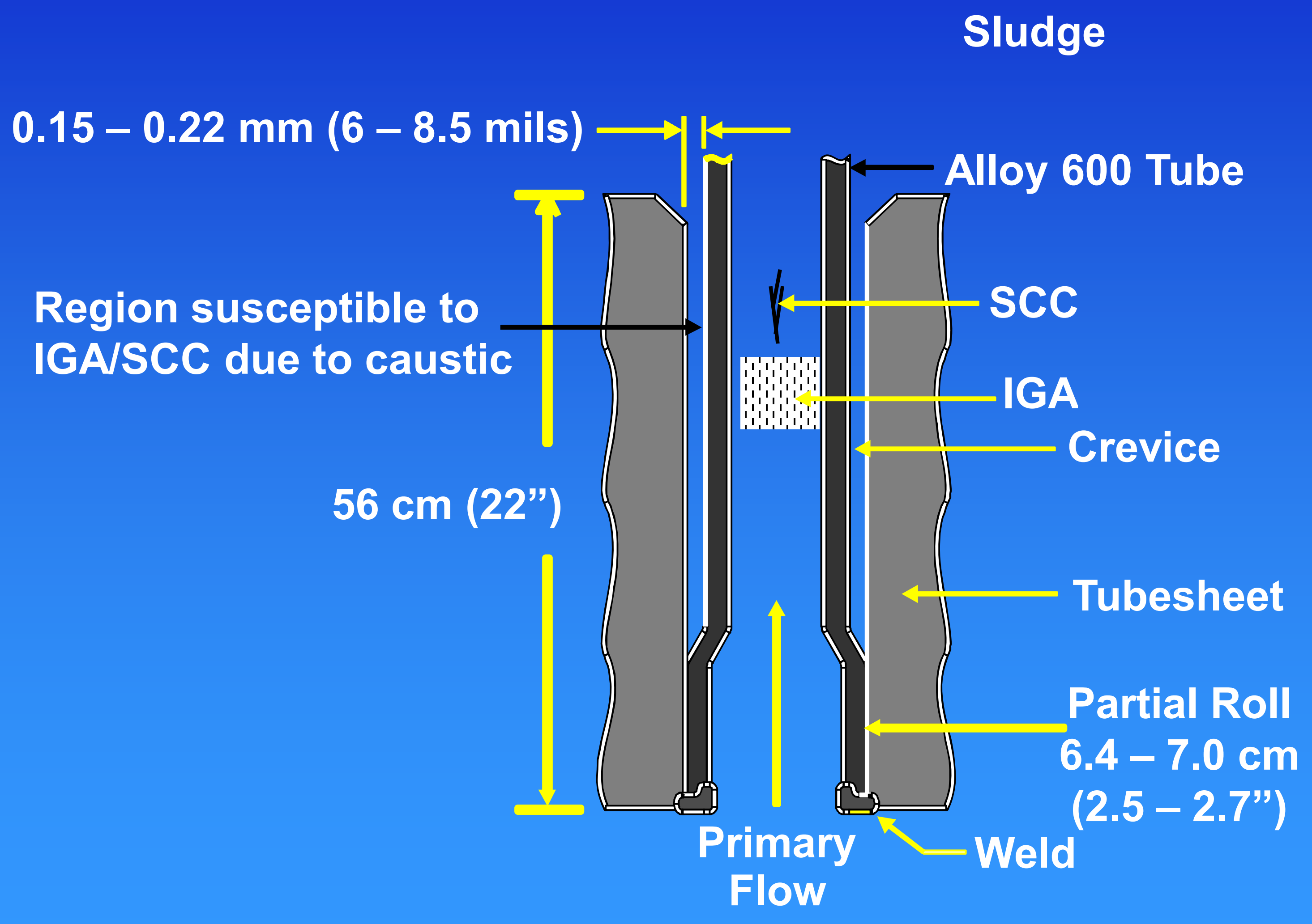
- PWR SG crevices are sites of concentrated impurities (Al_2O_3, SiO_2, $SO_4^{=}$, Cu, Cl^-, Pb, B, Ti, Zn, etc.) due to heat transfer, not differences in corrosion potential between the bulk solution and the crevice
- Heat transfer crevices control secondary side corrosion in SGs
- Three types/locations of SG heat transfer crevices
  - Top of tubesheet
  - Sludge
  - Tube support plate

Crevice Microcell in a Deaerated Environment



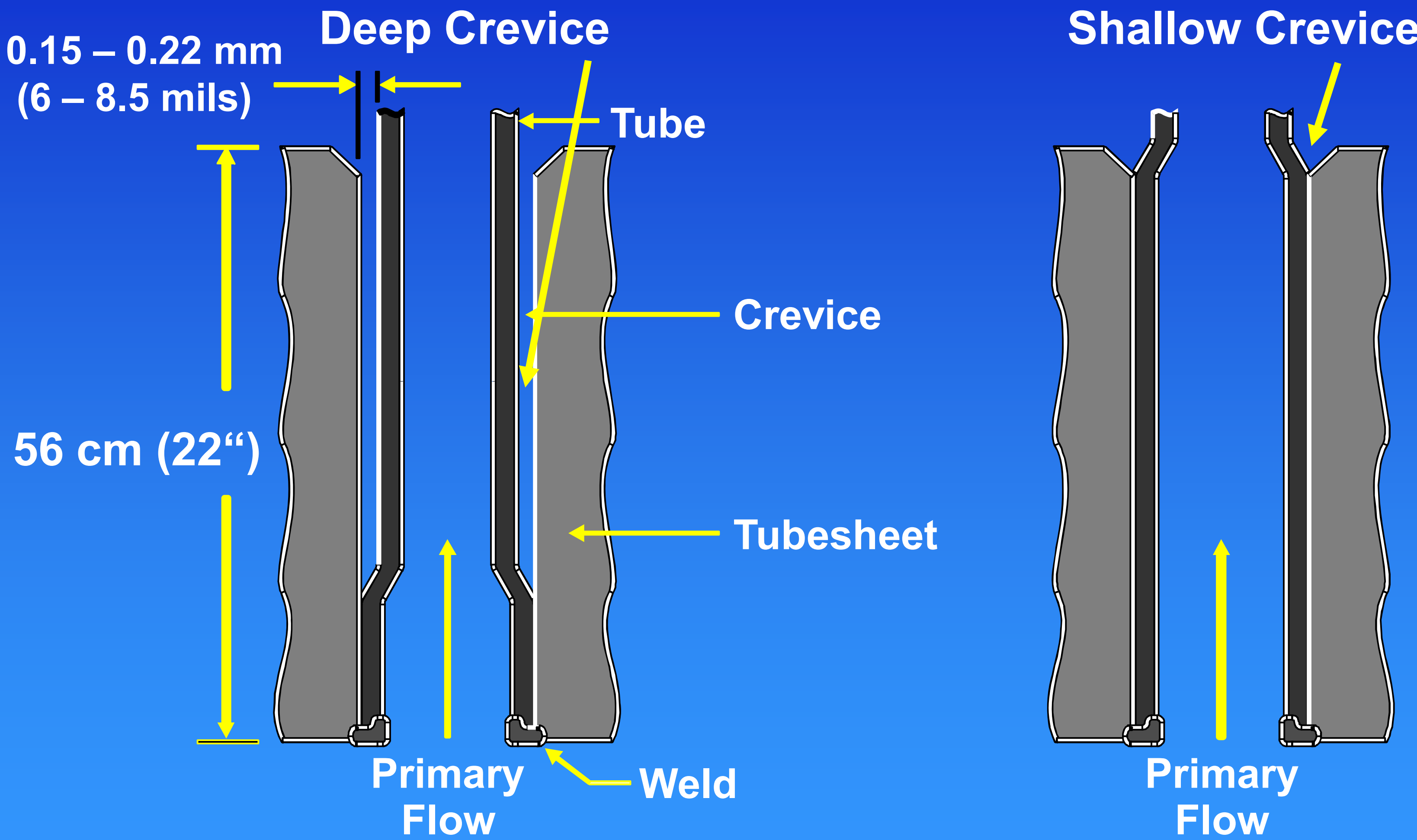
No corrosion potential gradient!

Steam Generator Tubing and Tubesheet Crevices



EPRI WS-80-157

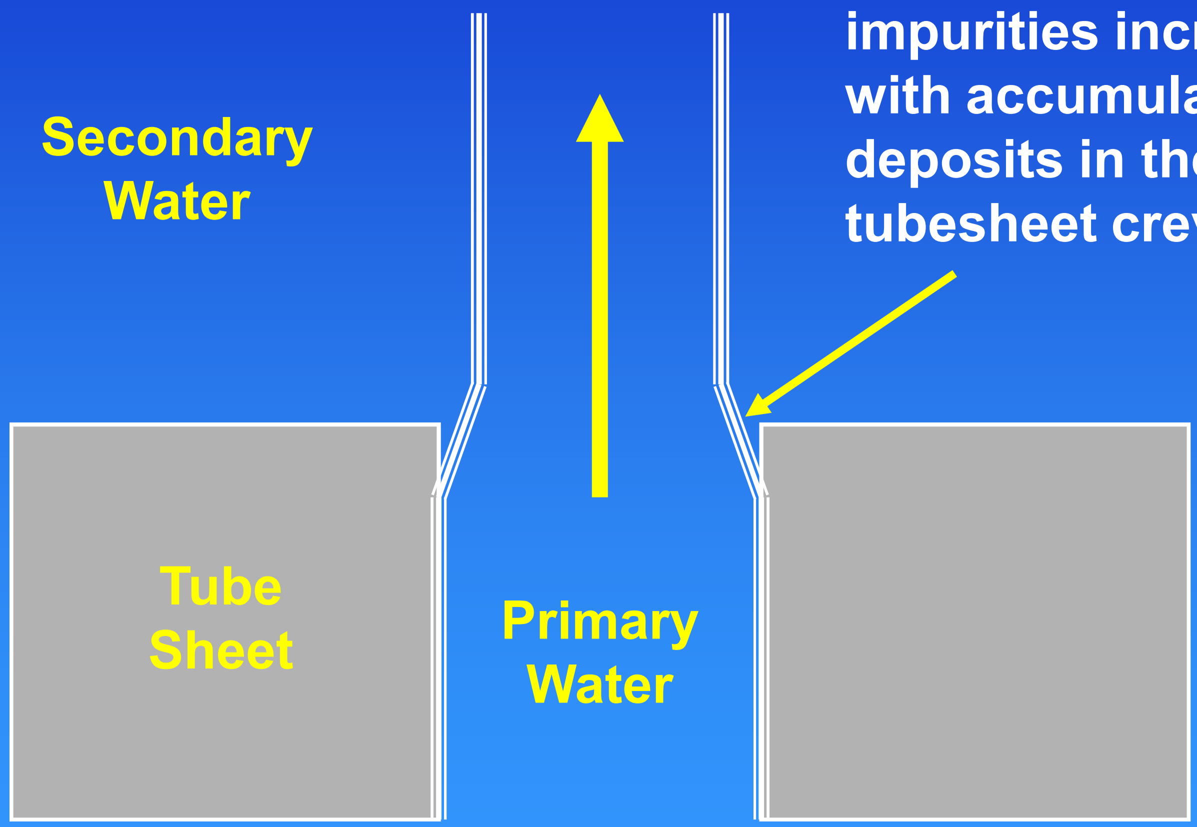
Design to Minimize Crevice Between SG Tubing and Tubesheet



94528r0

D. Jones, Principals and Prevention of Corrosion, 1992

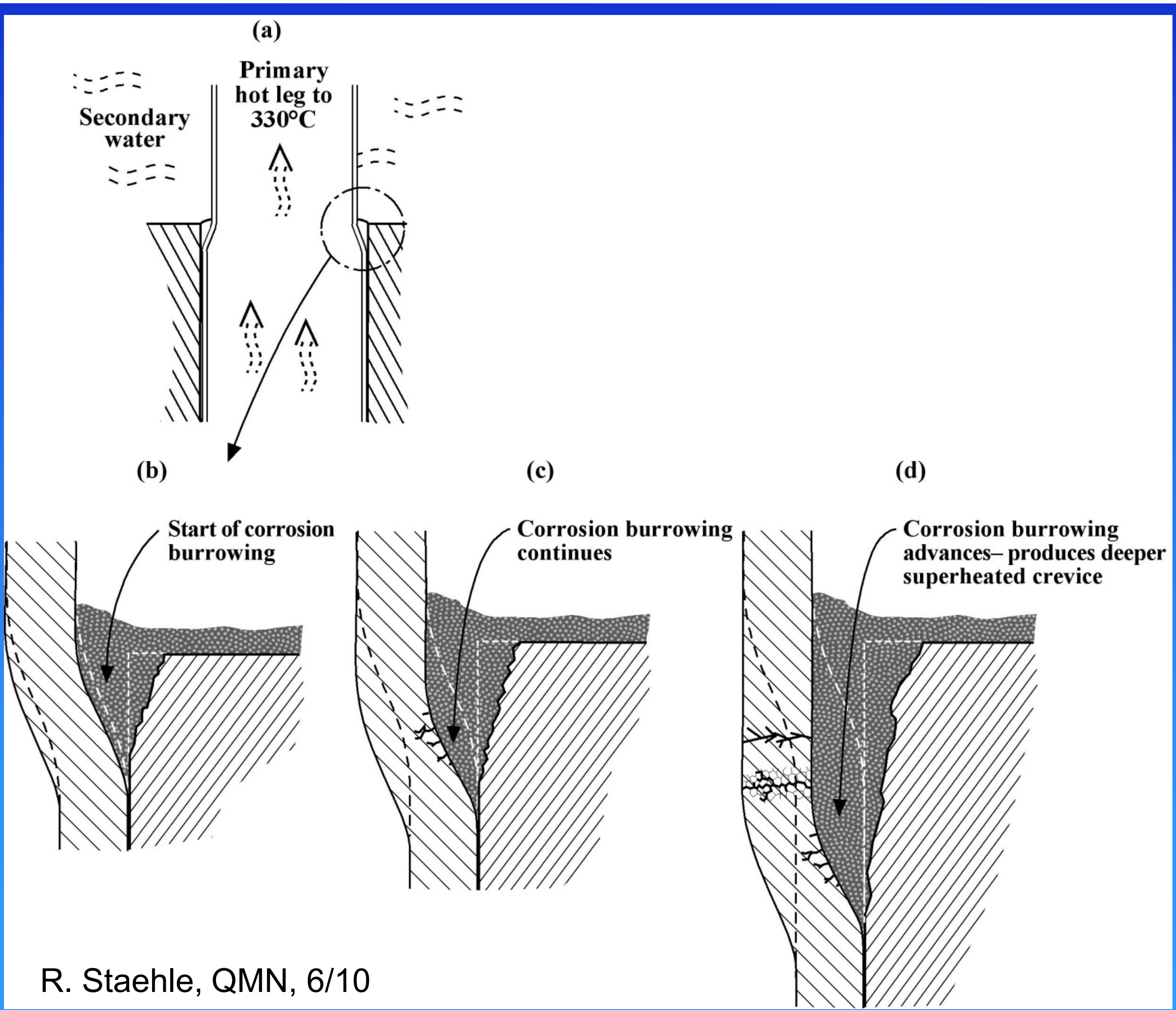
SG Top of Tubesheet Crevice



Concentration of impurities increases with accumulation of deposits in the top of tubesheet crevice

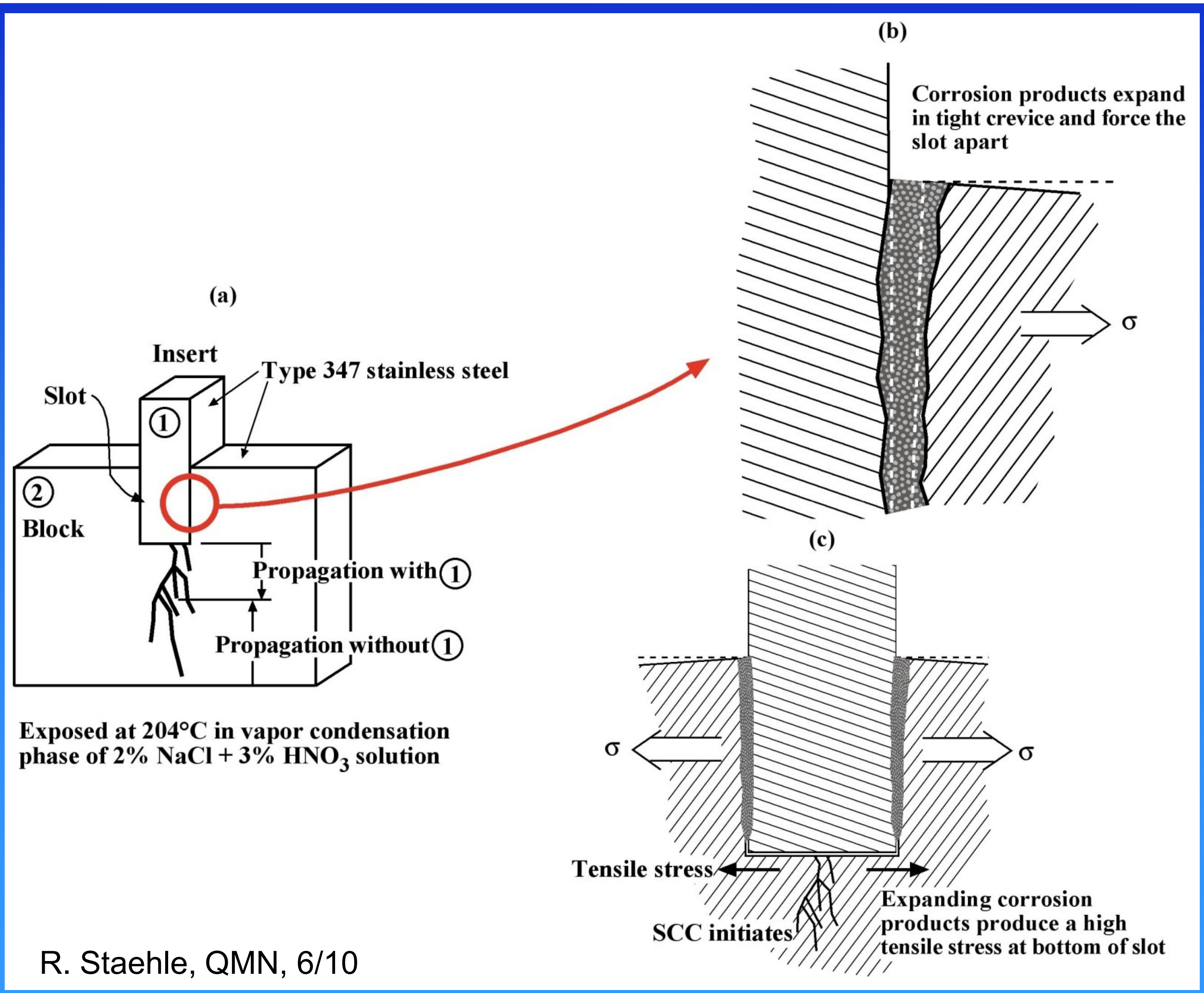
R. Staehle and J. Gorman, Corrosion, Vol. 59, No. 11, 2003

SG Top of Tubesheet Crevice Detail

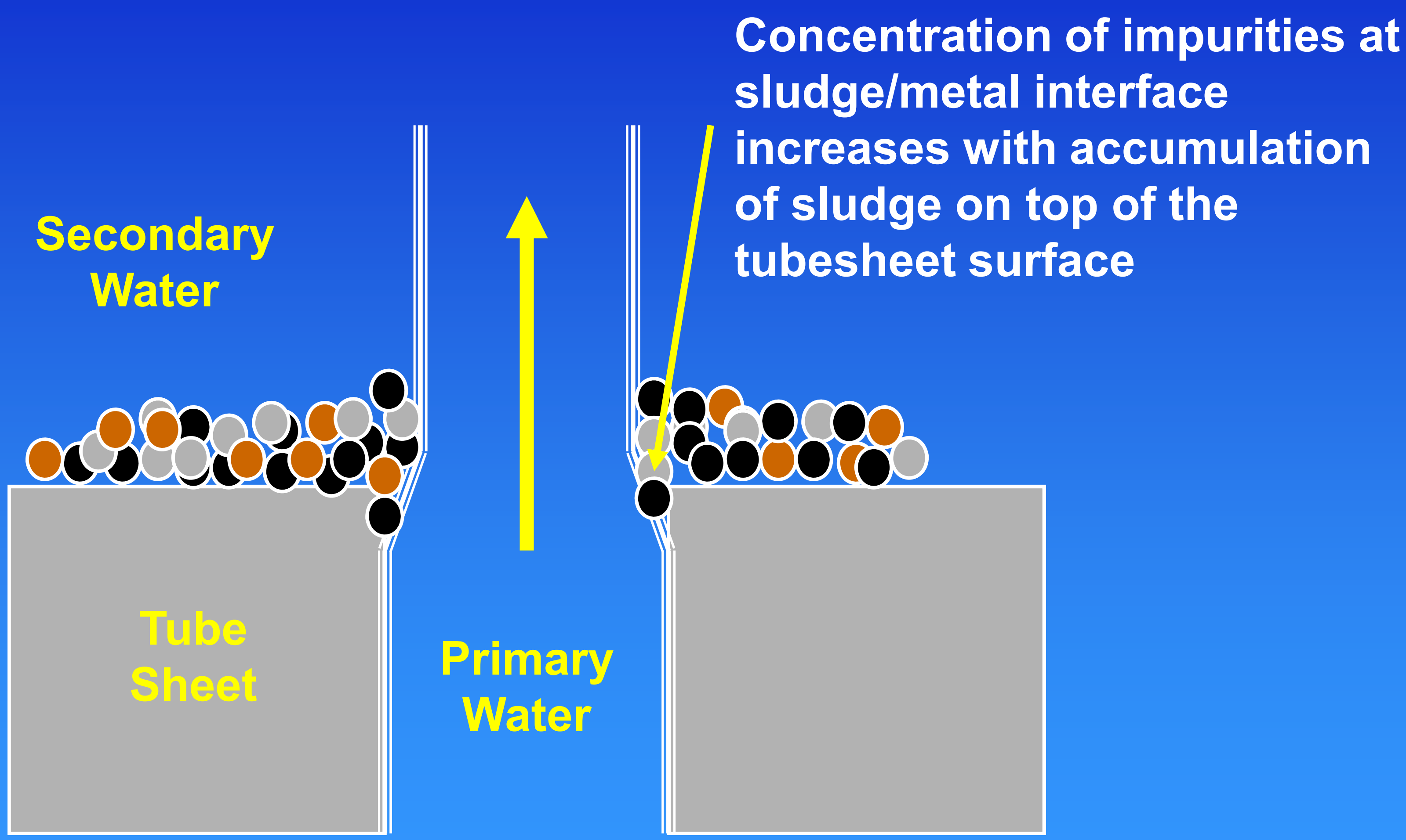


R. Staehle, QMN, 6/10

Expanding Corrosion Products Produce Large Stresses and SCC

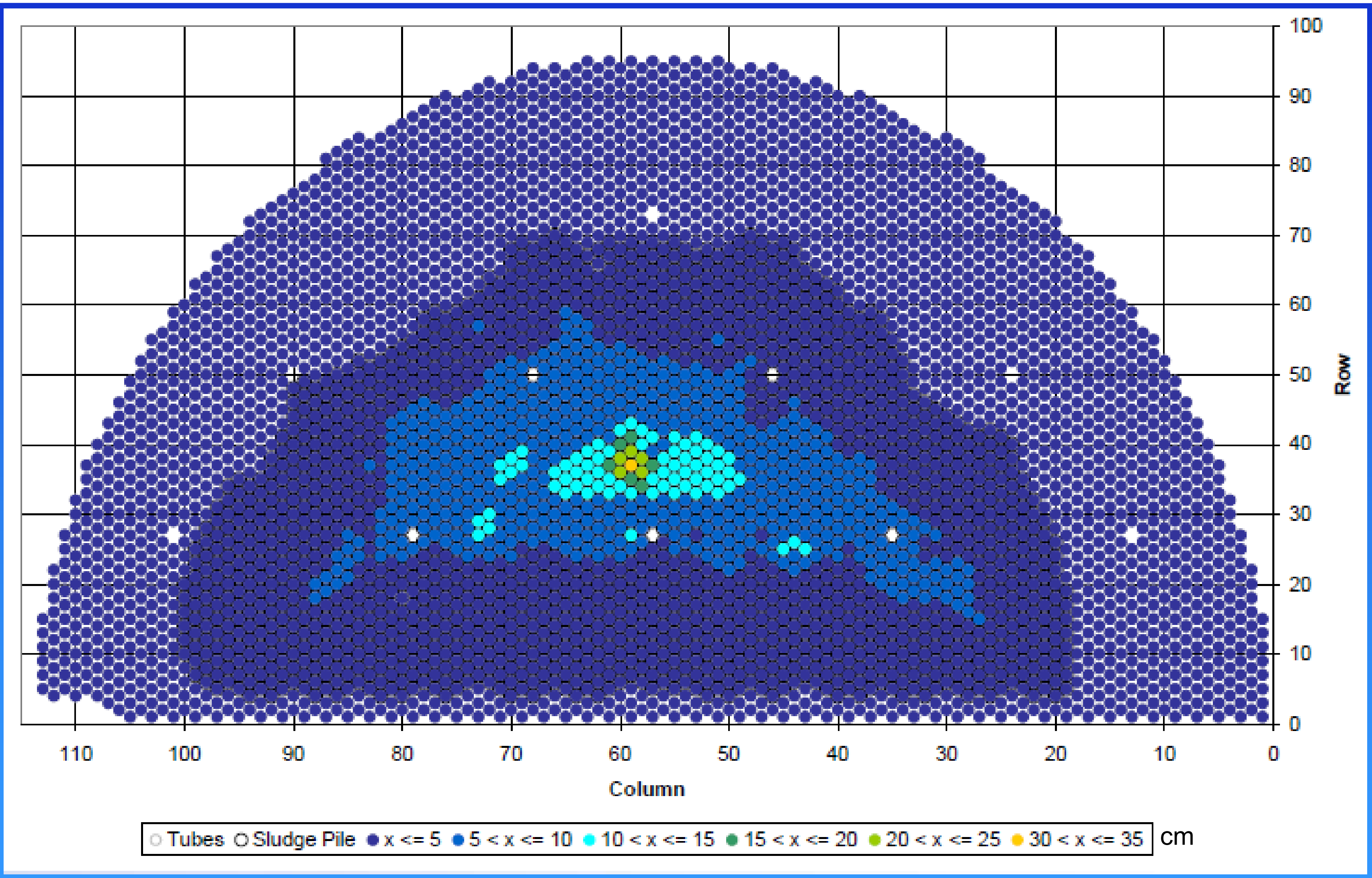


SG Sludge on Tubesheet Crevice



R. Staehle and J. Gorman, Corrosion, Vol. 59, No. 11, 2003

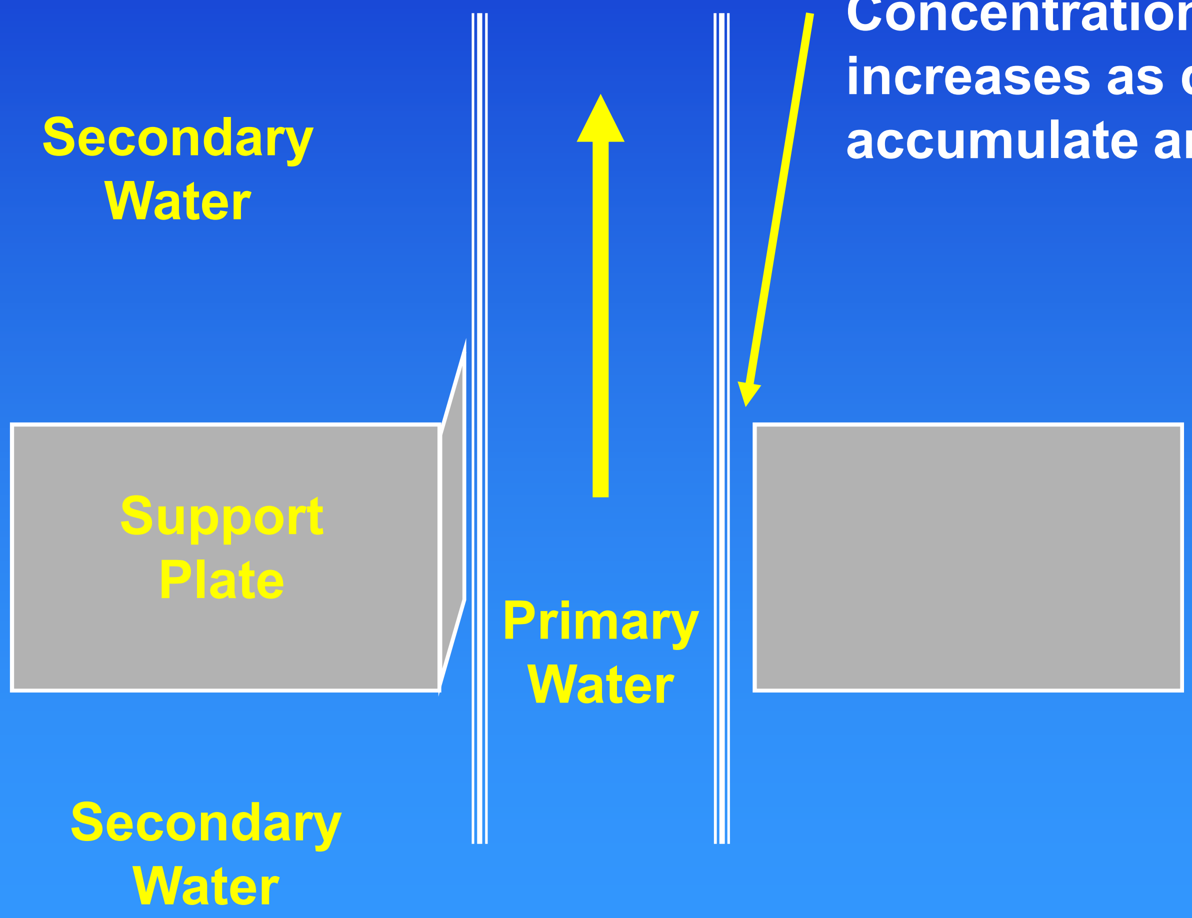
Example of Sludge Pile Height - CANDU



J. Riznic, SGAM, IAEA, 6/09

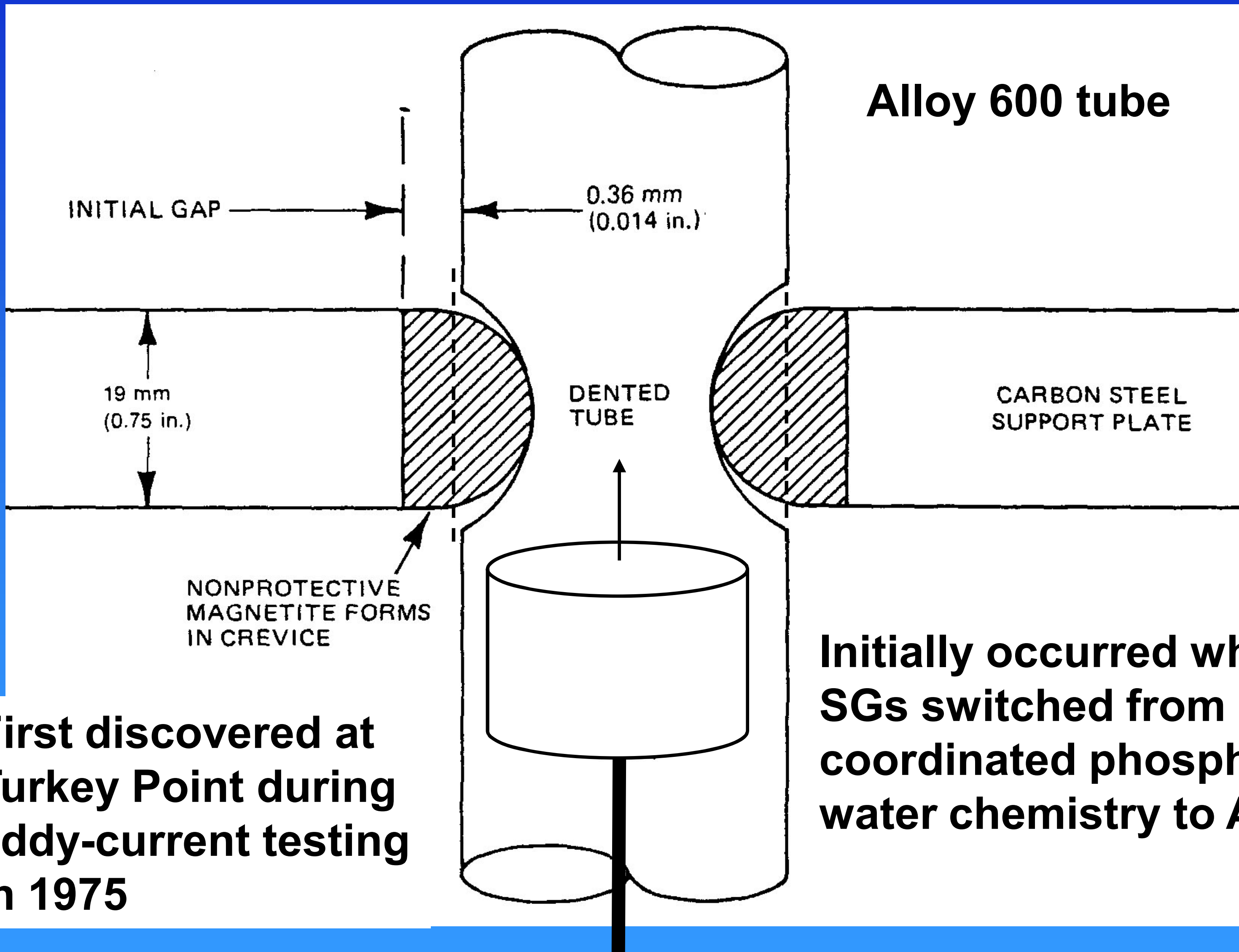
SG Tube Support Plate Crevice

Initial concentration of impurities on contacting side. Concentration of impurities increases as deposits accumulate around periphery



R. Staehle and J. Gorman, Corrosion, Vol. 59, No. 11, 2003

Denting of Alloy 600 SG Tubes

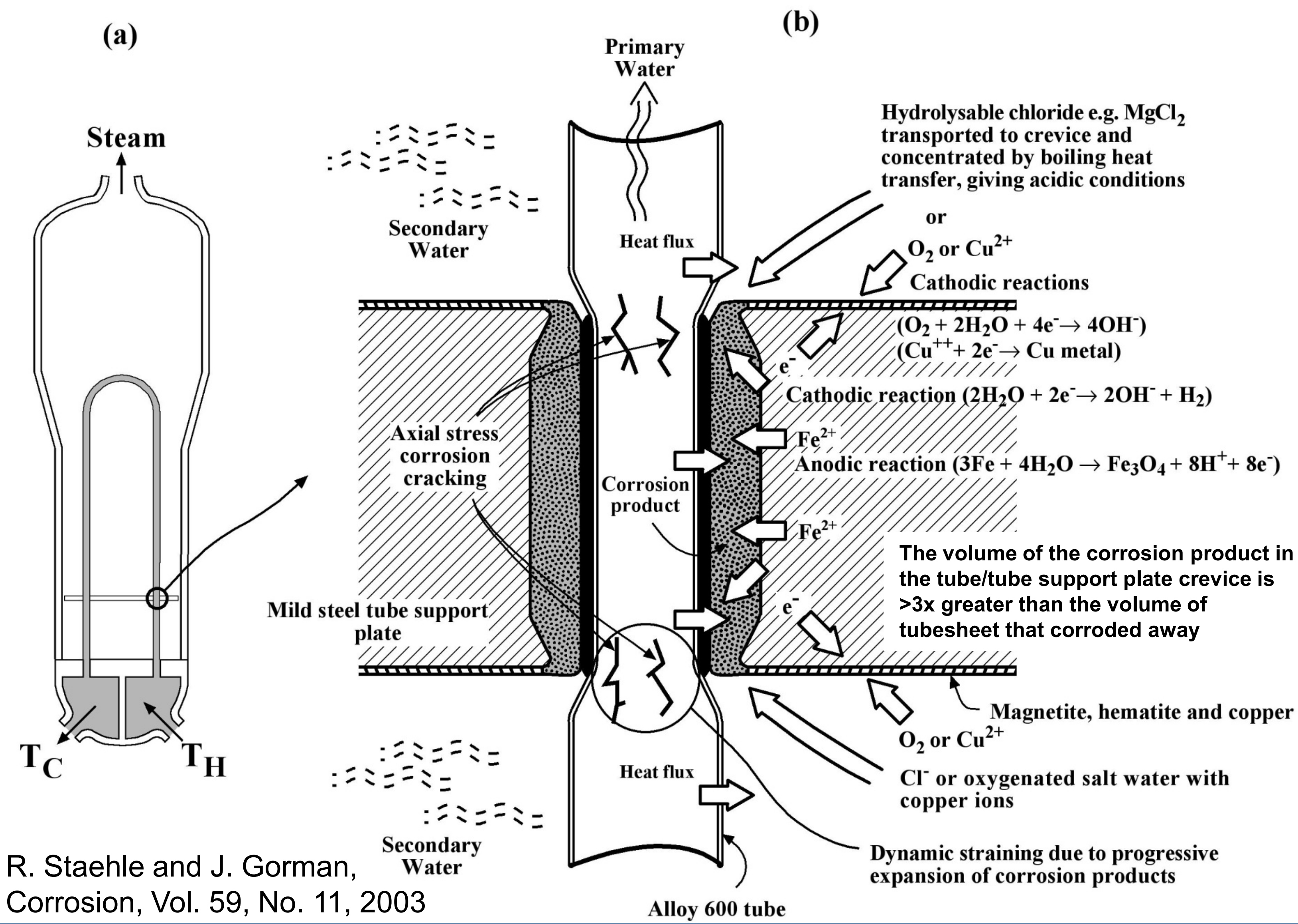


Alloy 600 tube

First discovered at Turkey Point during eddy-current testing in 1975

Initially occurred when SGs switched from coordinated phosphate water chemistry to AVT

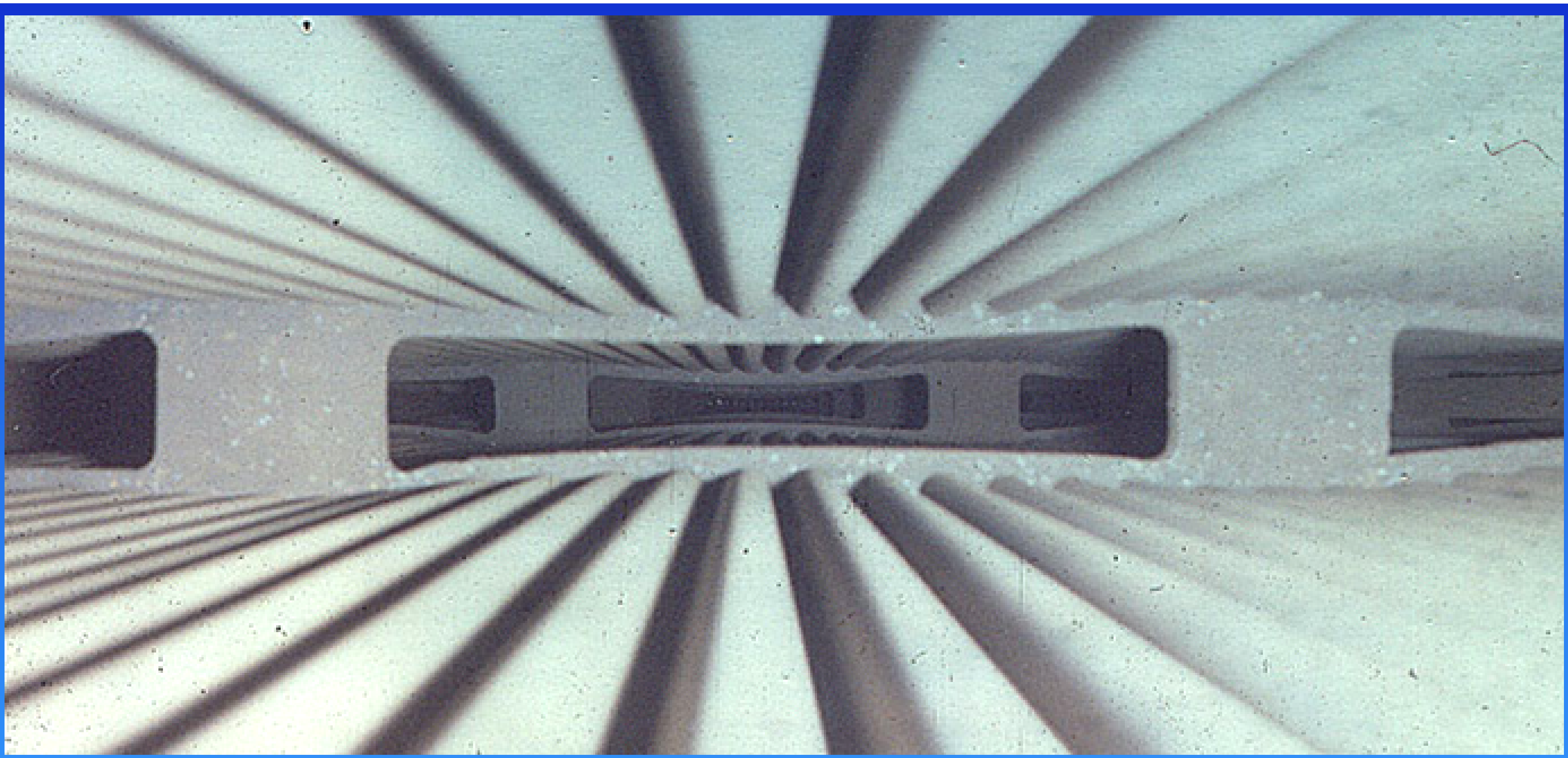
Corrosion Mechanism of SG Tube Denting

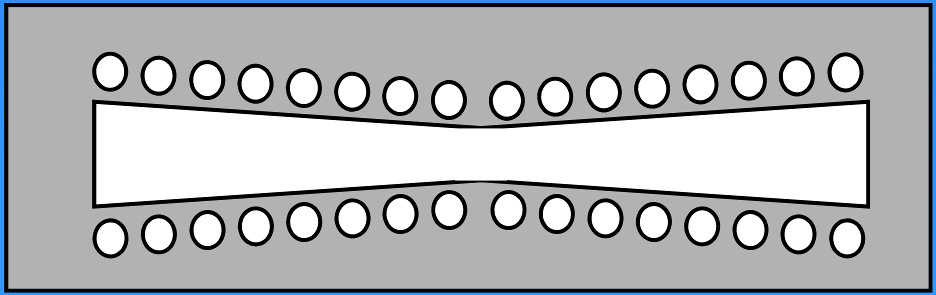


The volume of the corrosion product in the tube/tube support plate crevice is >3x greater than the volume of tubesheet that corroded away

R. Staehle and J. Gorman, Corrosion, Vol. 59, No. 11, 2003

"Hour Glassing" of SG Support Plate





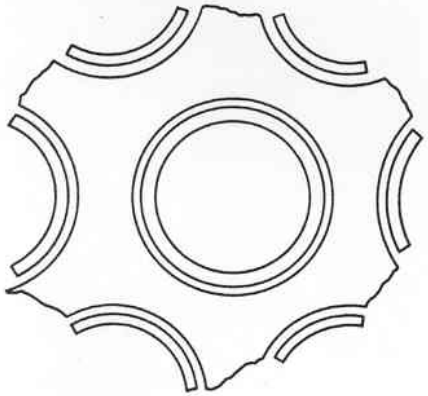
S. Rothstein

Structural Integrity Associates

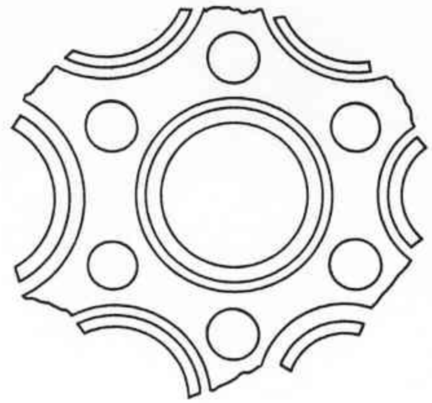
Steam Generator Tubing Crevices

- Heat transfer crevices, not electrochemical crevices
- Crevice dynamics unclear
  - Power operation
  - Start –up/shutdown
  - w/wo sludge filling in crevice
- Corrosion mechanism
  - OD initiation
  - SCC, IGA or both
- Thermal gradients and boiling
  - Boiling is the most potent concentrator and will be much worse in crevices and sludge piles
- Possible elevation in corrosion potential from oxidants

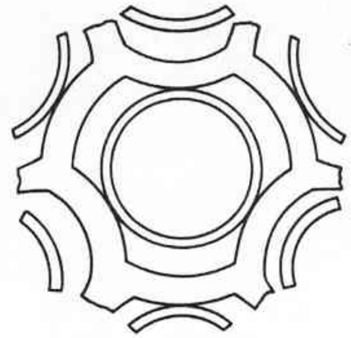
Steam Generator Tube Support Designs



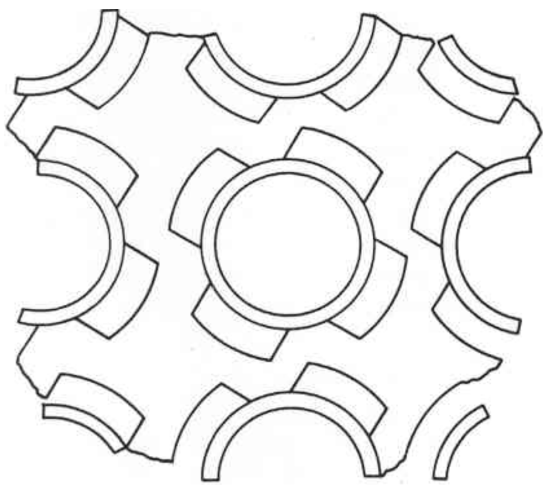
Drilled



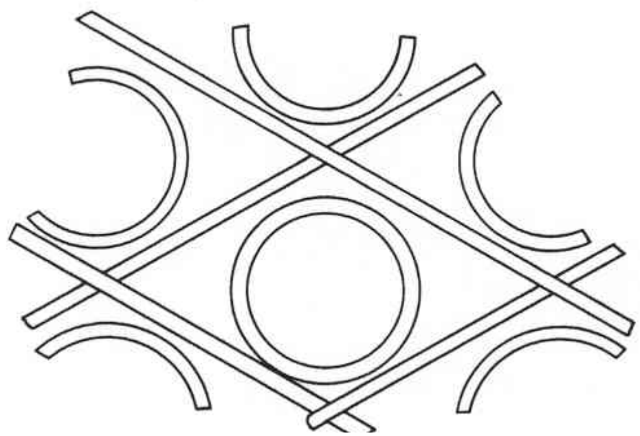
Drilled
w/Flow Holes



Broached trefoil



Broached quatrefoil



Egg crate (lattice bars)

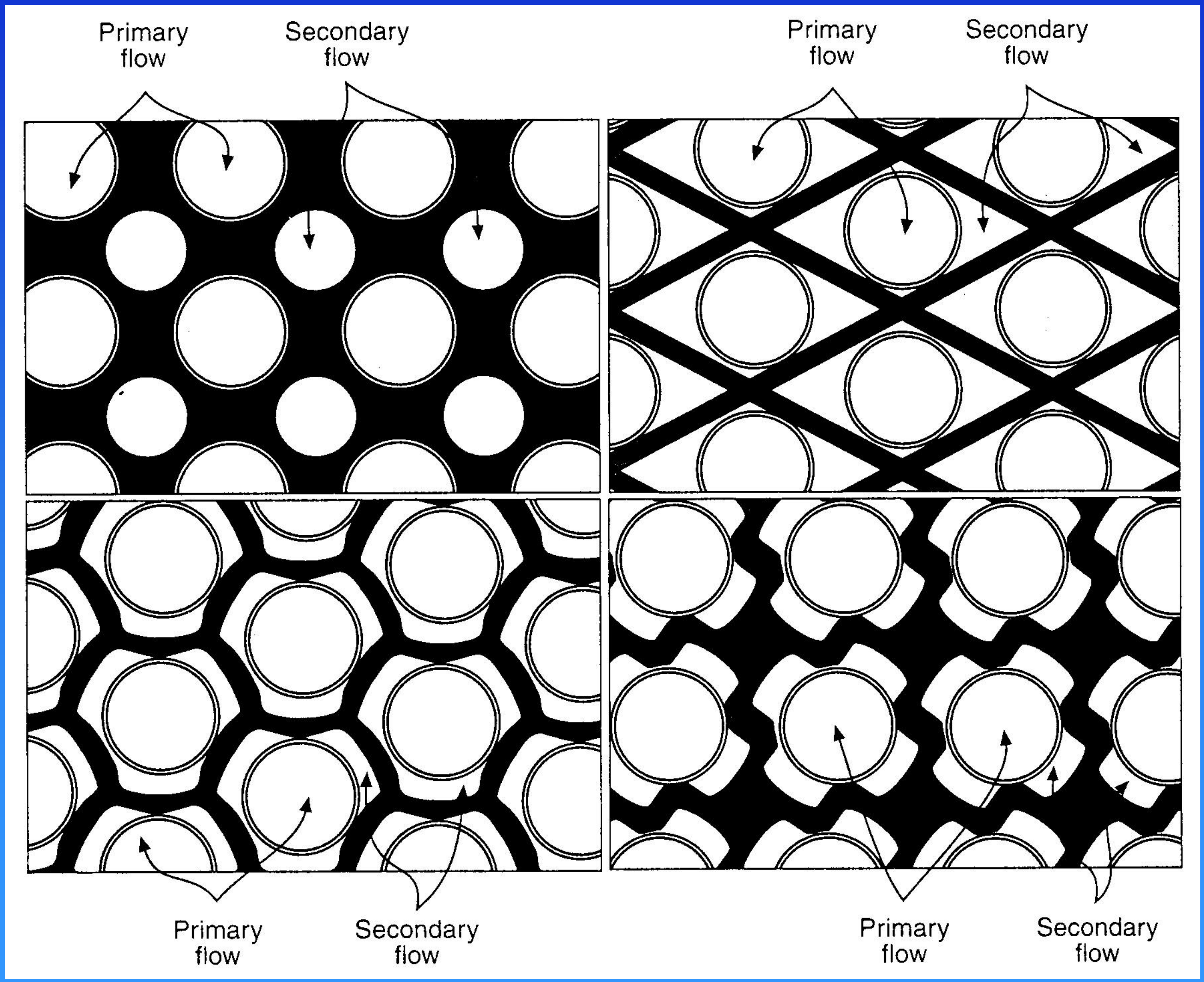
Broached Trefoil SG Support Plate

P. King, 12th Env. Deg., 8/05

SG Support Plate Designs by Company

Drilled hole – Early W

Broached trefoil – B&W

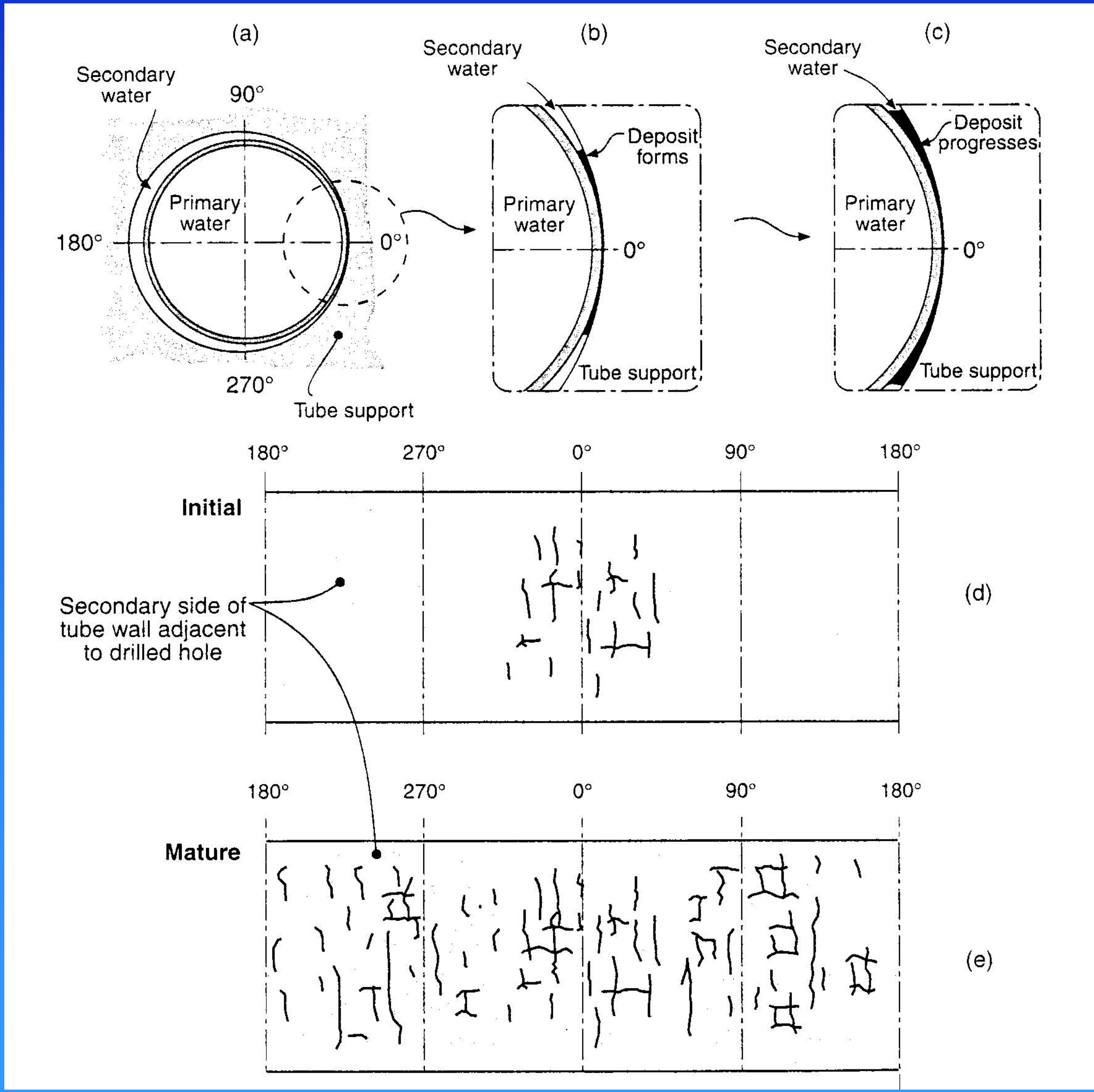


Egg crate – Siemens and CE

Broached quatrefoil – later W

R. Staehle and J. Gorman, Corrosion, Vol. 59, No. 11, 2003

Accumulation of Deposits and SCC in Drilled Support Plates



Progressive accumulation of deposits in drilled hole support plates

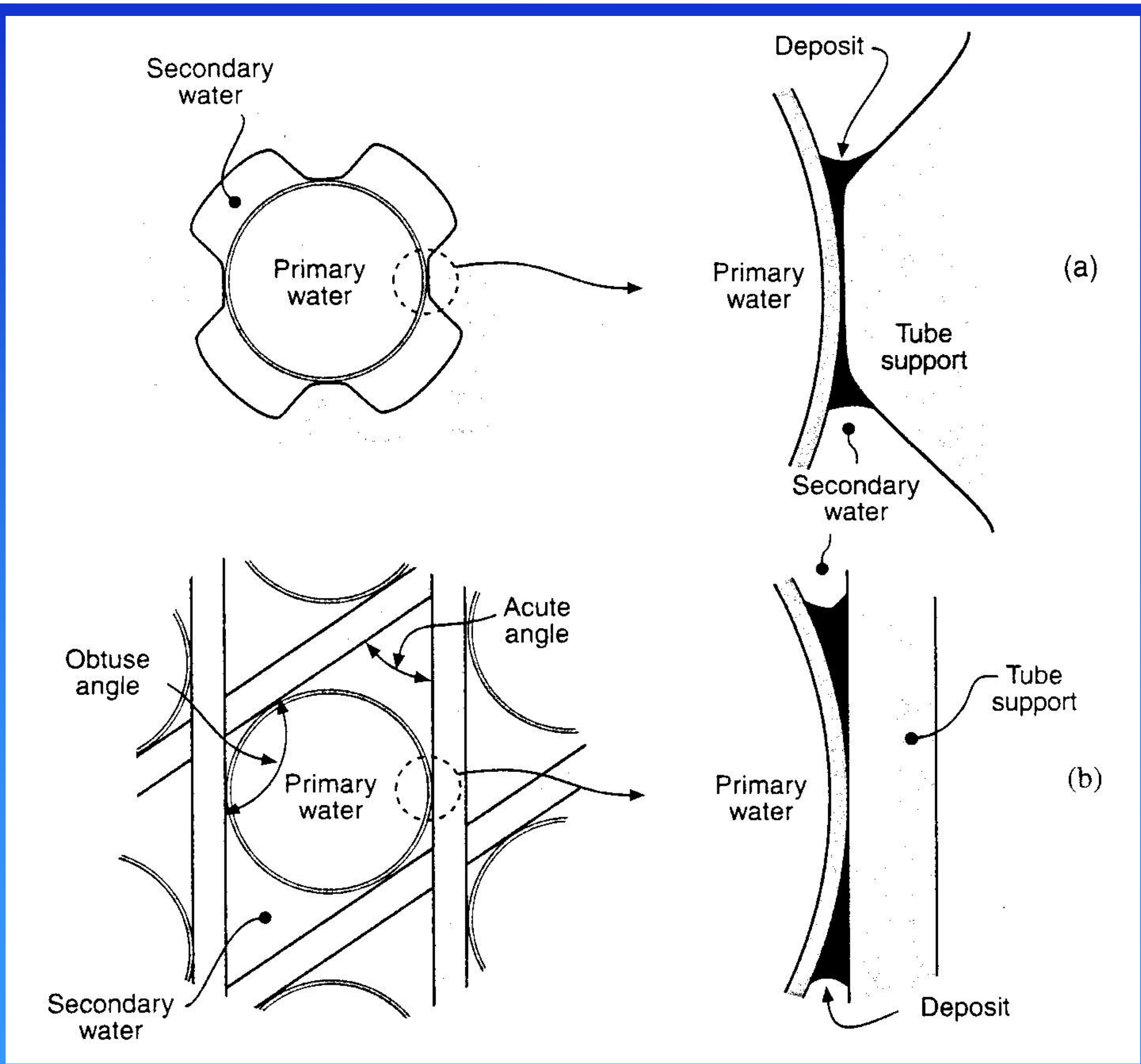
Progression of SCC in association with deposit accumulation

R. Staehle and J. Gorman, Corrosion, Vol. 59, No. 11, 2003

Newer Support Plate Design Cervices

Broached quatrefoil – later W

Egg crate – Siemens and CE



R. Staehle and J. Gorman, Corrosion, Vol. 59, No. 11, 2003

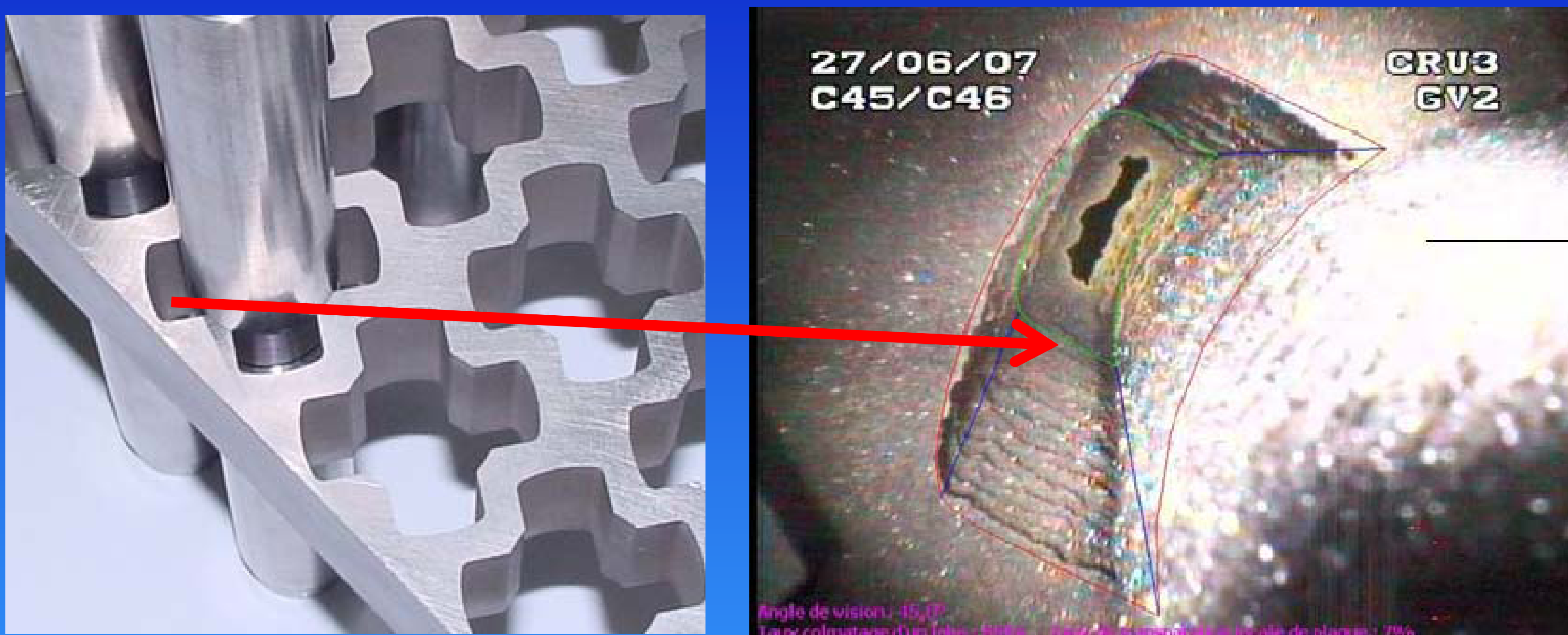
Broached Quatrefoil Support Plate Fouling and Spalling

FOULING

SPALLING

H. Bodineau, et al., Eurosafe, 2008

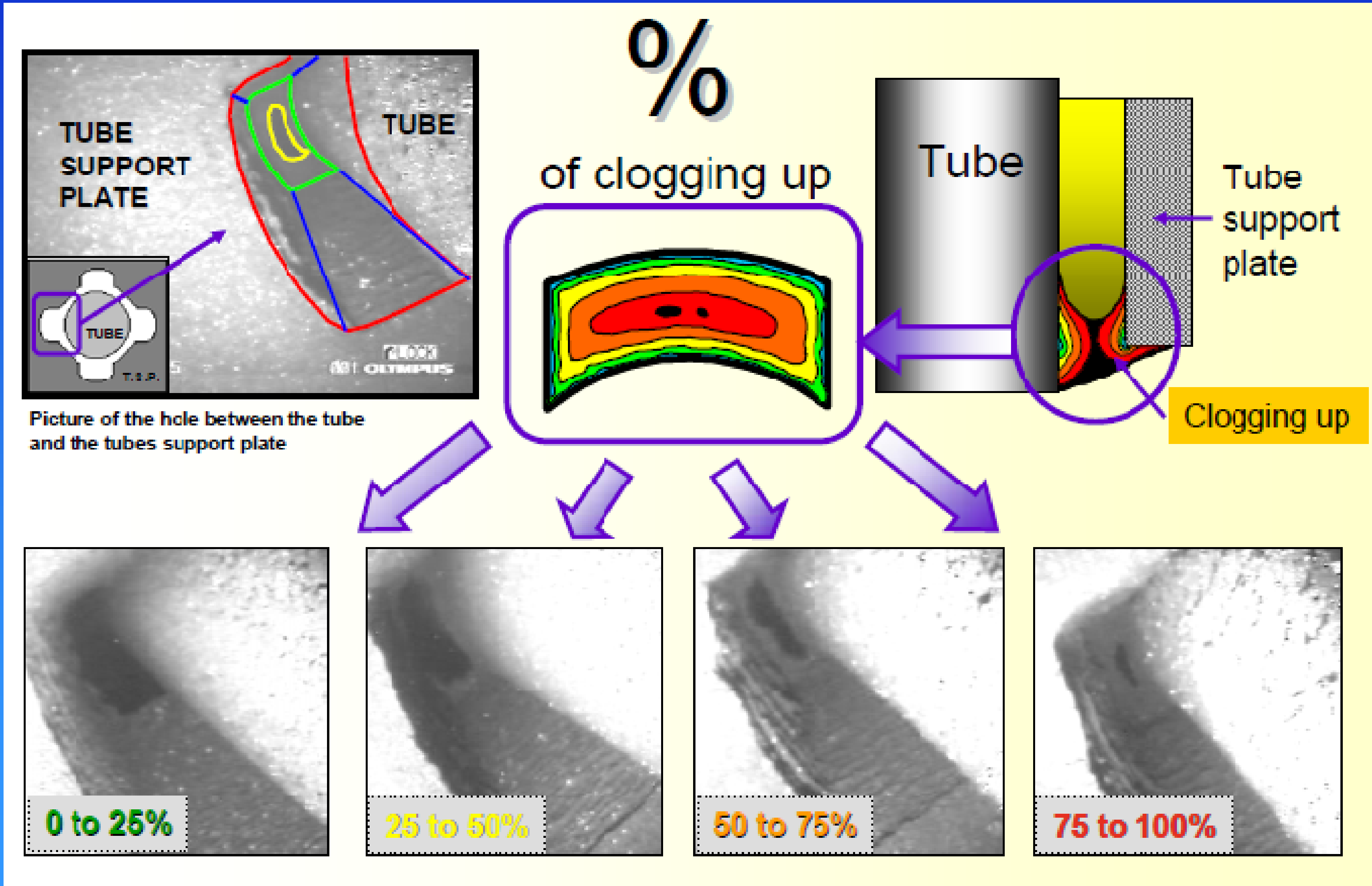
Tube Support Plate Clogging of French PWR Steam Generators



Leaks at the 8th TPS were due to circumferential cracks of SG tubes Cracking due to high cycle corrosion fatigue

H. Bodineau, et al., Eurosafe, 2008

Tube Support Plate Clogging of French PWR Steam Generators



Picture of the hole between the tube and the tubes support plate

H. Bodineau, et al., Eurosafe, 2008

Steam Generator Tubing Corrosion Mitigation

- Crevice flushing
  - improved with slow depressurization
  - improved if preceded by sludge lancing
- Crevice soaking (not very effective)
- Annual cleaning
- Temperature reduction
- Additives
  - Boric acid
  - Others – citric acid, phosphoric acid
- Tube sleeving, plugging, pulling

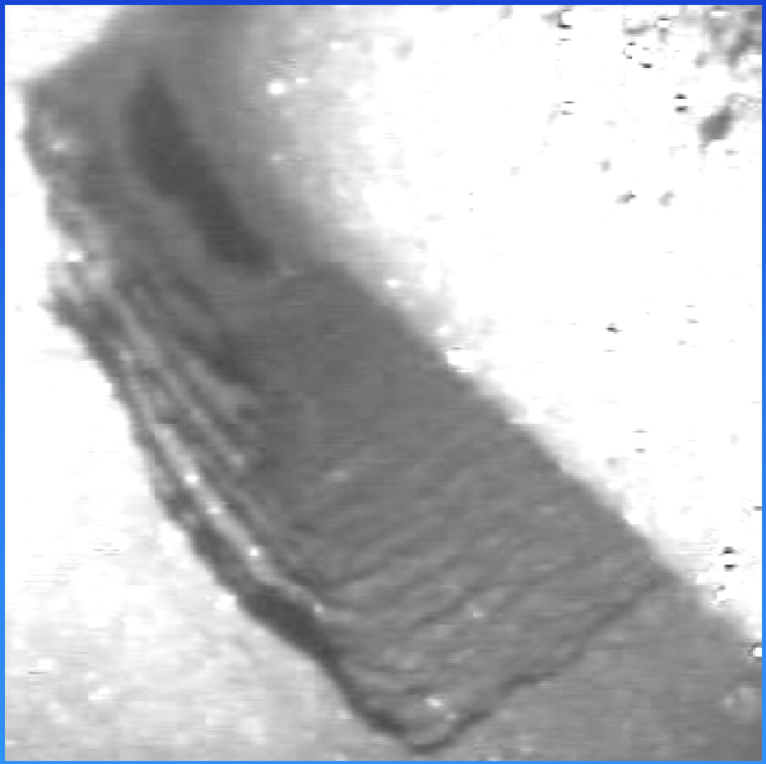
Steam Generator Corrosion Product Removal

- A clean SG is the key to long-term operation
- US utilities spend ~$25M/y cleaning SGs
- 1980s - SG chemical cleaning involved introducing chemicals during shutdown to dissolve magnetite (Fe_3O_4) and Cu-based deposits – only cost effective for huge amounts of sludge (1360 kg [3000 lbs]/SG)
- 1999 – Scale conditioning agents (SCAs) of patented mixtures of ~500 ppm of organic amines at 21 to >77°C (70 to >170°F) to soften deposits combined with mechanical cleaning techniques (e.g., sludge lancing). Not very effective.
- 2000 – Advanced SCAs 24h/77°C (170°F) for 3 specific types of deposits – bundle maintenance, top of tubesheet and Cu/Pb (5000 and 500 ppm, respectively, in older PWRs)

P. Battaglia and K. Prentice, NPJ, Vol. 21, No. 3

Effects of Cleaning on Clogged Quatrefoil TSPs

Before



Average clogging of 70% at 8th TSP

After

Average clogging of <15% at 8th TSP

H. Bodineau, et al., Eurosafe, 2008

Pitting Corrosion

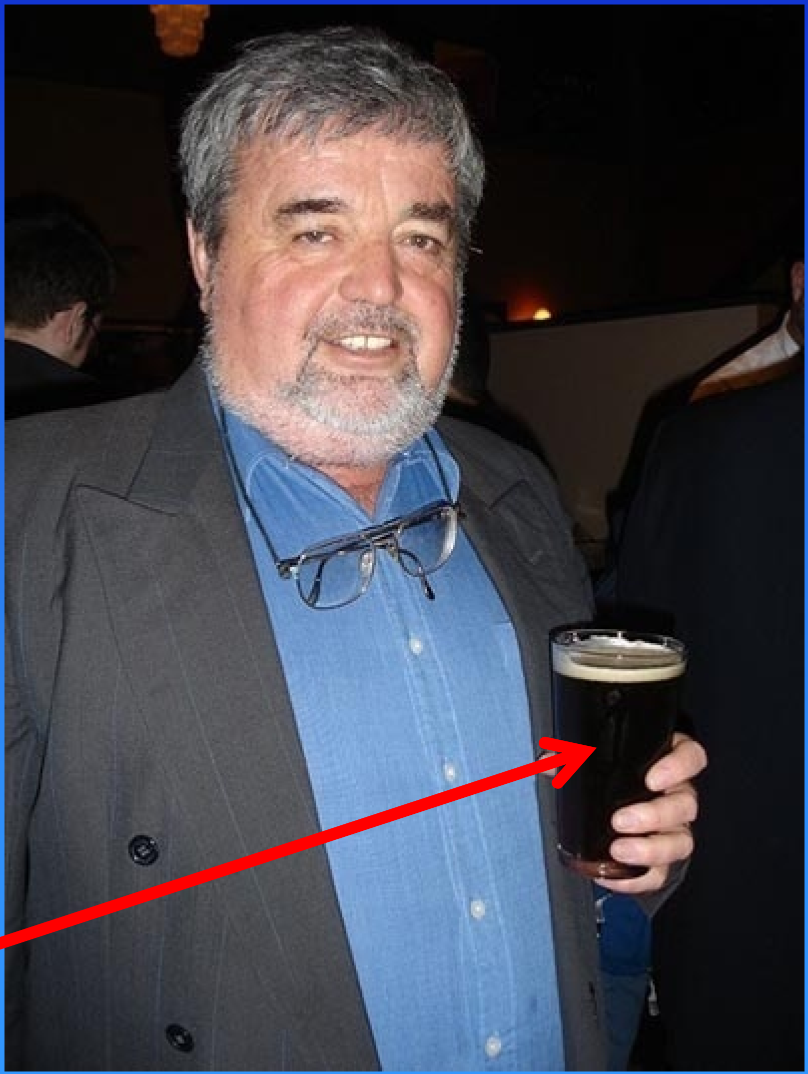
Pitting Corrosion

- **Mechanism**
- **LWR Case Study Example**
  - ♦ **Copper**
  - ♦ **Carbon steel**
  - ♦ **Al fuel storage racks**

"Pits Are Like People"

- Pits are like people:
  - They are born …
  - And they grow and …
  - They die
- Most pits are stillborn
- Pits die from:
  - Old age
  - Misadventure
  - Competition

Glass of Electrolyte



Digby Macdonald, 1/02

Having a Pot to Pit in

Note: Just because a surface appears "pitted" does not mean that the corrosion degradation mechanism is pitting corrosion!!

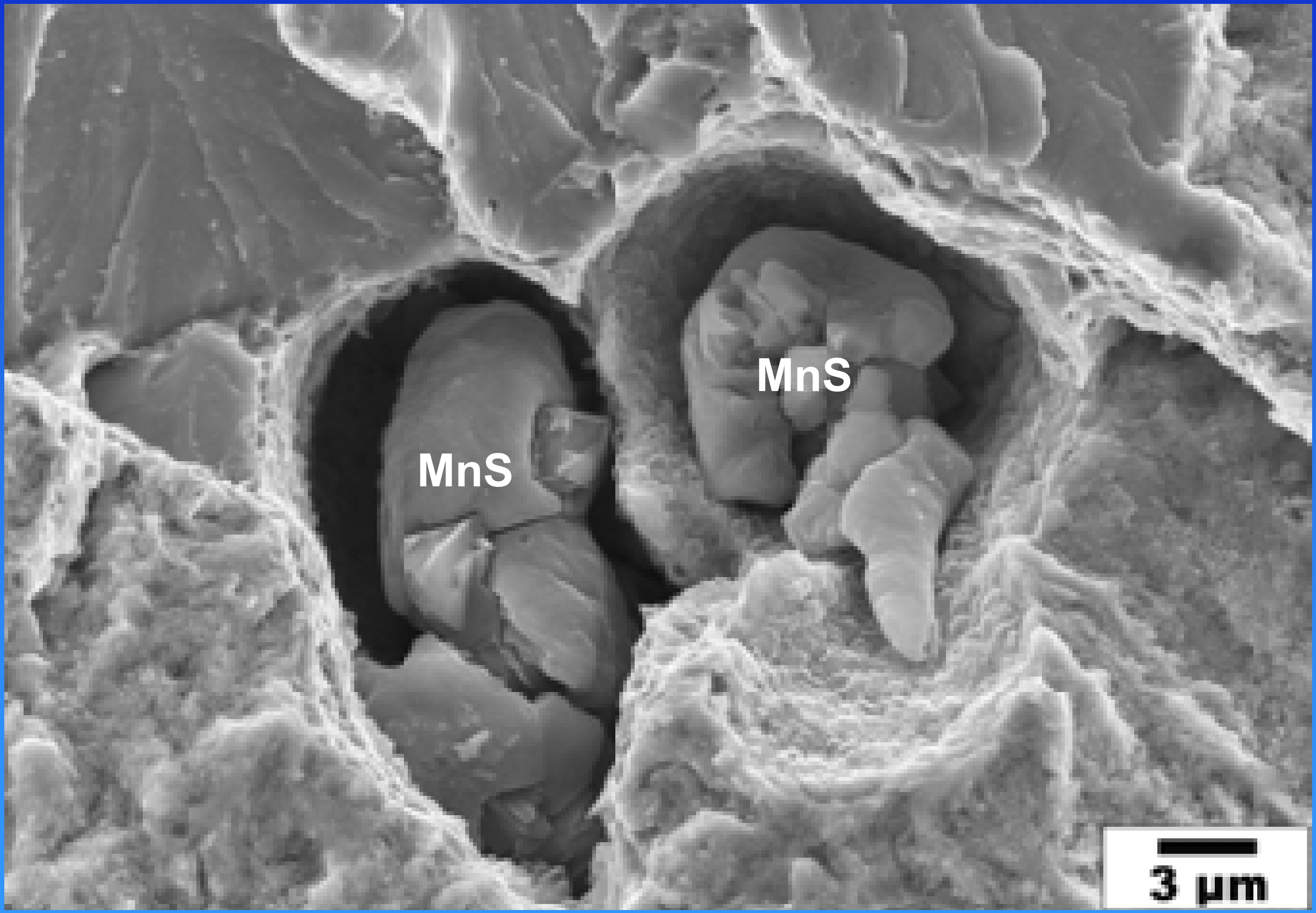
Pitting Corrosion

- Pitting corrosion is localized accelerated dissolution that occurs as a result of a breakdown of the otherwise protective passive film on the metal surface
- Such passive films, however, are often susceptible to localized breakdown resulting in accelerated dissolution of the underlying metal
  - If the attack initiates on an open surface, it is called pitting corrosion
  - If the attack initiates at an occluded site, it is called crevice corrosion

Pitting Corrosion

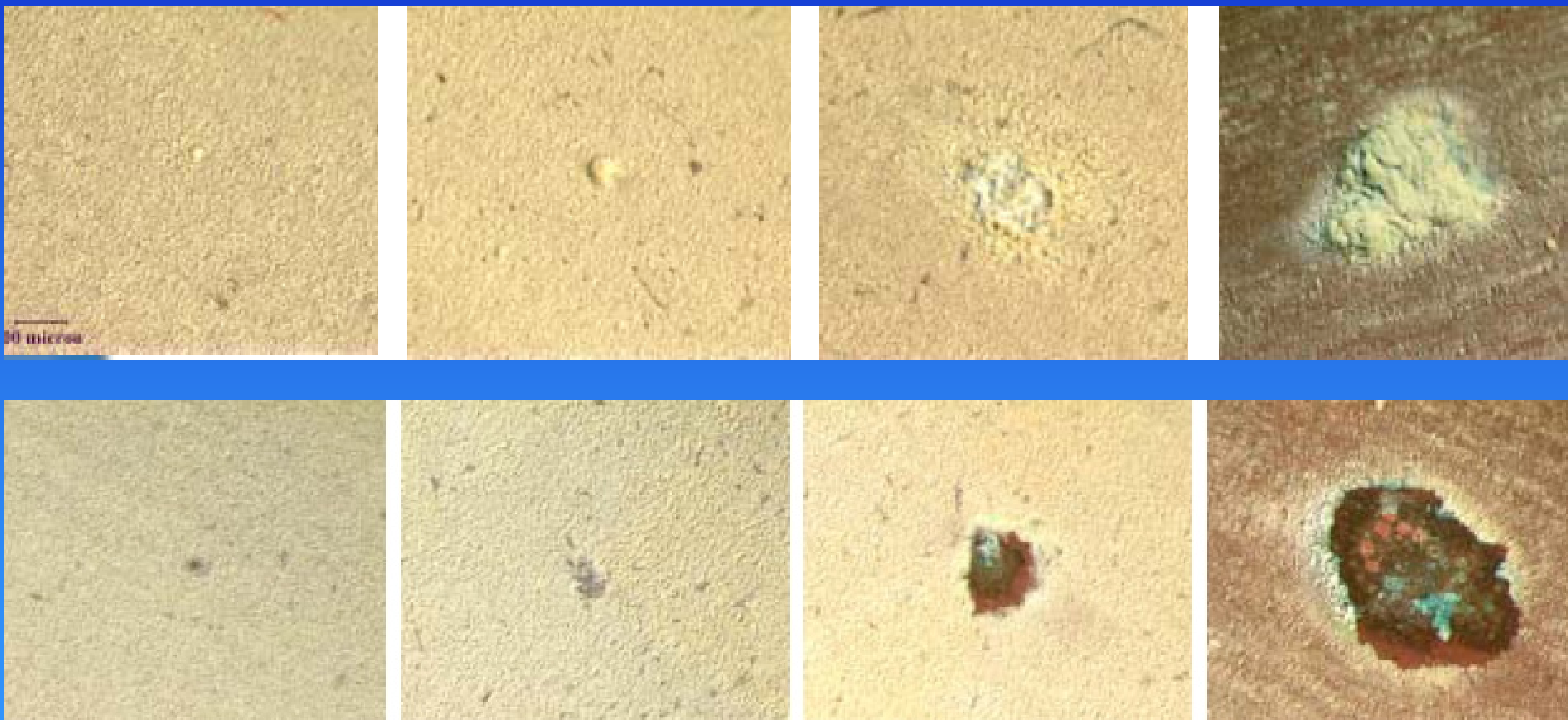
- **Stationary electrodes**
- **Very destructive**
- **A limiting case of localized attack**
- **Shielded from view and remain undetected until leakage occurs**
- **Occurs on passive surfaces due to:**
  - **Second phase particles (MnS) – provide SO_4^{2-}, HS^-, S^{2-}**
  - **Dislocation intersections**
  - **Defects such as scratches**
  - **Any area of high local anodic activity**
- **Maintenance of the aggressive pit chemistry is facilitated by the possibility that solid corrosion product can form at the mouth of the pit, thereby hindering flushing out of local pit environment**

Dissolvable MnS Inclusions



H-P. Seifert and S. Ritter, SKI Report 2005:60, 11/05

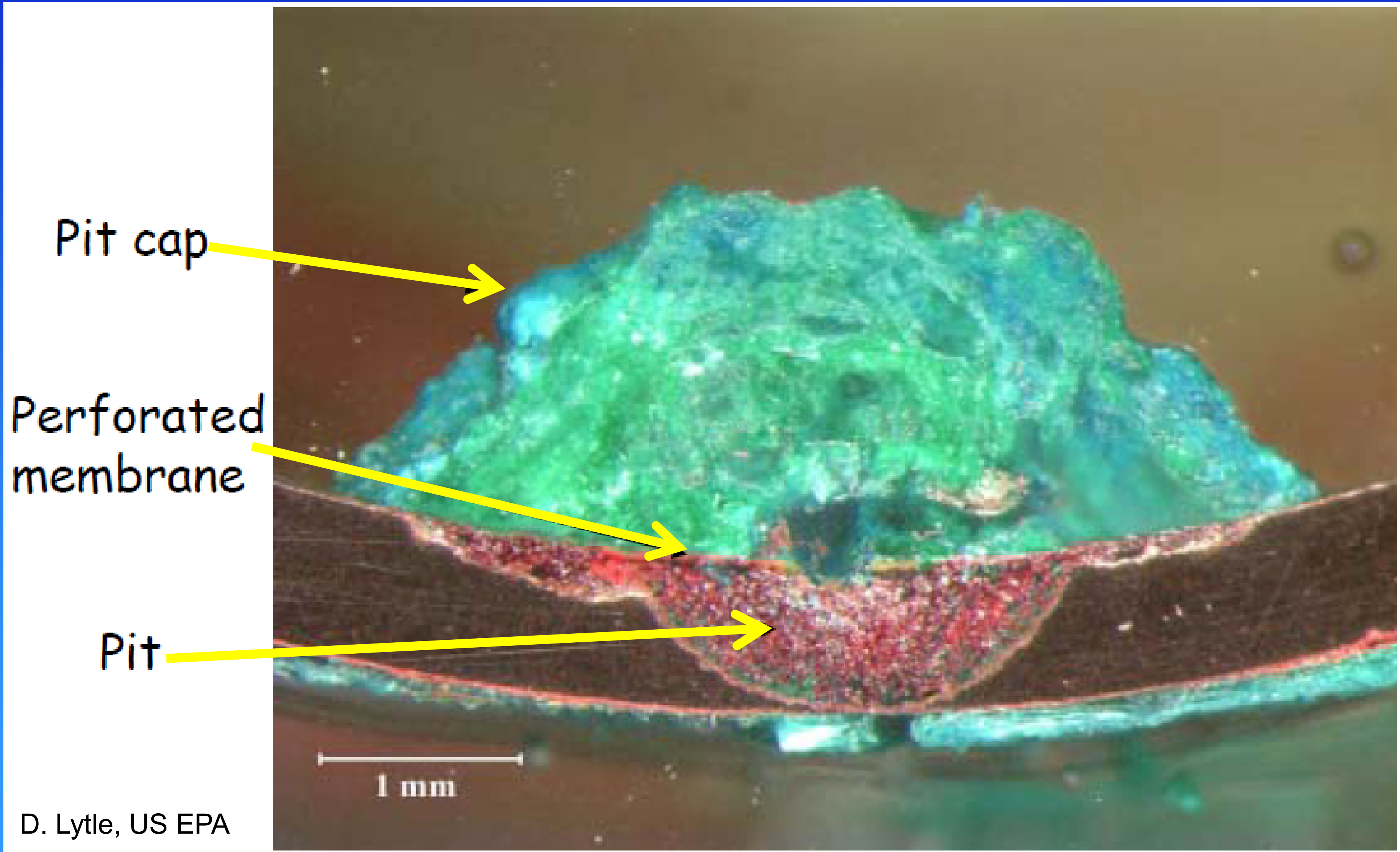
Pit Propagation due to Particle Deposition



Particle Deposition, Particle Growth and Corrosion Cell Formation

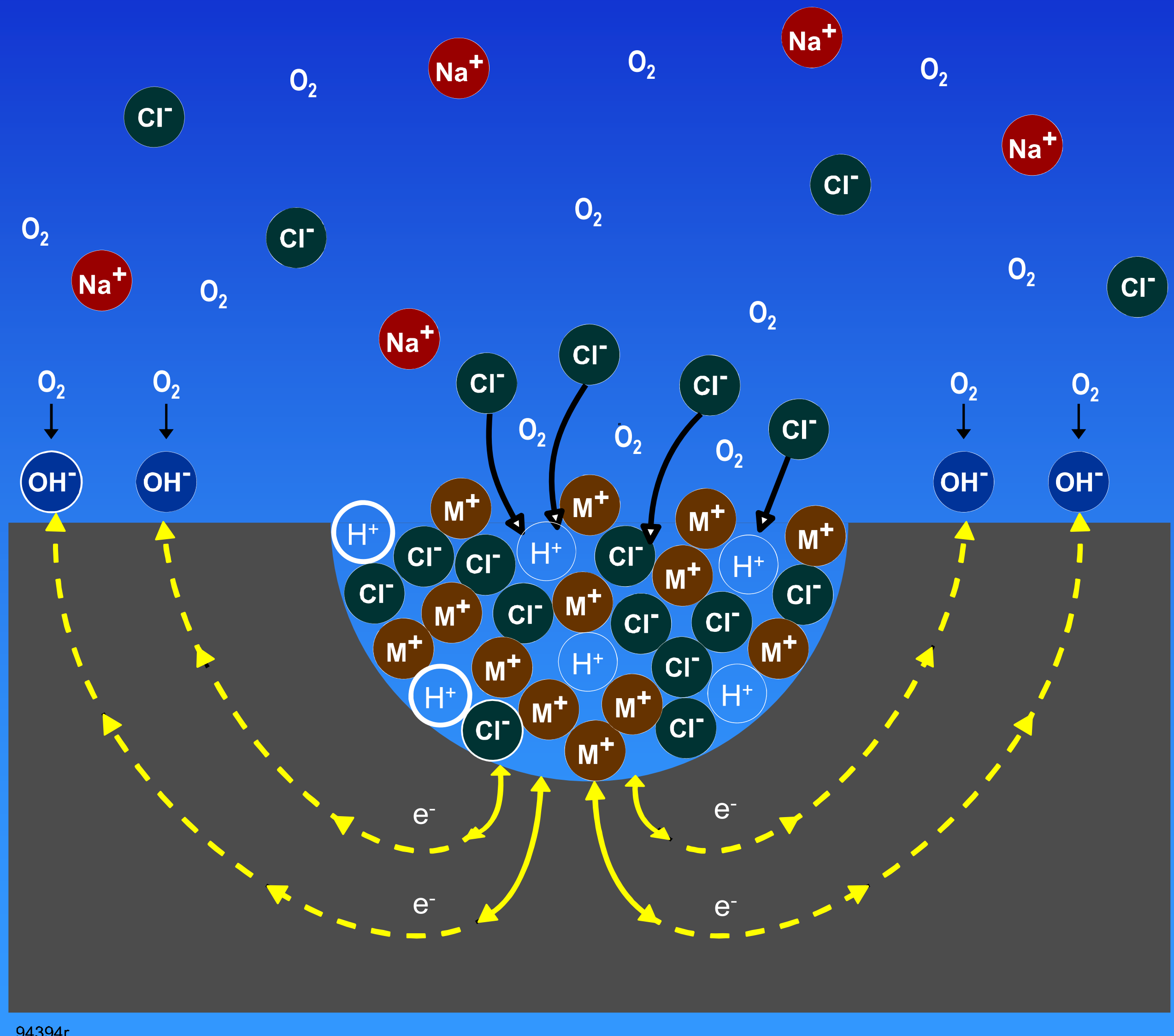
D. Lytle, US EPA

Anatomy of a Copper Corrosion Pit



D. Lytle, US EPA

Autocatalytic Process Occurring in a Corrosion Pit

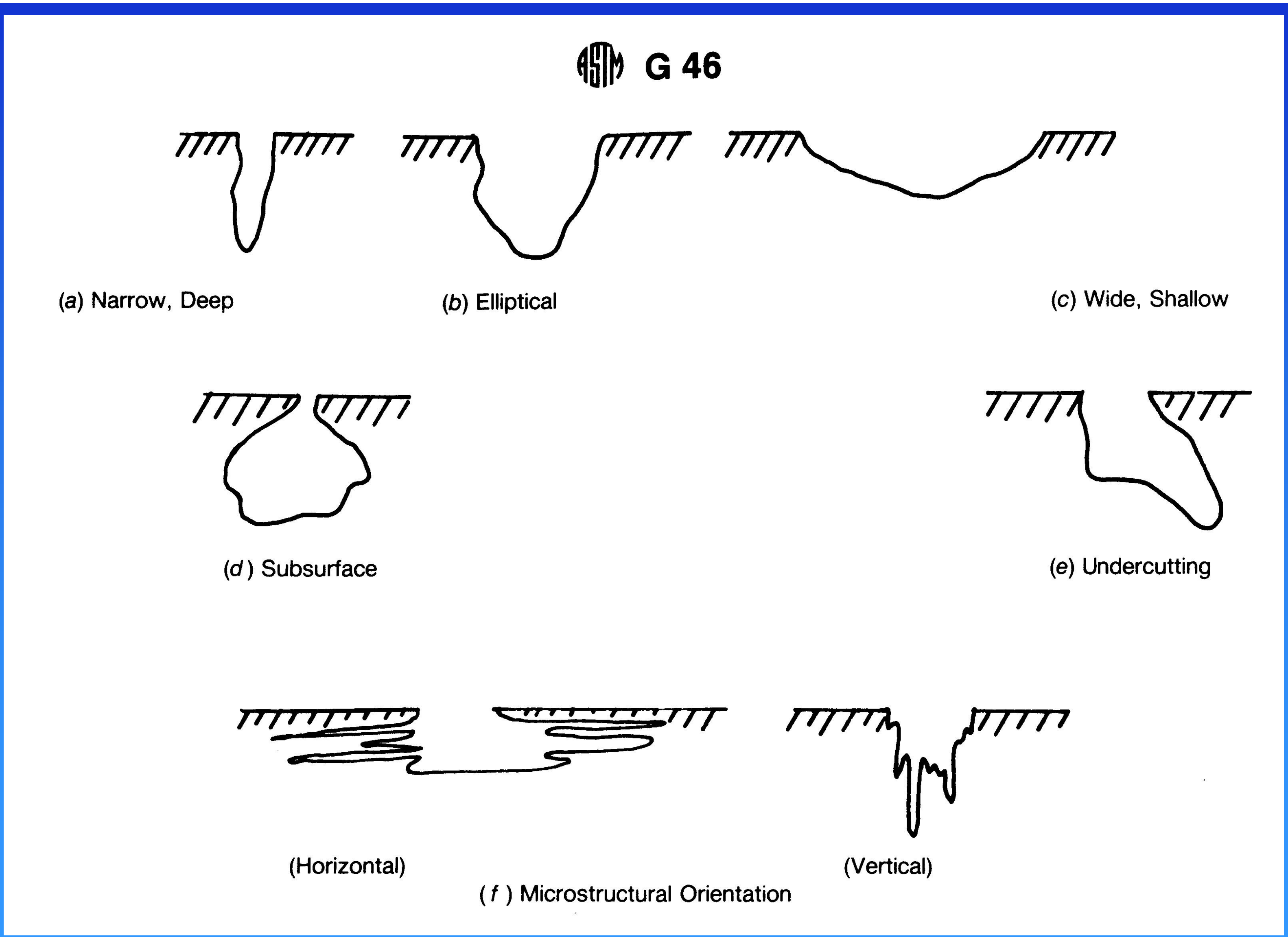


Pitting Corrosion

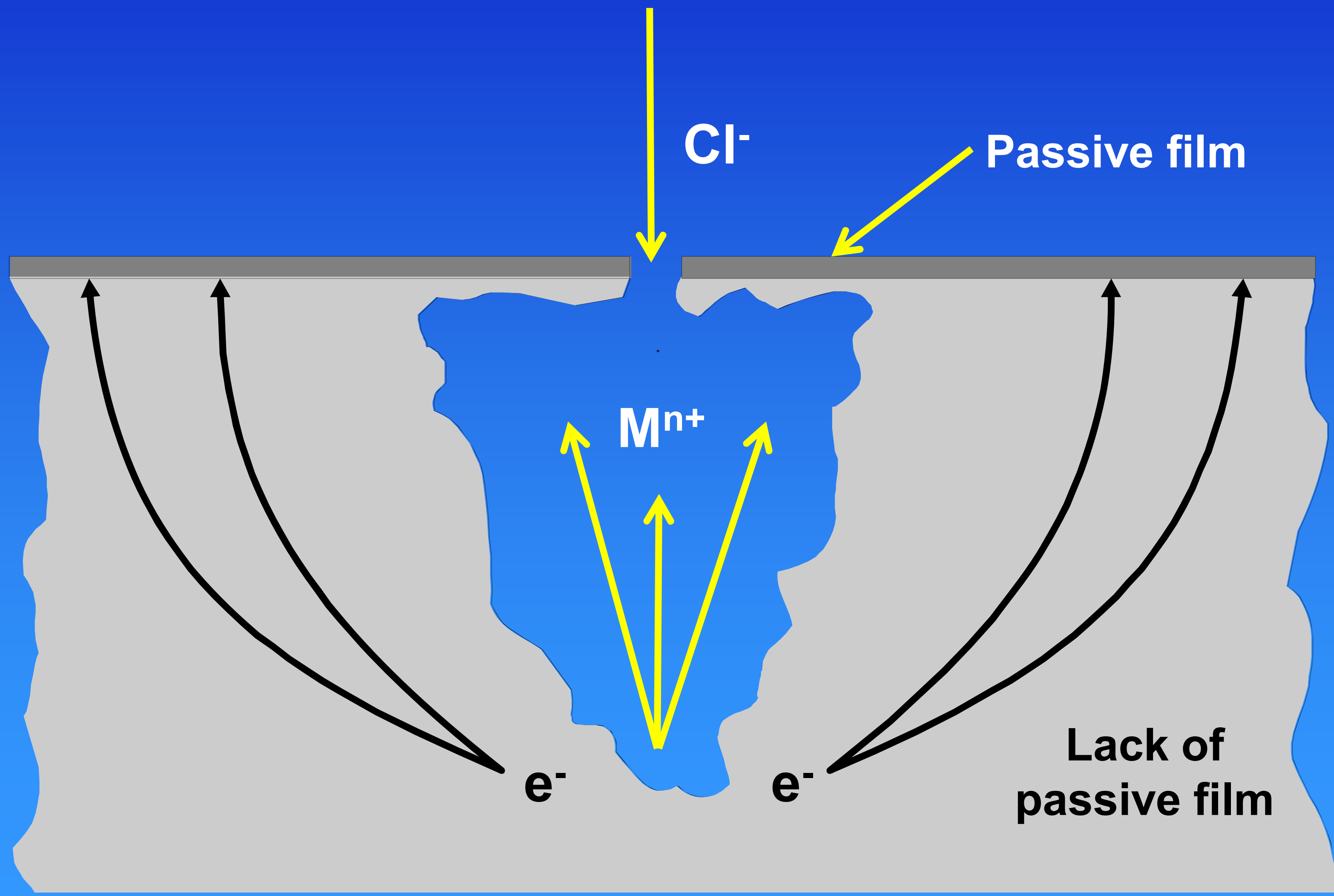
- Pits usually grow in the direction of gravity
- Long initiation period followed by rapid autocatalytic growth
- Several shapes (ASTM)

Narrow, deep
Elliptical
Wide, shallow
Subsurface
Undercutting
Horizontal
Vertical

ASTM Pit Shapes

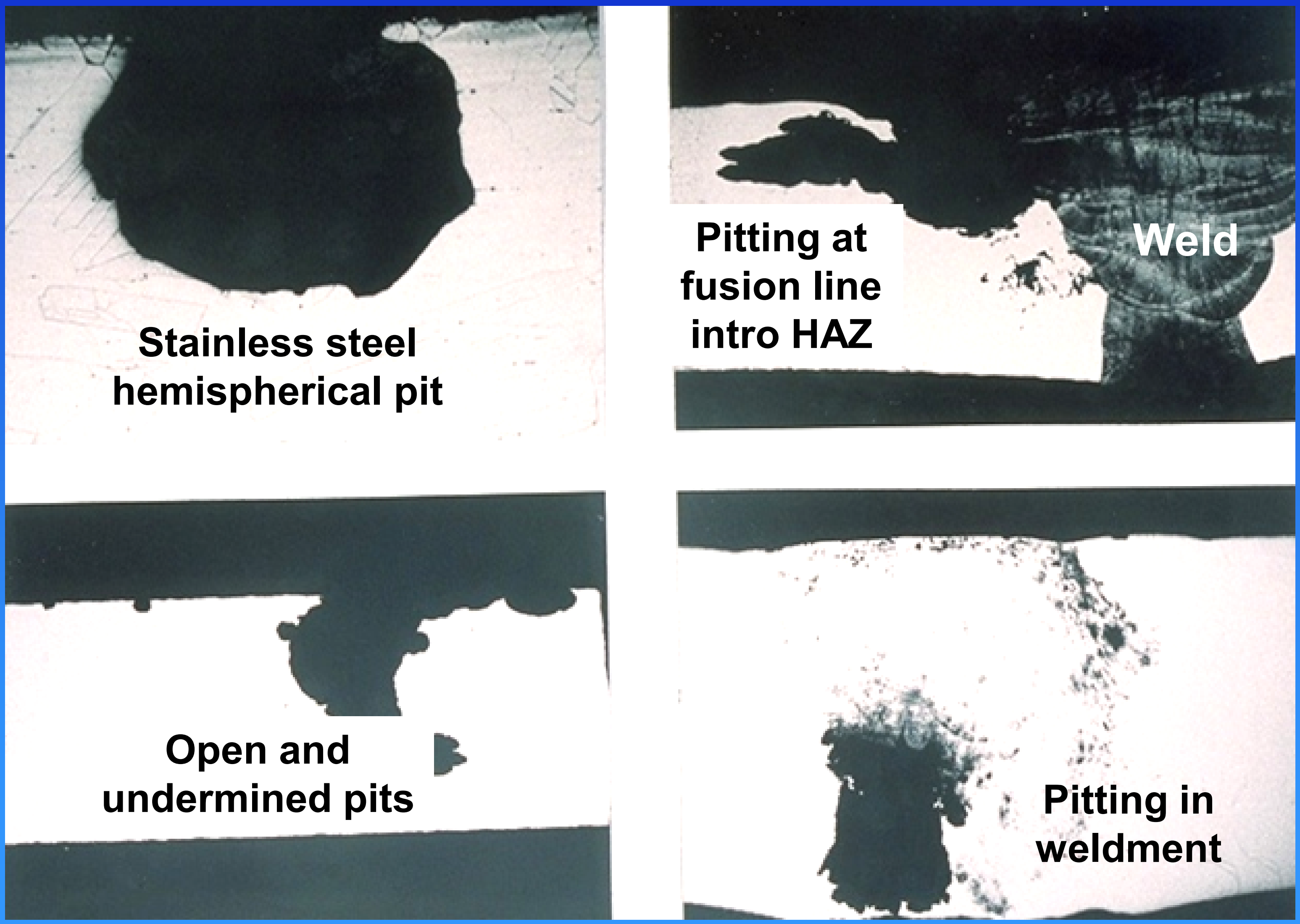


Subsurface Pit



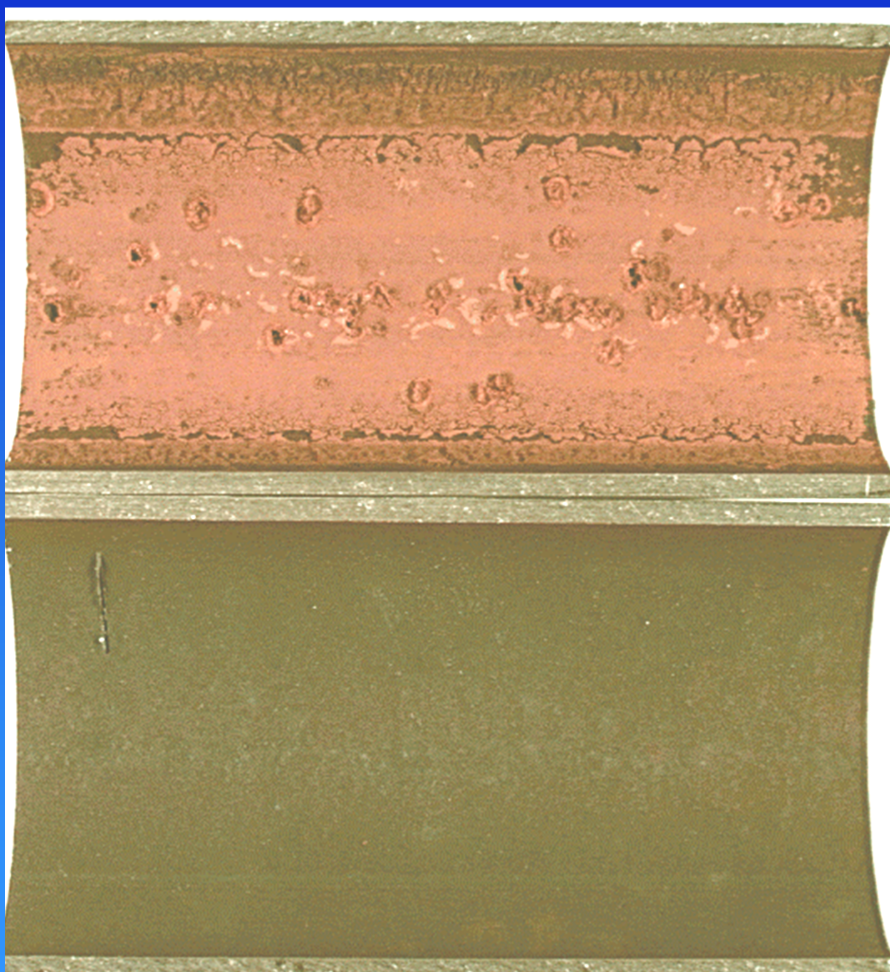
92380r0

Pitting Corrosion

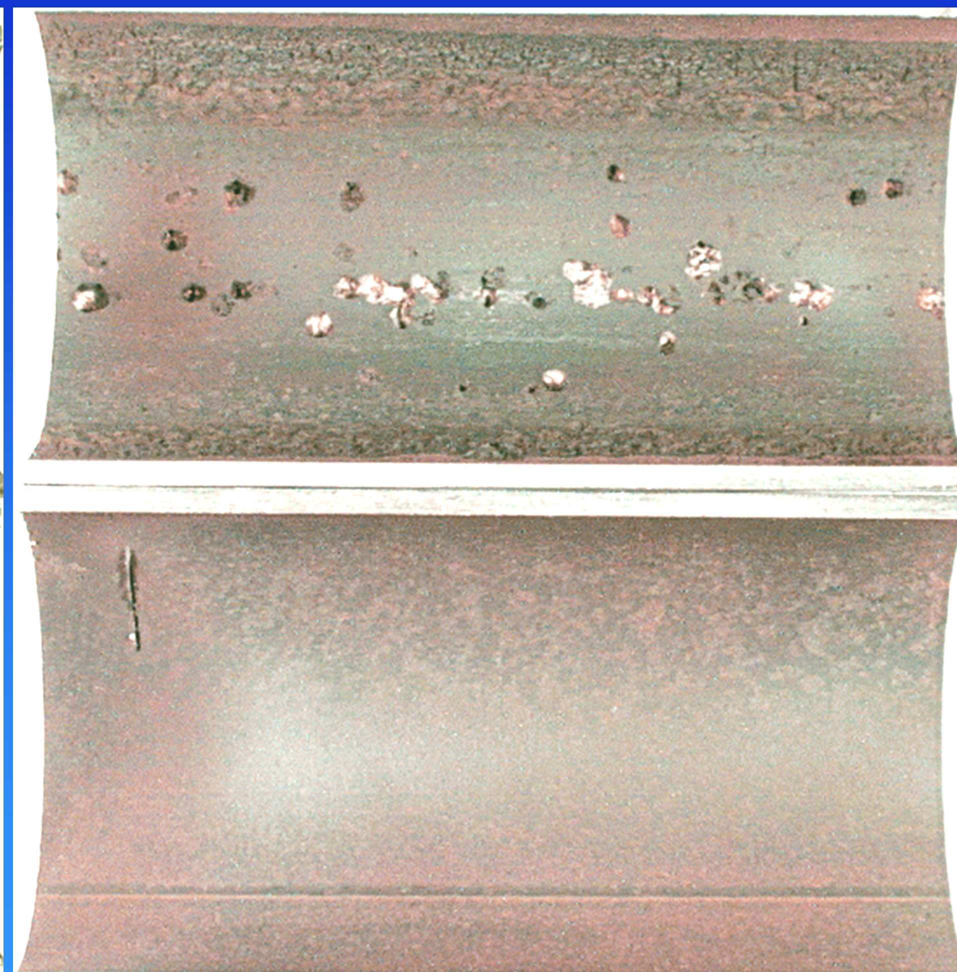


S. Borestein, EPRI 1004924 2003

Carbon Steel Condensate Line Pitting

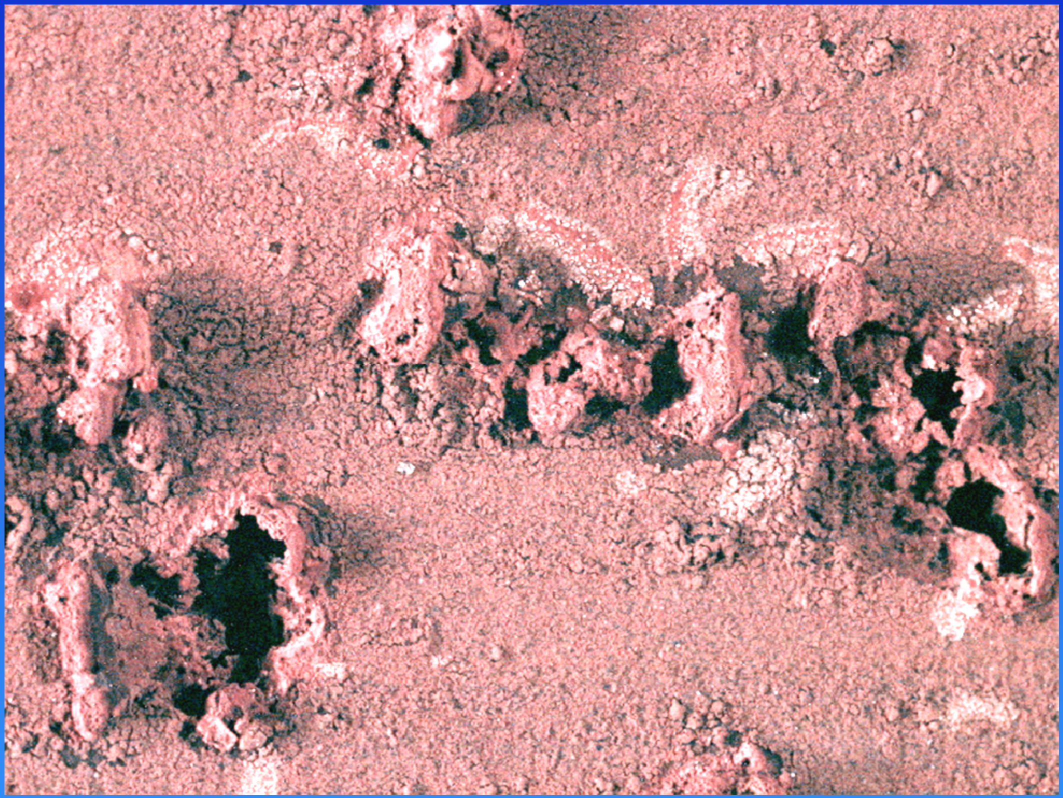


Pit Tubercles



After Bead Blasting

Pitting of Carbon Steel



Pit Tubercles - hollow mounds of corrosion product and deposits that cap the pit and trap acidic environments

Tubercles are often the result of re-deposition of soluble ferrous (Fe^{+2}) following its oxidation to the insoluble ferric (Fe^{+3}) state

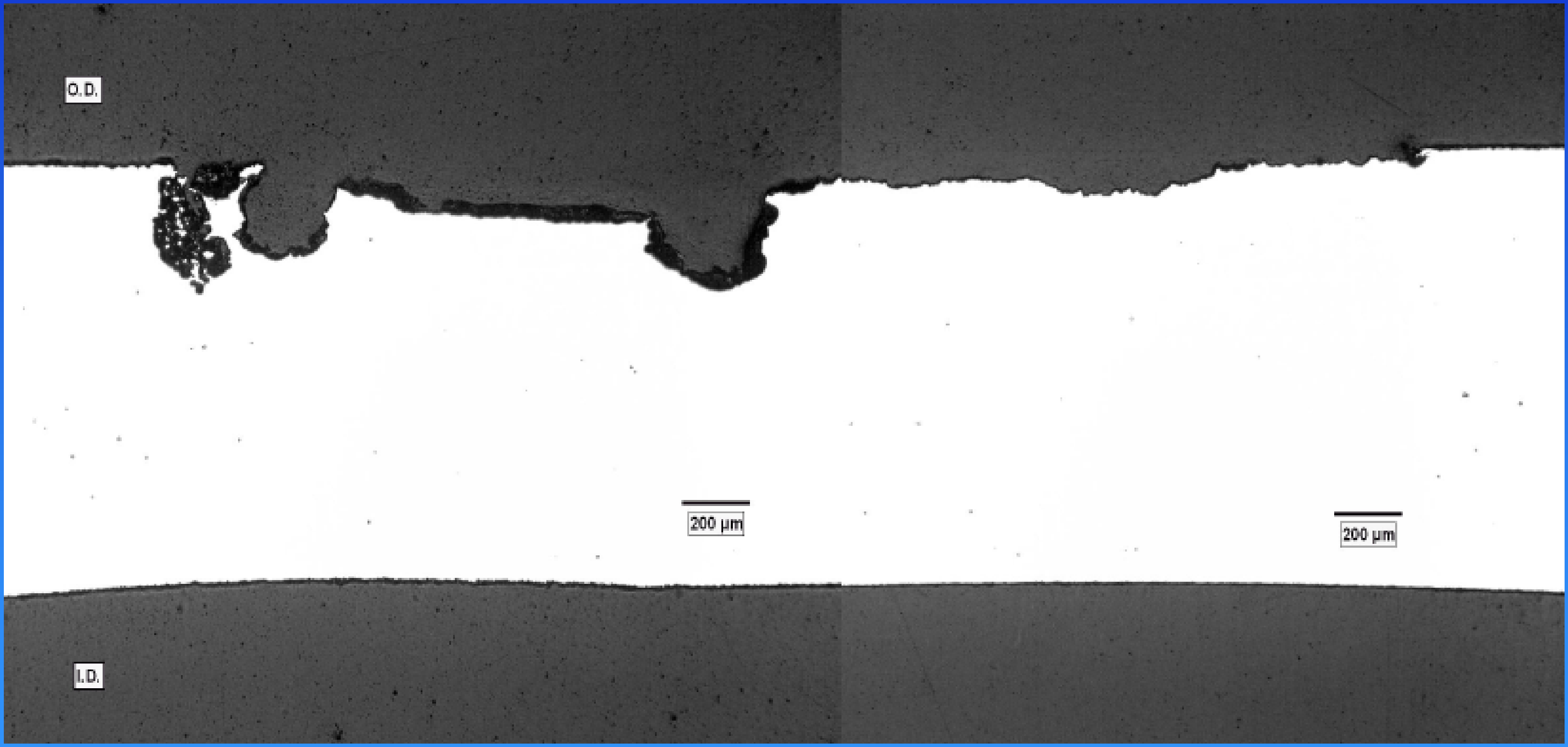
Not only due to MIC!

Can cause blockage!

Cross section

Occluded Pipe at Kewaunee due to Pitting and Tubercles

Pitting Alloy 600 SG Tube - CANDU

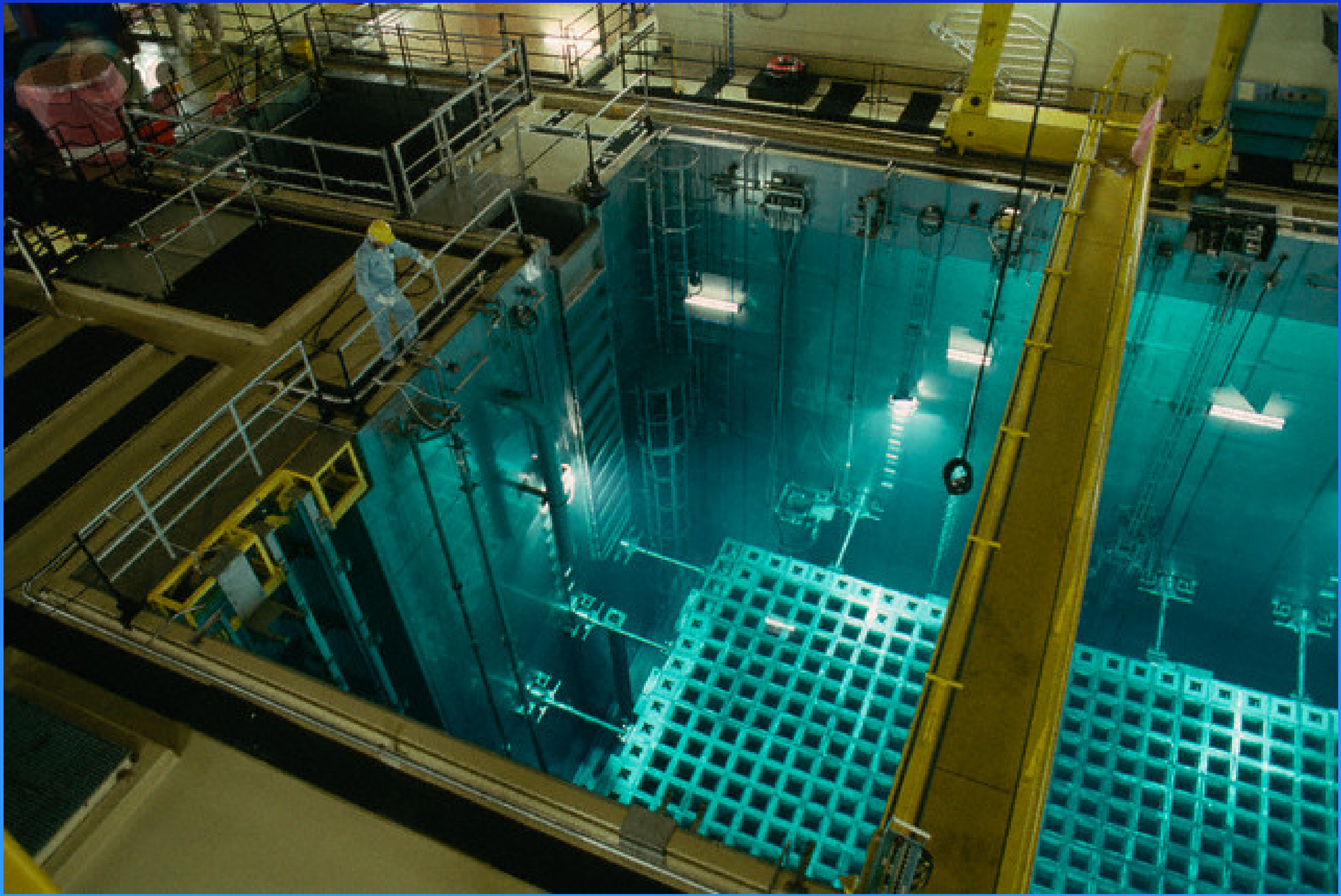


J. Riznic, SGAM, IAEA, 6/09

Al Fuel Storage Racks

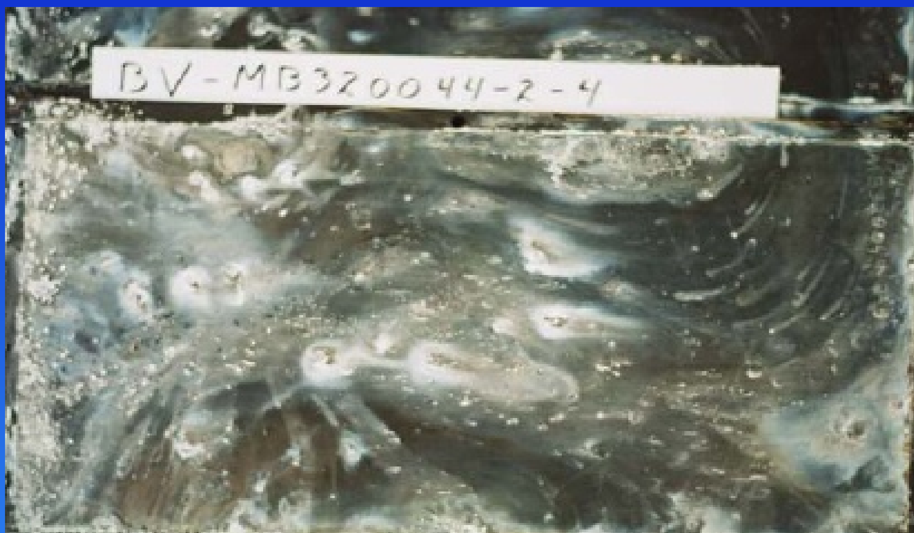
- NRC Information Notice 2009-26
- Neutron absorber materials (e.g., B_4C or BORAL®) are used in spent fuel storage racks to control the reactivity of spent nuclear fuel
  - BORAL® - hot-rolled composite plate of a core of mixed Al and B_4C particles with Al cladding on both external surfaces
- Al square tubes can be fixed in a stainless steel grid that fit between and is in contact with the Al tubes at the top and bottom
  - Galvanically induced pitting

Example of Fuel Storage Rack



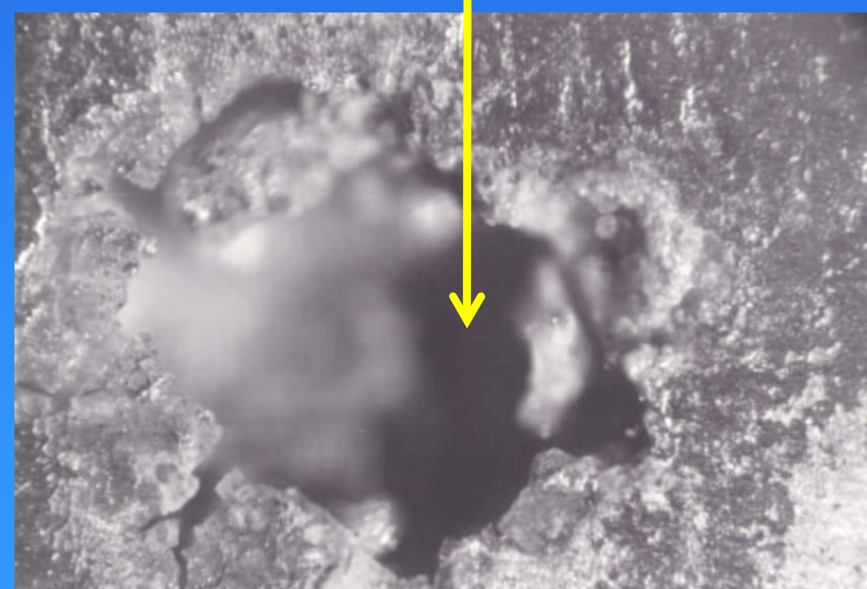
© Roger Ressmeyer/CORBIS, 1990

Pitting of BORAL™



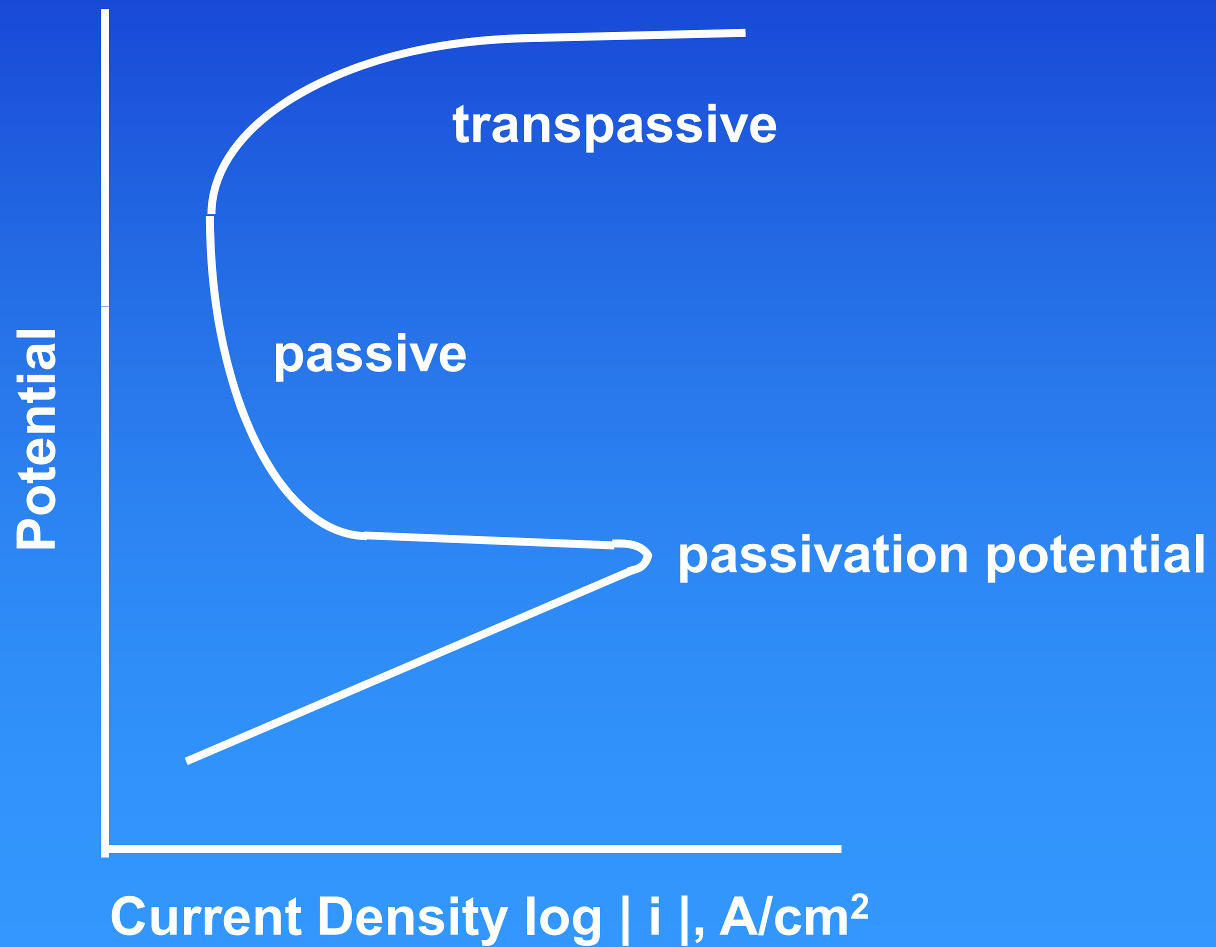
Pitting initiated by residual contaminants on BORAL™ surfaces

Through-wall pit in BORAL™



Anodic Scan for a Passive Alloy

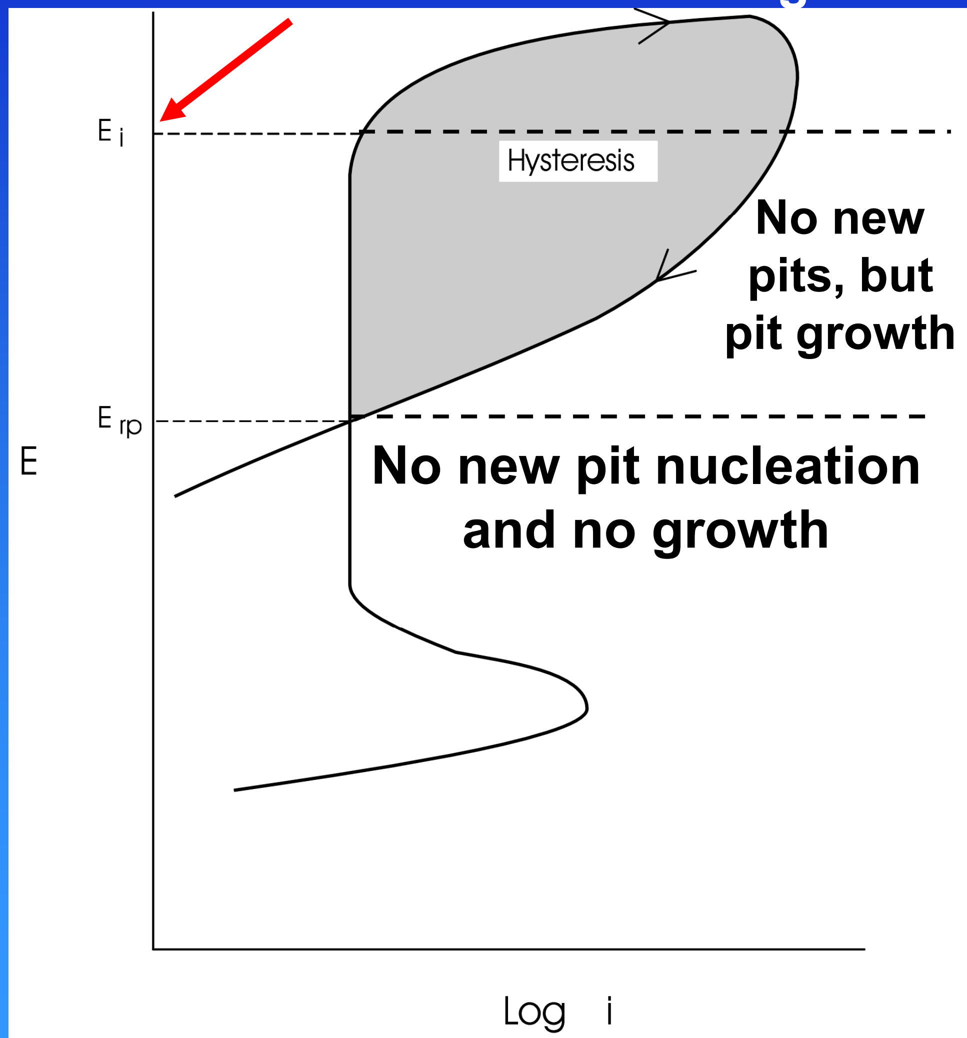
Evans Diagram



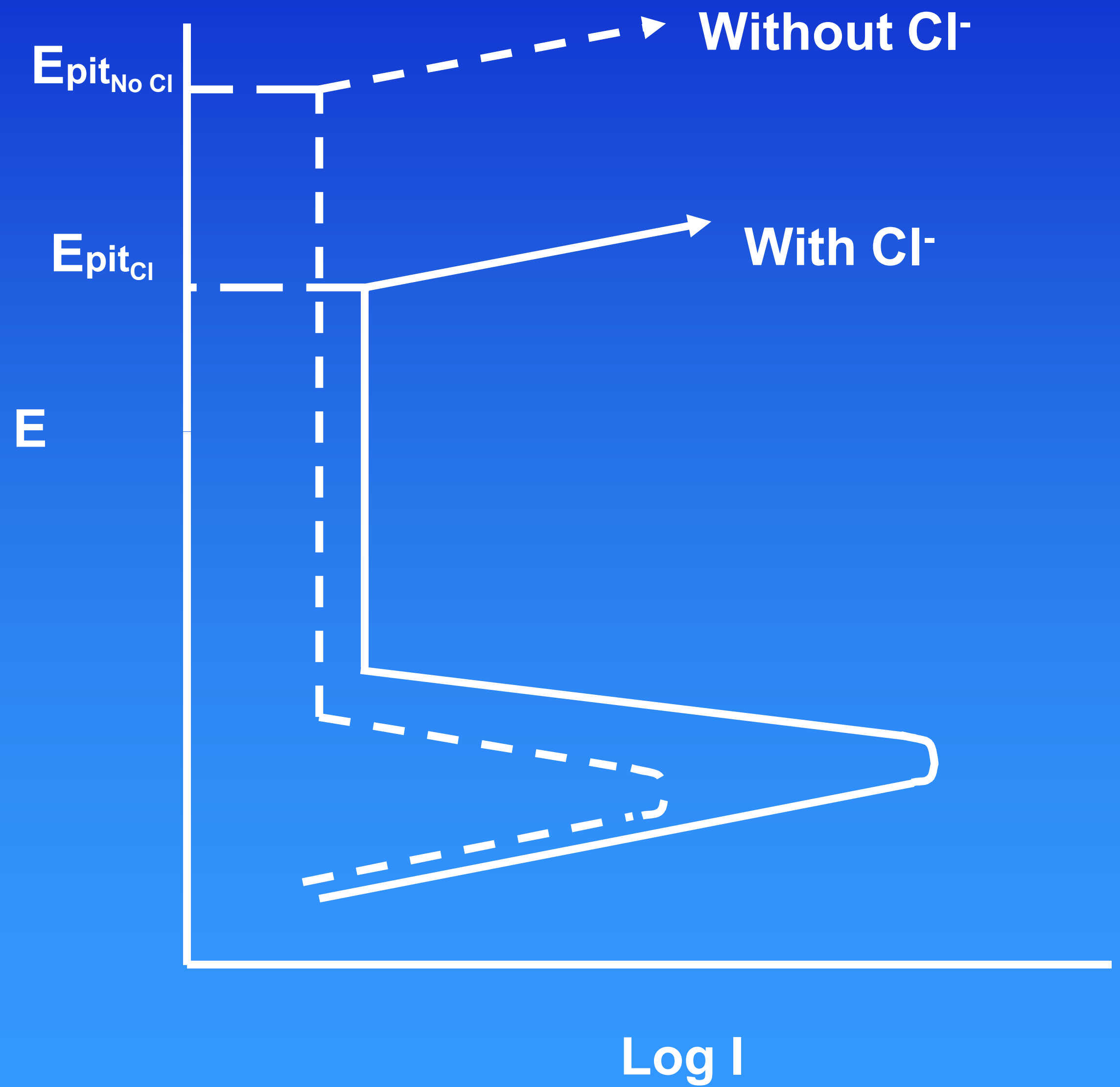
Passive Alloy Susceptible to Pitting

- At $E > E_i$ ($= E_{pit}$) pits will nucleate and grow
- At $E < E_{rp}$ (repassivation E) no new pits will initiate and existing pits will stop growing
- At $E_{rp} < E < E_i$ (E_{pit}) no new pits will initiate, but existing pits will grow

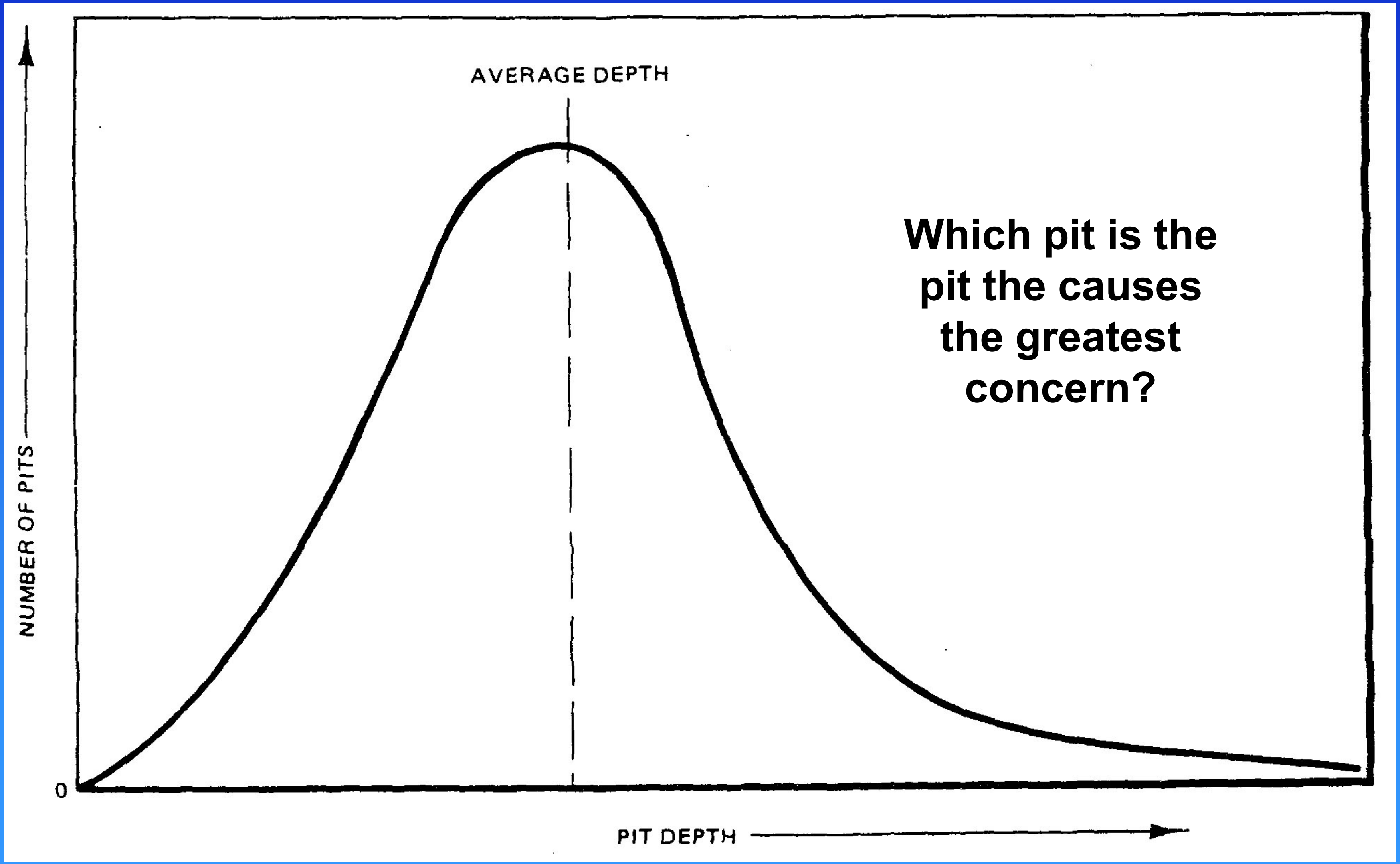
Pit nucleation and growth



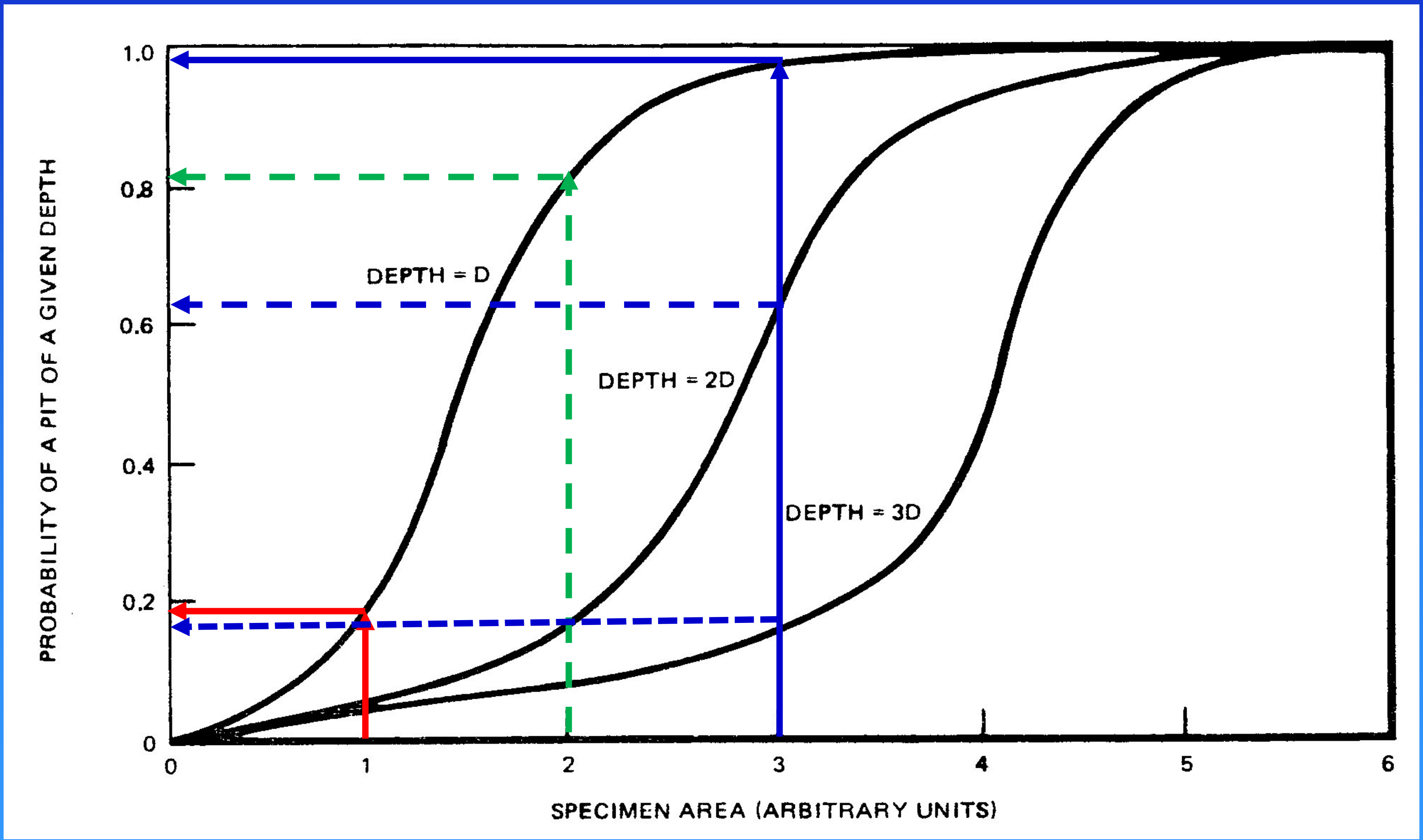
Critical Pitting Potential with and without Chloride



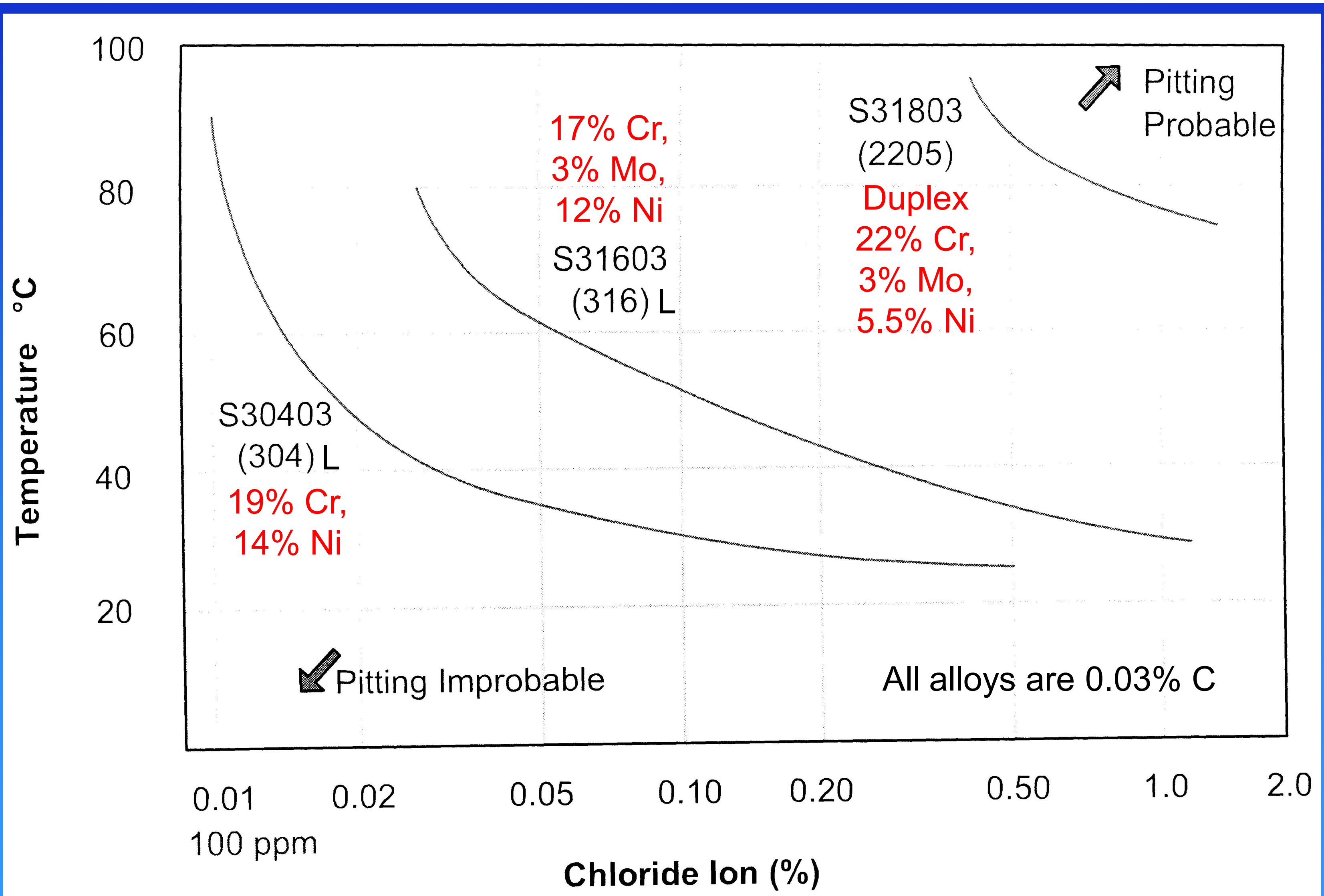
Relationship Between Pit Depth and the Number of Pits on a Surface



Pit Depth as a Function of Area

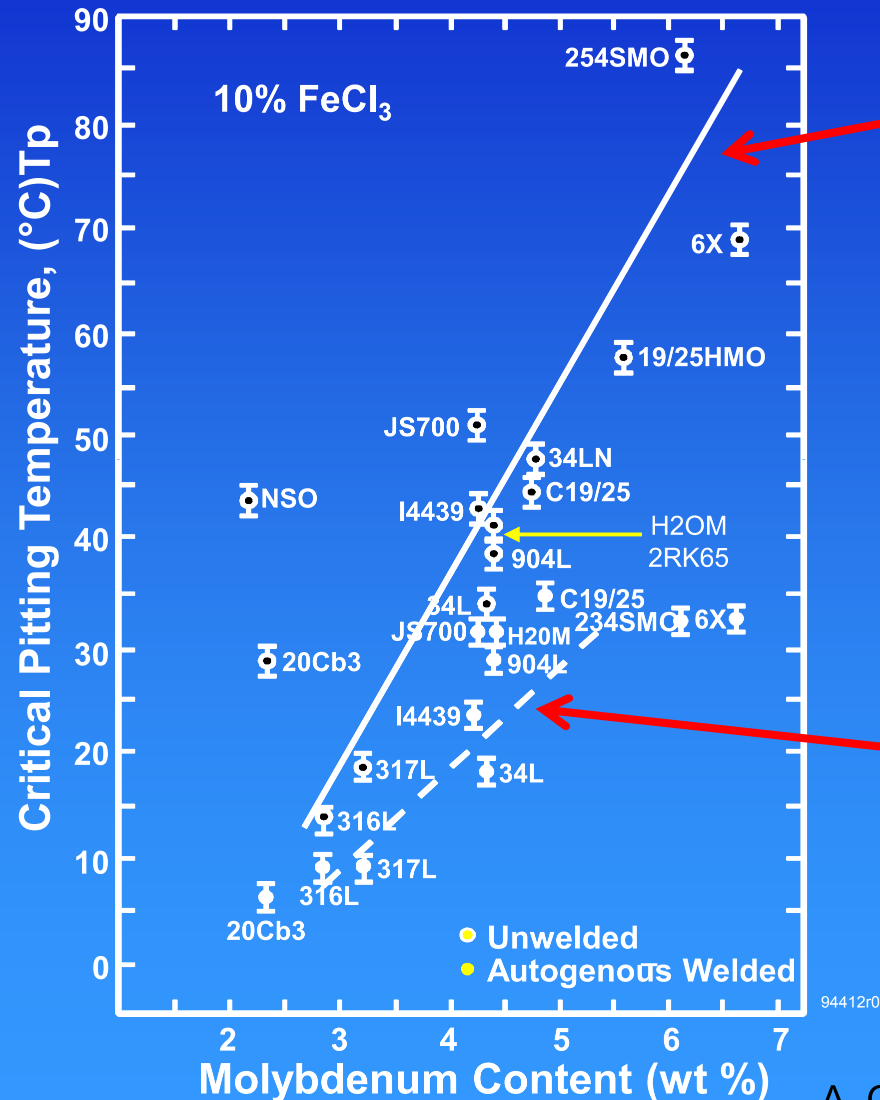


Effect of Temperature and Cl^- on Pitting of Stainless Steels



Pitting Resistance - Effect of Mo

Dunk Test
2 days exposure then expose at higher Ts

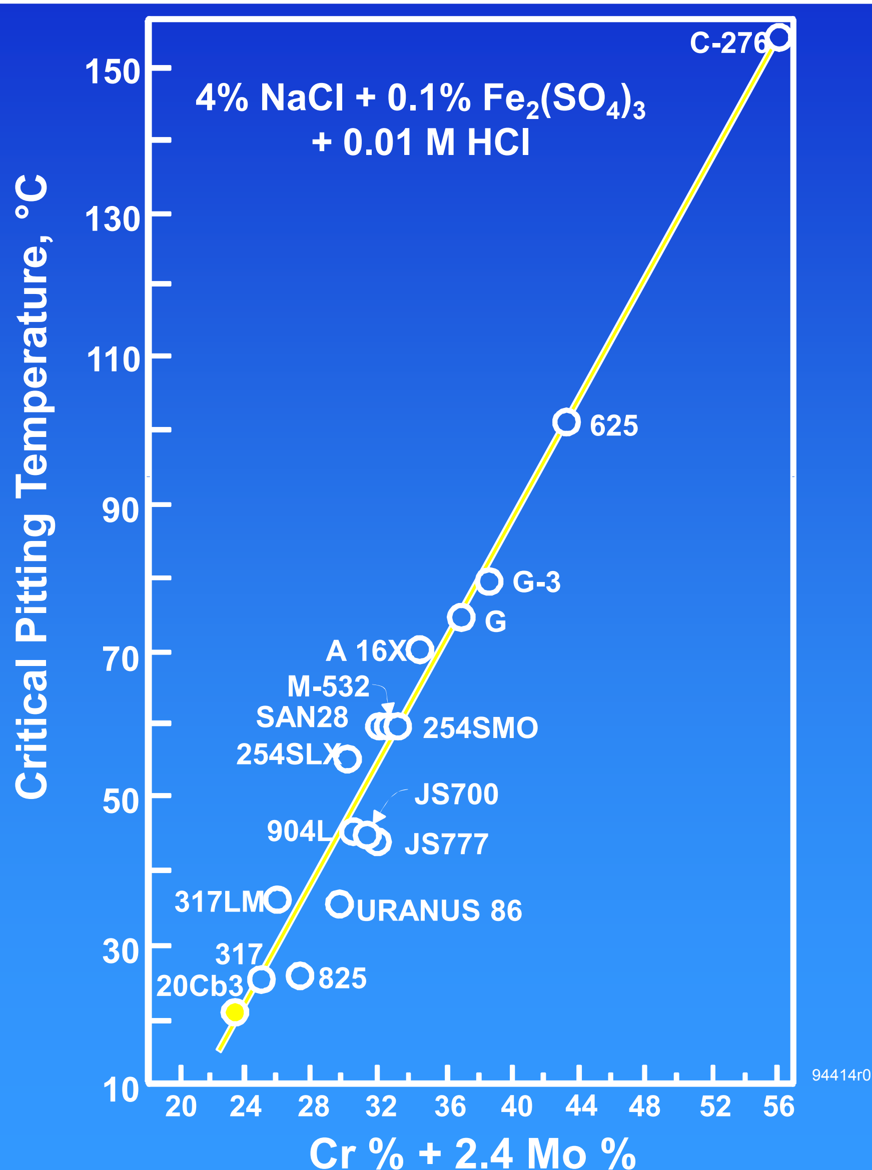


As-received material

Heat of Welding

A. Garner, Materials Performance
Vol. 20, No. 8, 1982

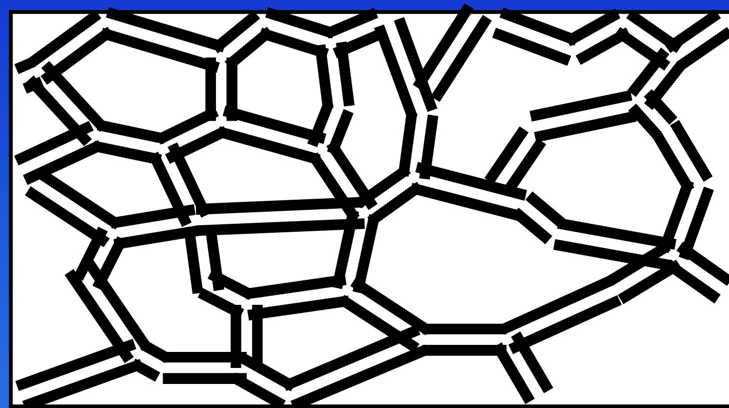
Pitting Resistance - Effect of Cr and Mo



J. Kolts and N. Sridhar, Corrosion of Nickel Base Alloys, ASM, 1985

Intergranular Attack (IGA)

Intergranular Attack (IGA)

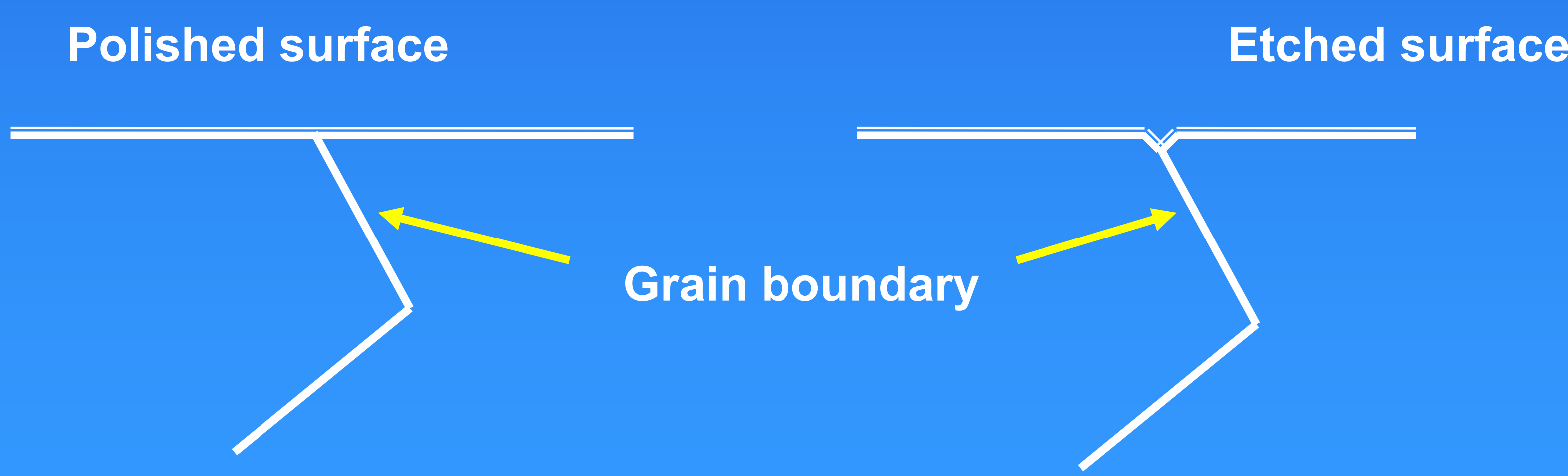


- Mechanism
- LWR Examples
  - BWR stainless steel piping sensitization
  - Decontamination solutions
  - BWR control rod index tubes
  - Alloy 600 steam generator tubes

IGA Mechanism

Intergranular Attack (IGA)

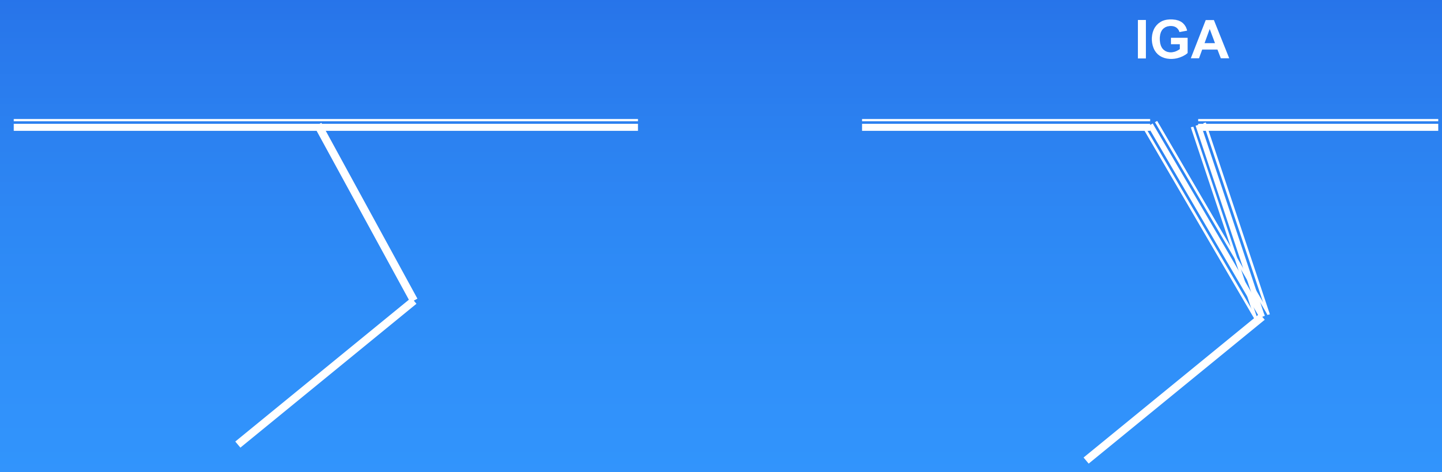
- a.k.a. “grain boundary corrosion”
- GBs are preferentially attacked during metallographic etching because gb atoms are more loosely packed and have higher disorder as compared to grain matrix. This is not IGA, per se.



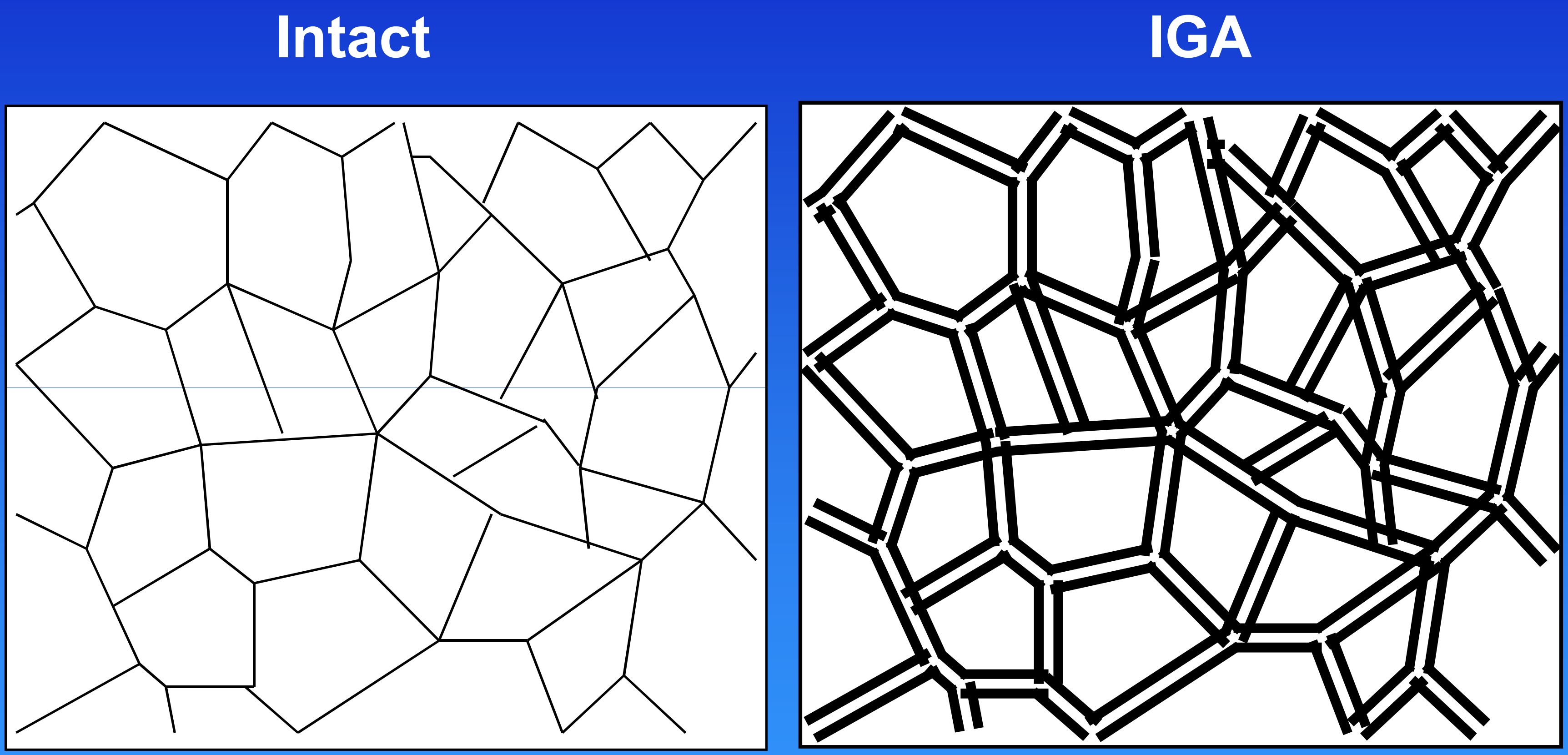
Intergranular Attack (IGA)

IGA is caused by:

- Impurity segregation
- Enrichment or depletion of alloying elements
- Heat treatment induced solid state reactions

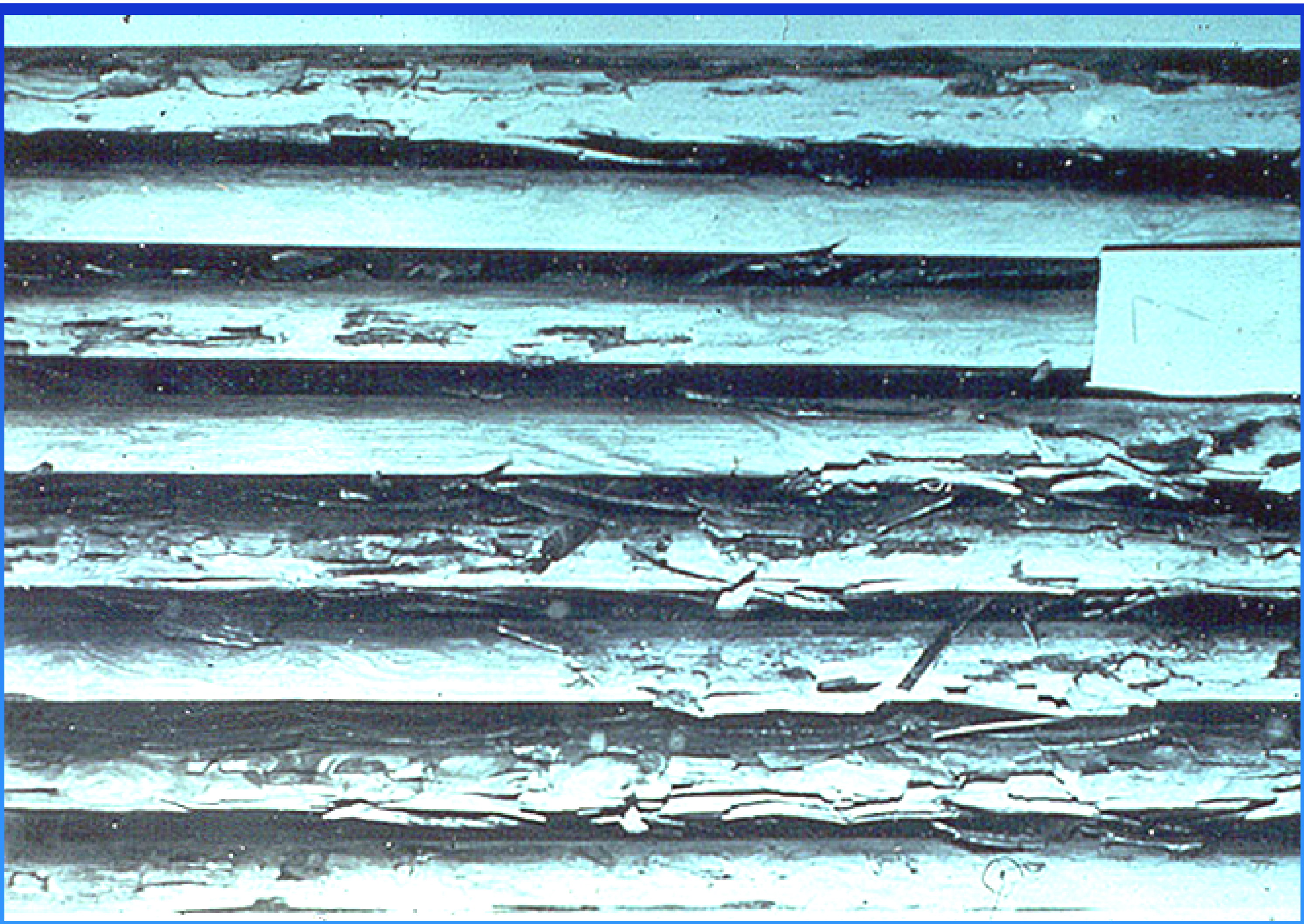


IGA



Analogous to removing mortar from a brick wall

Exfoliation of 70-30 Cu-Ni Condenser Tubes



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

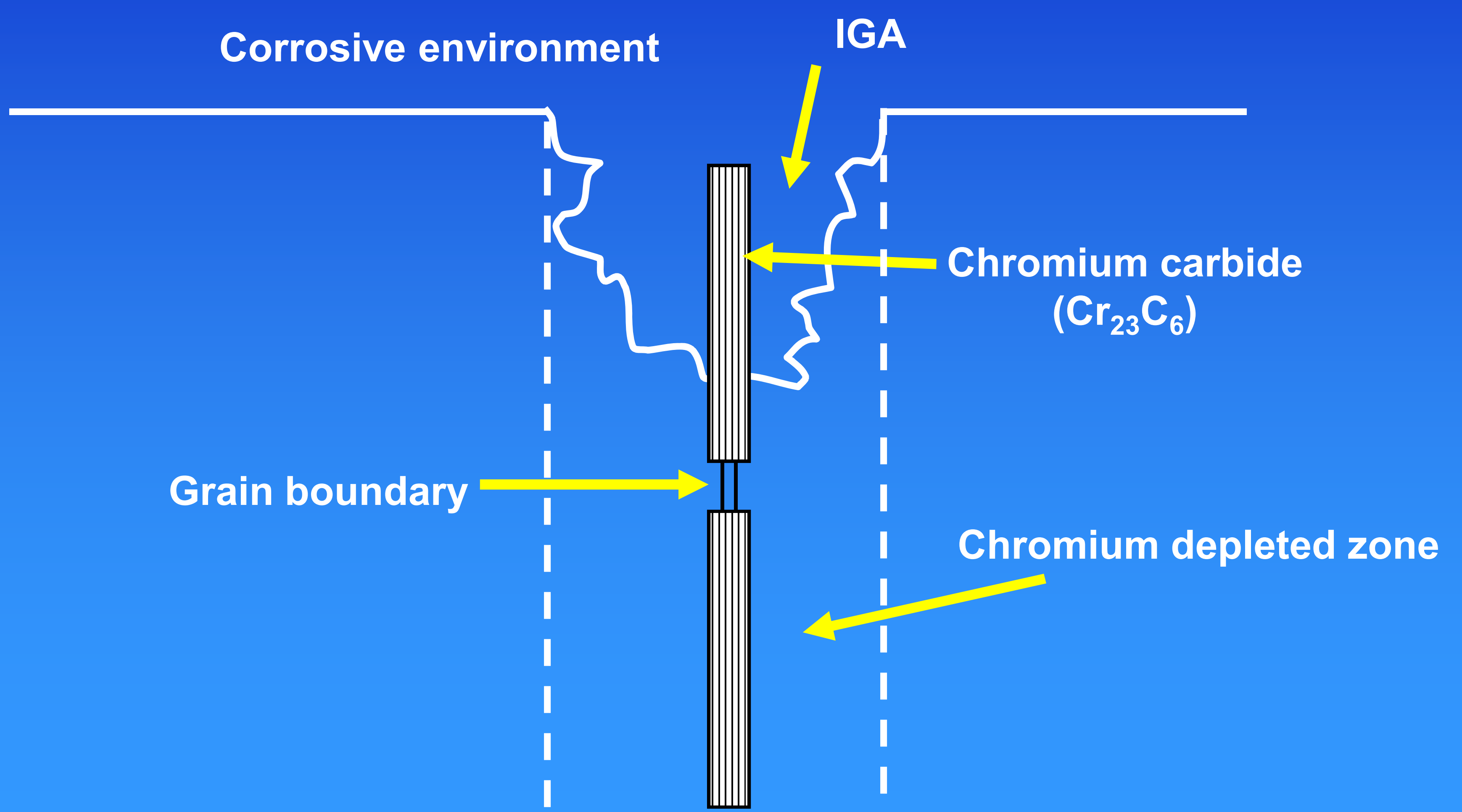
Exfoliation of Al Water Pipe

Certain gb precipitate phases (e.g., Mg_5Al_8, Mg_2Si, $MgZn_2$, $MnAl_6$, etc.) cause or enhance IGA of high strength Al alloys, particularly in chloride-rich media.

Lyon Laboratoire de Physicochimie Industrielle 2009

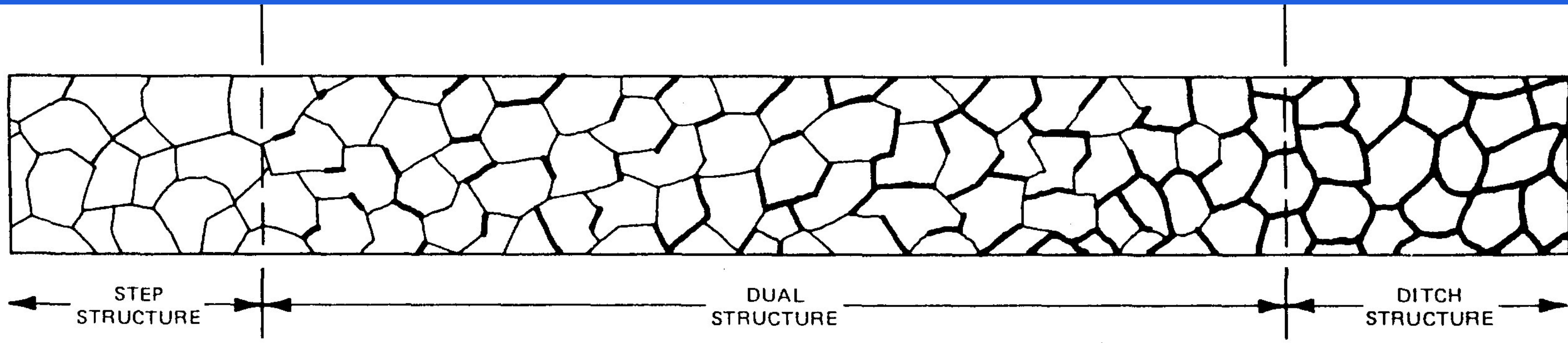
Intergranular Attack (IGA) of a Sensitized SS Grain Boundary

IGA of sensitized stainless steel



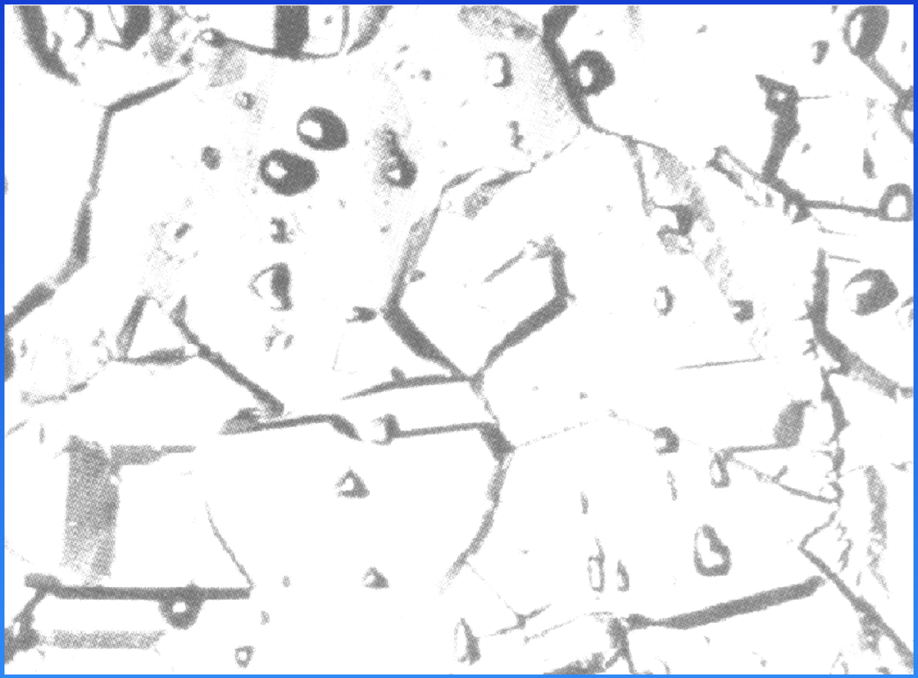
Oxalic Acid Test (ASTM A262)

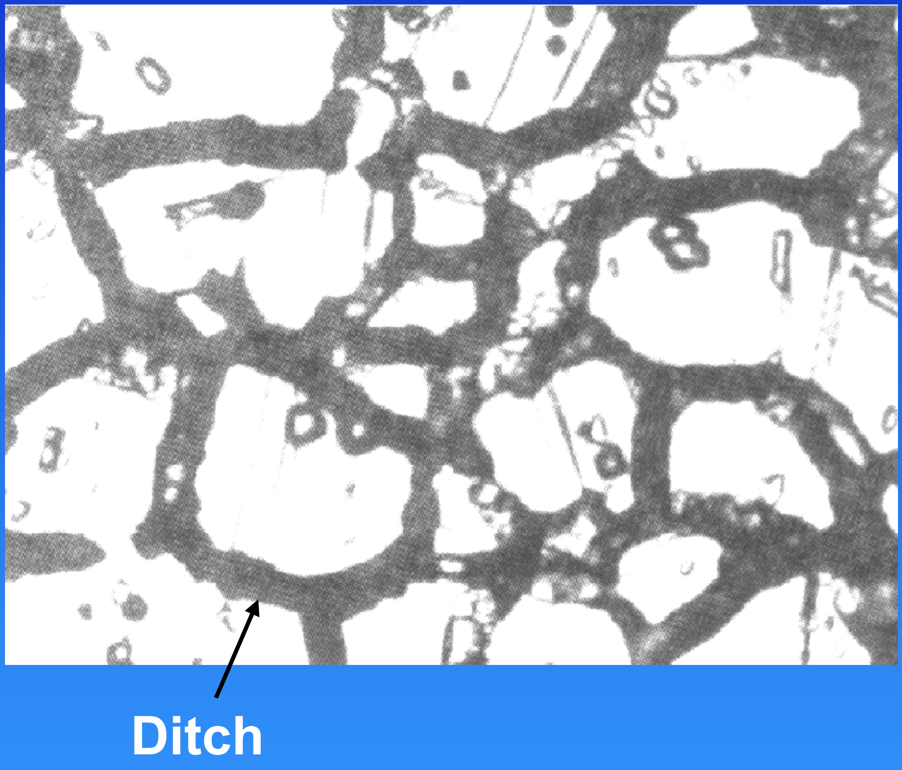
- Specimen etched 10% oxalic acid for 90 s at 1 A/cm^2
- Etched surface examined at 250-500x for “step,” “dual” or “ditch”



STEP STRUCTURE – "STEPS ONLY BETWEEN GRAINS, NO DITCHES AT GRAIN BOUNDARIES"
DUAL STRUCTURE – "SOME DITCHES AT GRAIN BOUNDARIES IN ADDITION TO STEPS, BUT NO SINGLE GRAIN COMPLETELY SURROUNDED BY DITCHES"
DITCH STRUCTURE – "ONE OR MORE GRAINS COMPLETELY SURROUNDED BY DITCHES"

IGA of Stainless Steel
Oxalic Acid Etch Test





No IGA **IGA**

Electrochemical Potentiokinetic Reactivation

- Response to a need for better, quantitative method was needed to measure the degree of sensitization (DOS)
- EPR - rapid, nondestructive, well-suited for in-situ field measurements
- Develop potentiokinetic curves of polarized specimen using a potentiodynamic sweep from the passive region back to the active region, stopping at E_{CORR}
- ASTM G 108

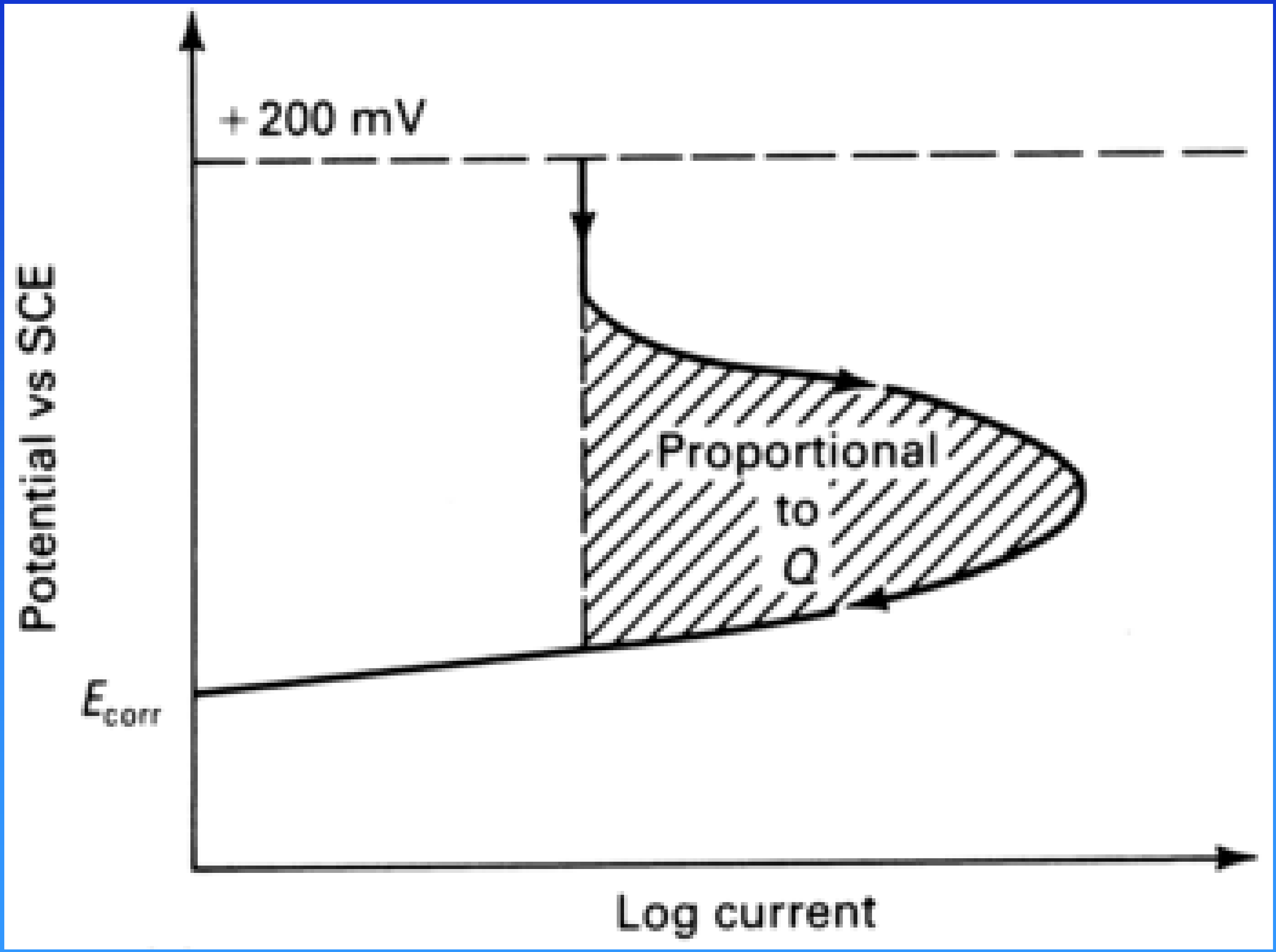
EPR

- To distinguish between annealed and sensitized materials:
  - Q, activation charge = integrated area below the reactivation peak
  - Sensitized materials are easily reactivated – show higher Qs
  - Q is normalized by both specimen size and grain size in single loop technique
    - P_a charge/cm^2 = C/cm^2 of grain boundary area
  - P_a >2 C/cm^2 is “sensitized”
  - WS ~15 C/cm^2, FS ~30 C/cm^2

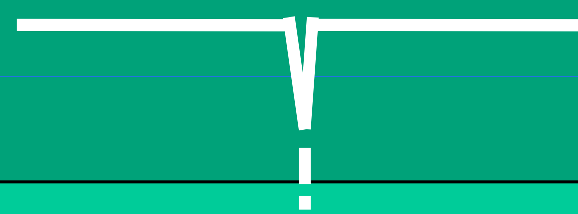
Single and Double Loop EPR

- Sweep is carried out in H_2SO_4 containing potassium thiocyanate (KSCN) to activates the Cr depleted gbs
- Current peak observed during the reactivation scan increases with DOS
- Charge Q is a measure of the DOS and used to determine a sensitization number, P_a, after normalization with the gb area
- Double-loop EPR test involves a scan from E_{CORR} to passive range, followed immediately by reverse polarization back to E_{CORR}
  - DOS is determined by the ratio I_r/I_a of the maximum current generated in the reverse scan (I_r)compared to that in the initial anodic scan (I_a)
  - No need for normalizing gb area, etc.

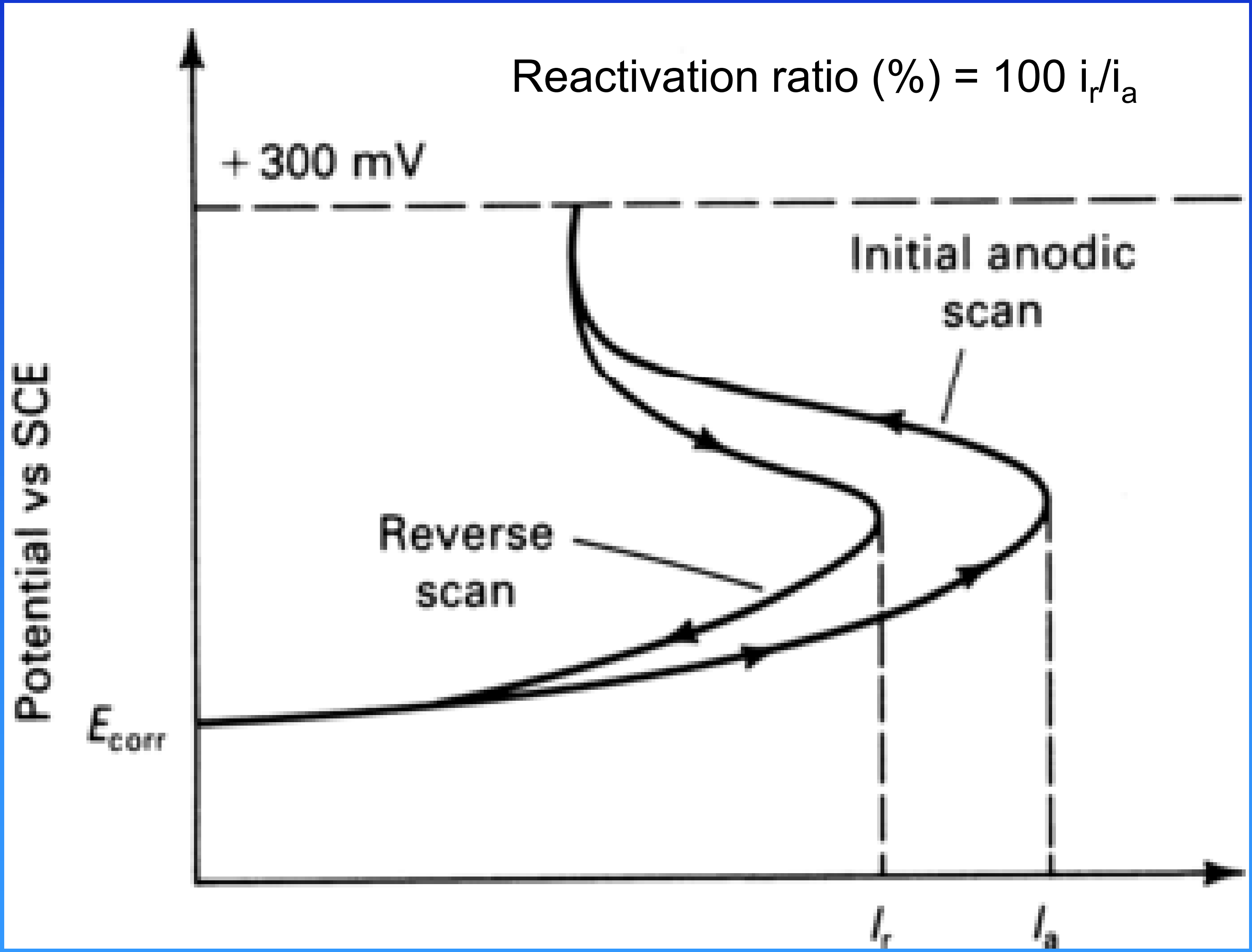
Single Loop EPR



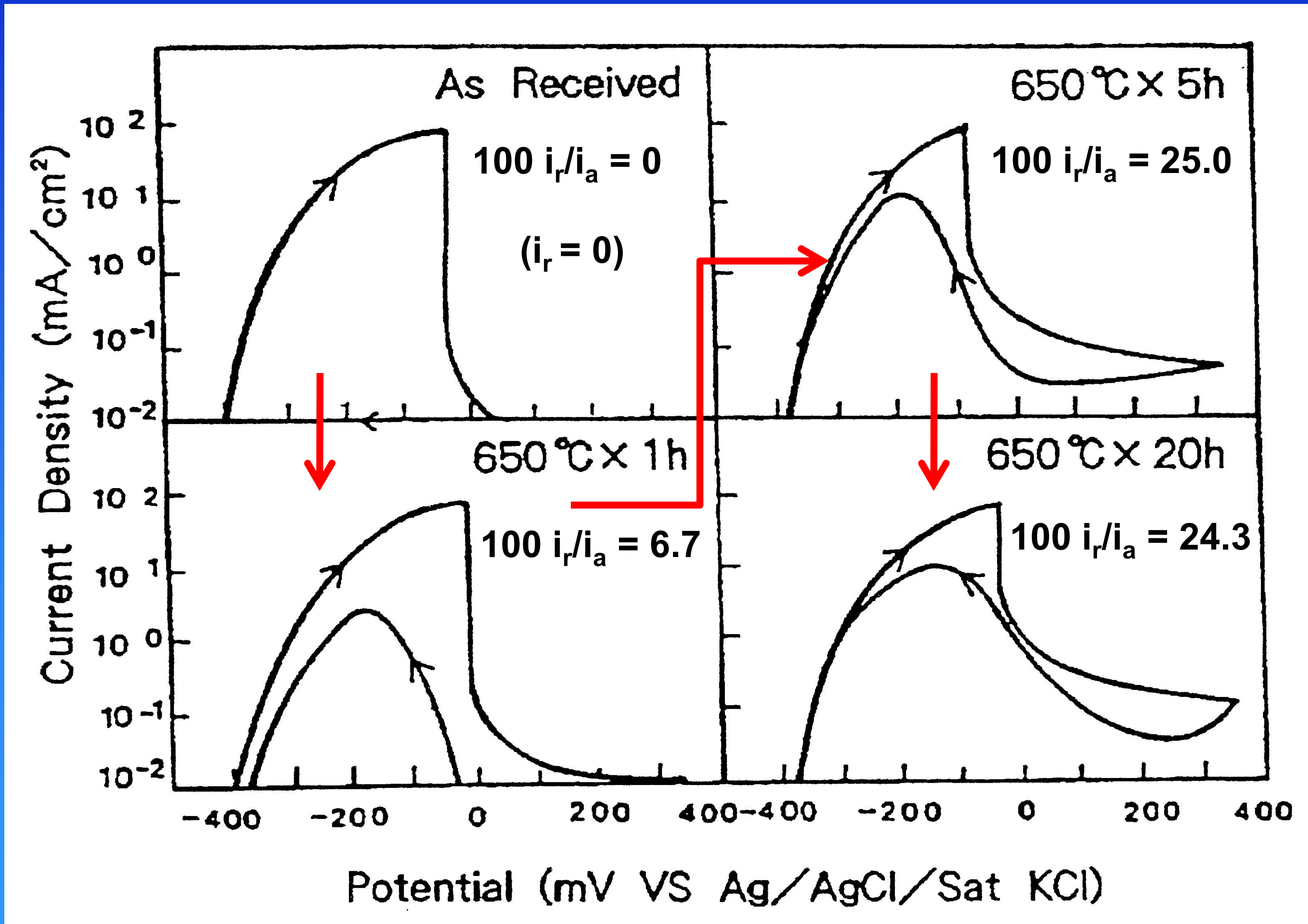
Single Loop EPR Values

EPR C/cm²	Physical Characteristics
2	
15 (Weld Sensitized)	
30 (Furnace sensitized)	

Double Loop EPR



Double Loop EPR

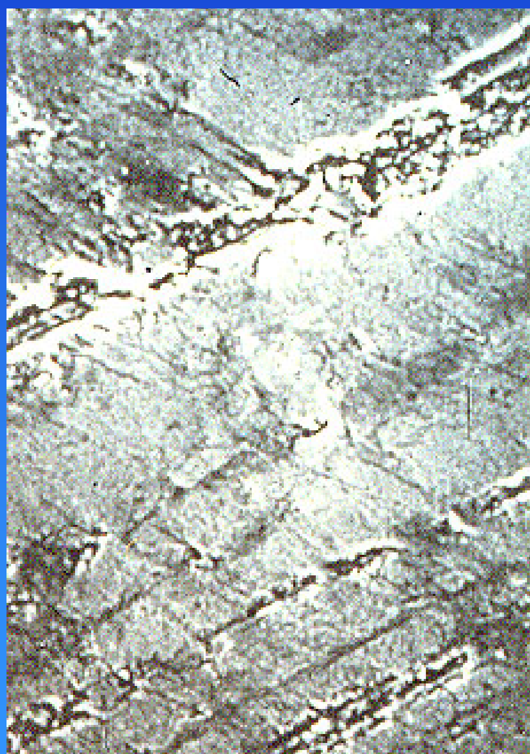


R. Katsura, et al., Corrosion, 5/92

LWR IGA Examples

CAN-DECON™ Decontamination Solution on Stainless Steel Specimens

Comparison of as-contaminated vs. CAN-DECON™ processed RWCU in Peach Bottom 2



As-contaminated
SEM 500x

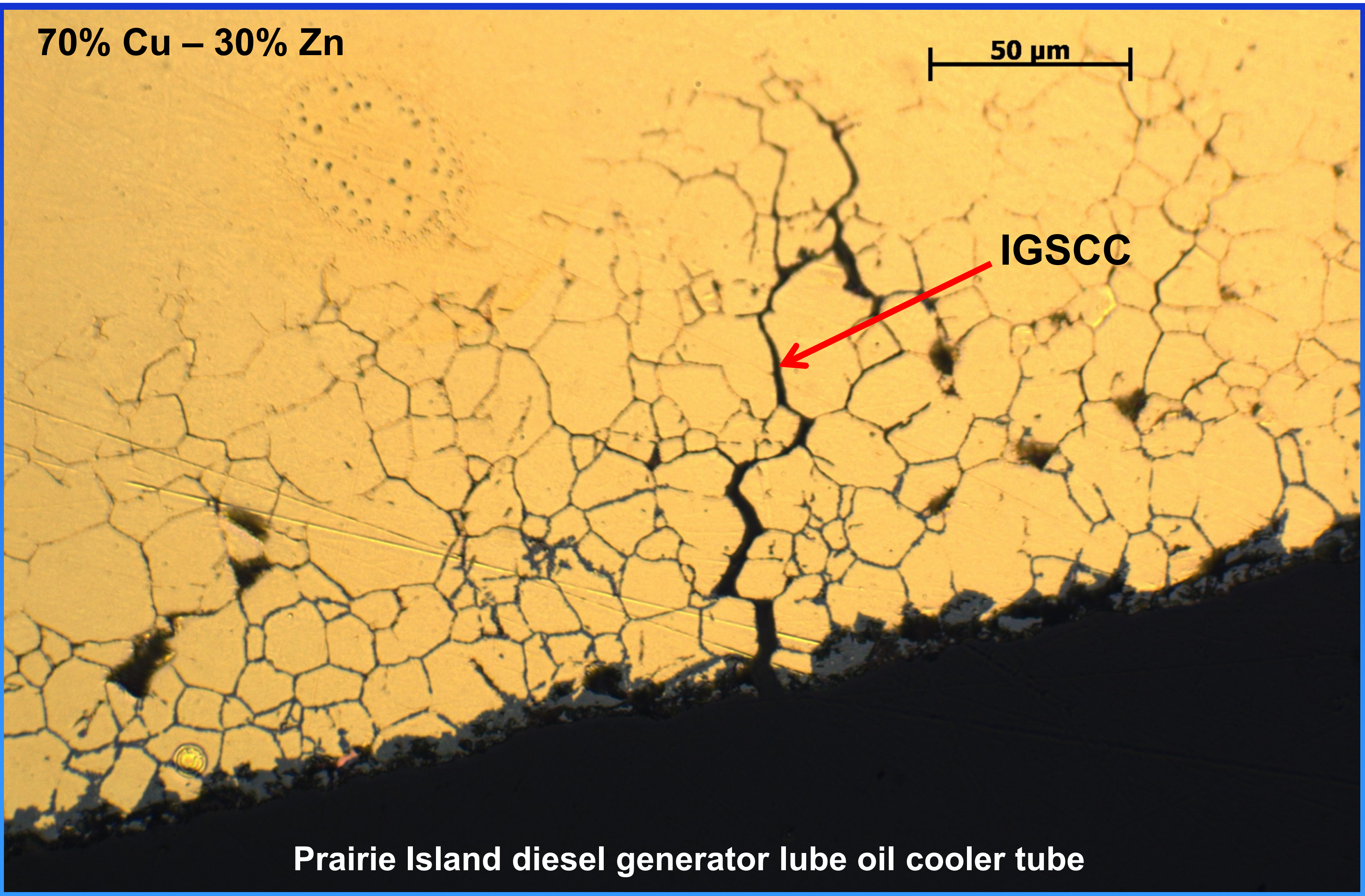
CAN-DECON Processed

CAN-DECON

EDTA
Citric Acid
Oxalic acid
pH 2.8
90-127°C
(195-260°F)
24-100 h

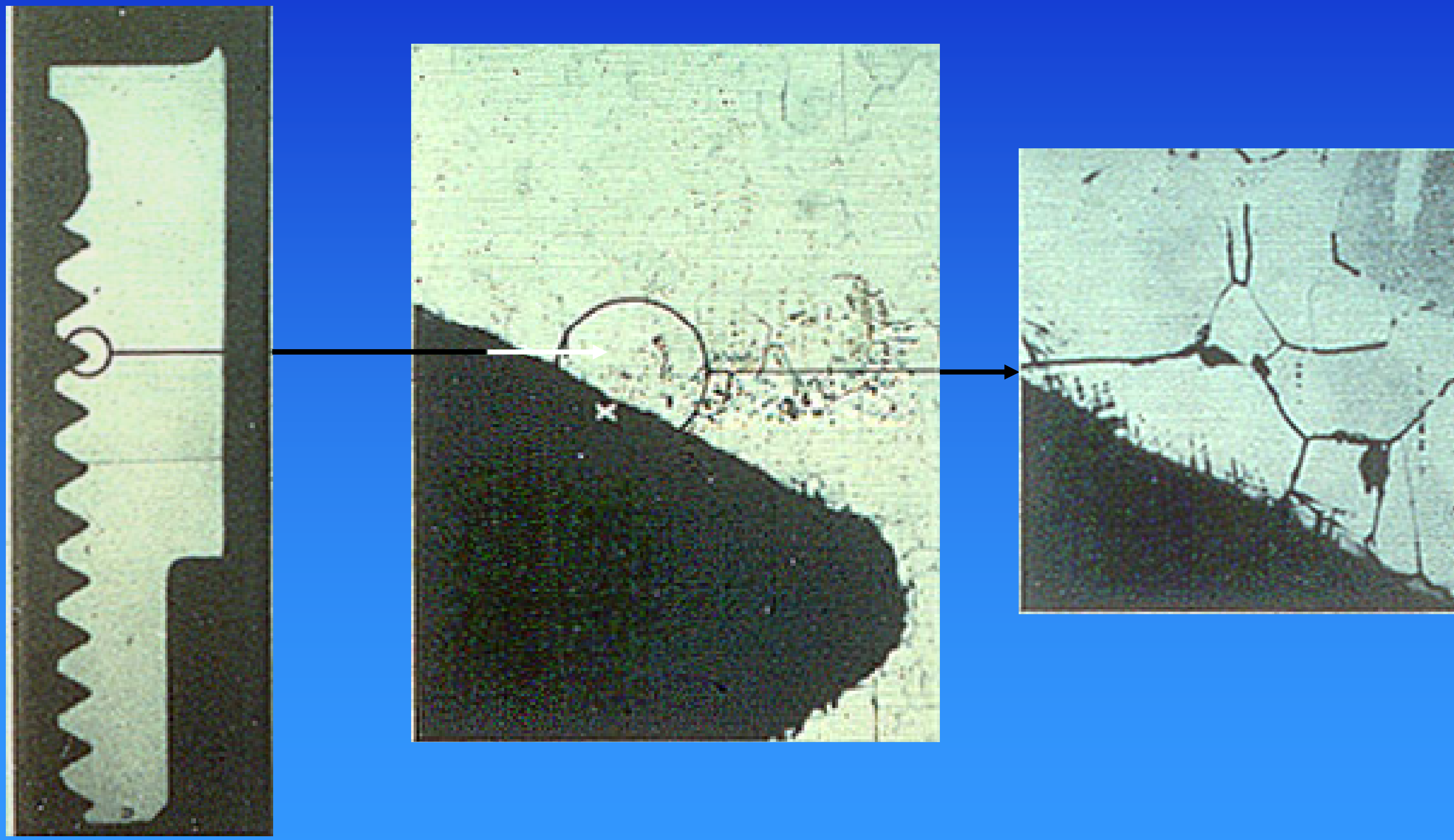
Chelating agent ethylene diamine tetraacetic acid (EDTA) ($C_{10}O_8N_2H_{11}$)

Admiralty Brass IGA

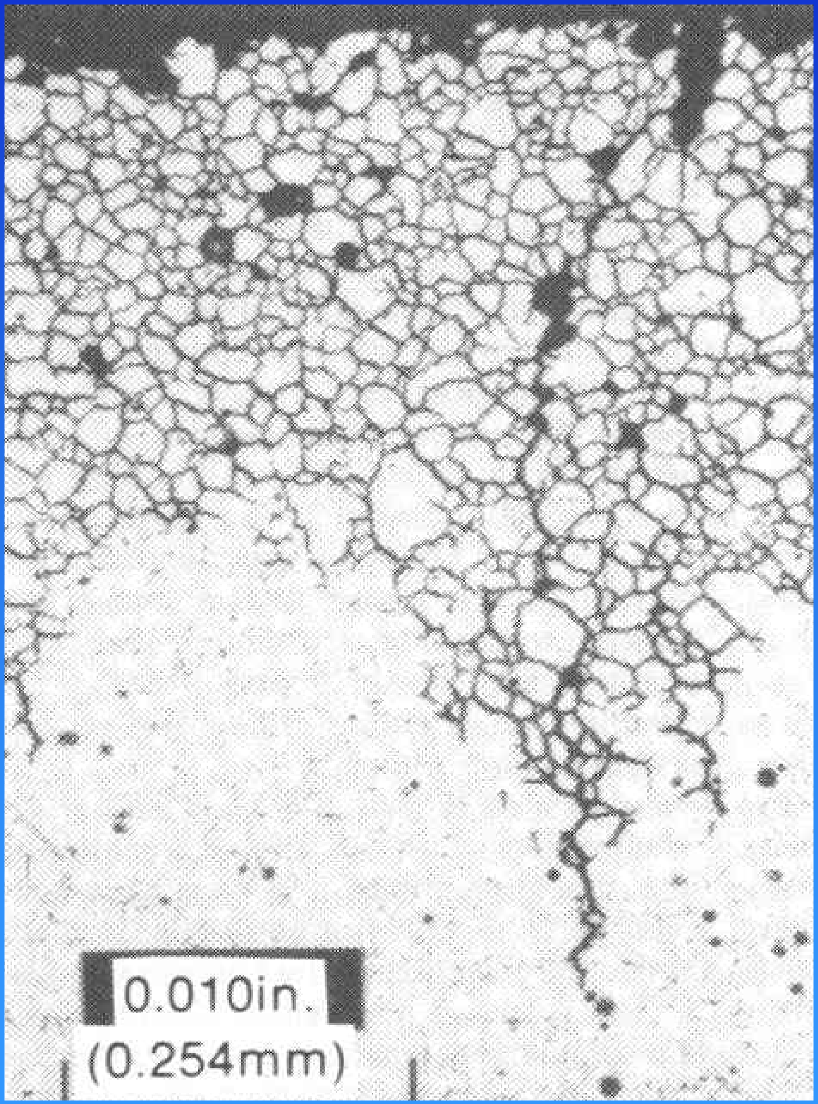


Prairie Island diesel generator lube oil cooler tube

BWR Control Rod Index Tube



Severe IGA of Alloy 600 SG Tube



S. Green, Vol. 13, ASM, 1987

Crevice Corrosion, Pitting Corrosion and IGA Summary

- **Mechanisms for crevices corrosion in oxygenated and deaerated environments are different**
  - **NWC BWR – potential gradient drives corrosion, concentrates detrimental anions in crevice**
  - **HWC BWR/PWR – heat transfer crevice effects**
- **Pitting is major concern for BOP, but not in primary systems due to high flow and material pitting resistance**
- **IGA due to grain boundary compositional differences**
  - **Often the precursor for IGSCC**