United States Nuclear Regulatory Commission

Protecting People and the Environment

General Corrosion

+ Introduction to LWR Alloys

Human Resources Training & Development

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General Corrosion Learning Objectives

- Review LWR structural materials and some metallurgy basics
- Understand the difference between general corrosion and the various forms localized of corrosion
- Learn the mechanism of general corrosion
- Learn about the kinetics of general corrosion
- Examine LWR containment corrosion
- Evaluate the mechanism of boric acid corrosion in PWRs

Introduction to LWR Alloys

and Metallurgy*

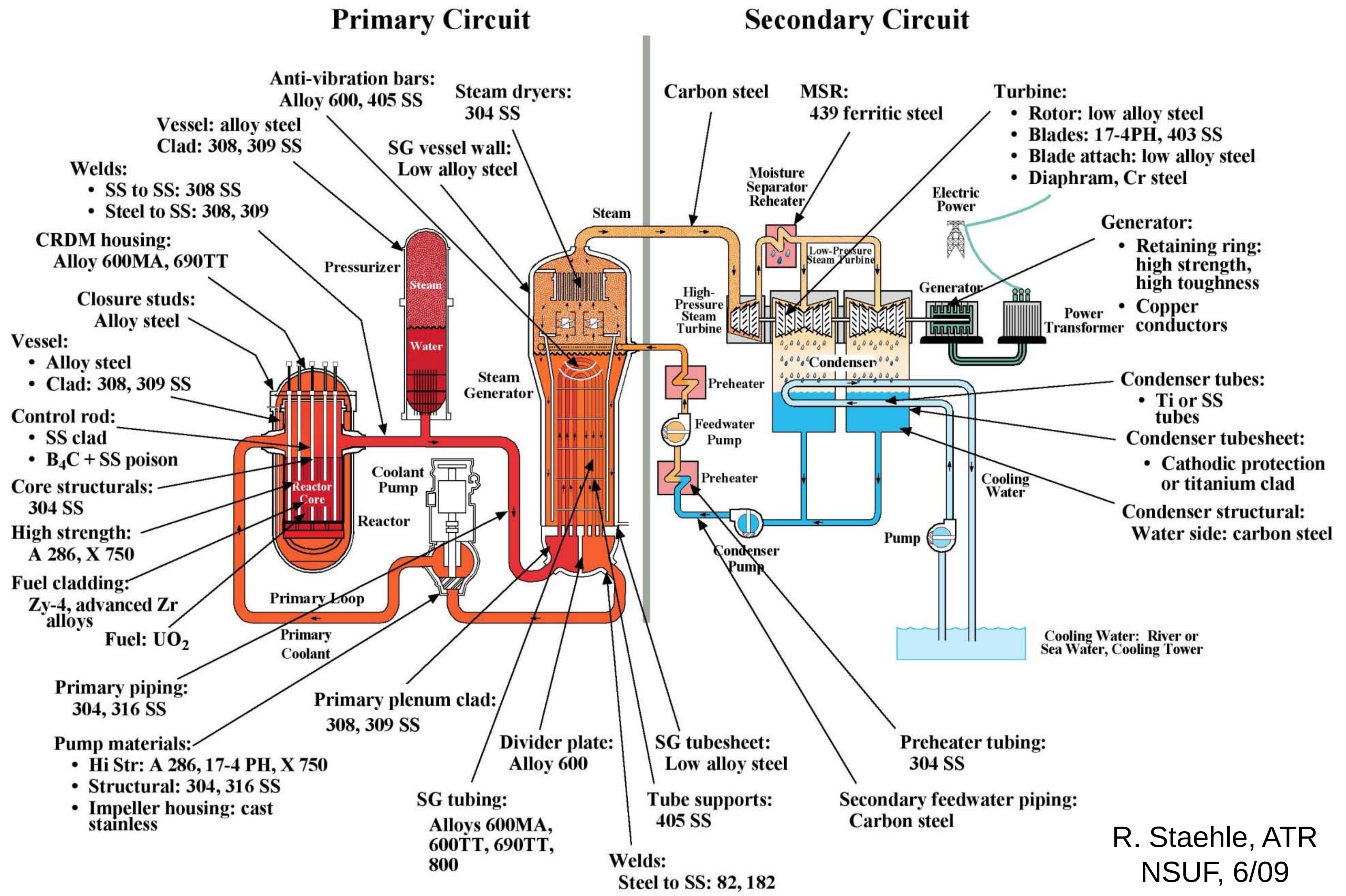
***Metallurgy is the only True Science**

LWR Materials of Construction

- **Large variety of alloys used in LWR pressure boundary and internal components:**
  - **Reactor Coolant Piping and Fittings – CS, LAS, cast and wrought SSs and various weld metals depending on the parent metal**
  - **RPV and PWR Pressurizer Vessel – LAS, SS cladding, wrought Ni-base penetrations and various weld metals**
  - **Reactor Internals – cast and wrought austenitic SS, Ni alloys and their associated weld metals**
  - **PWR Steam Generator – LAS and CS, SS cladding, Ni-base alloys and various weld metals**
  - **Pumps – cast and wrought austenitic SS for pressure boundary materials; various high alloy steels for bolting and austenitic or martensitic SS for pump shafts and other internal components**

NUREG/CR-6923, 2/07

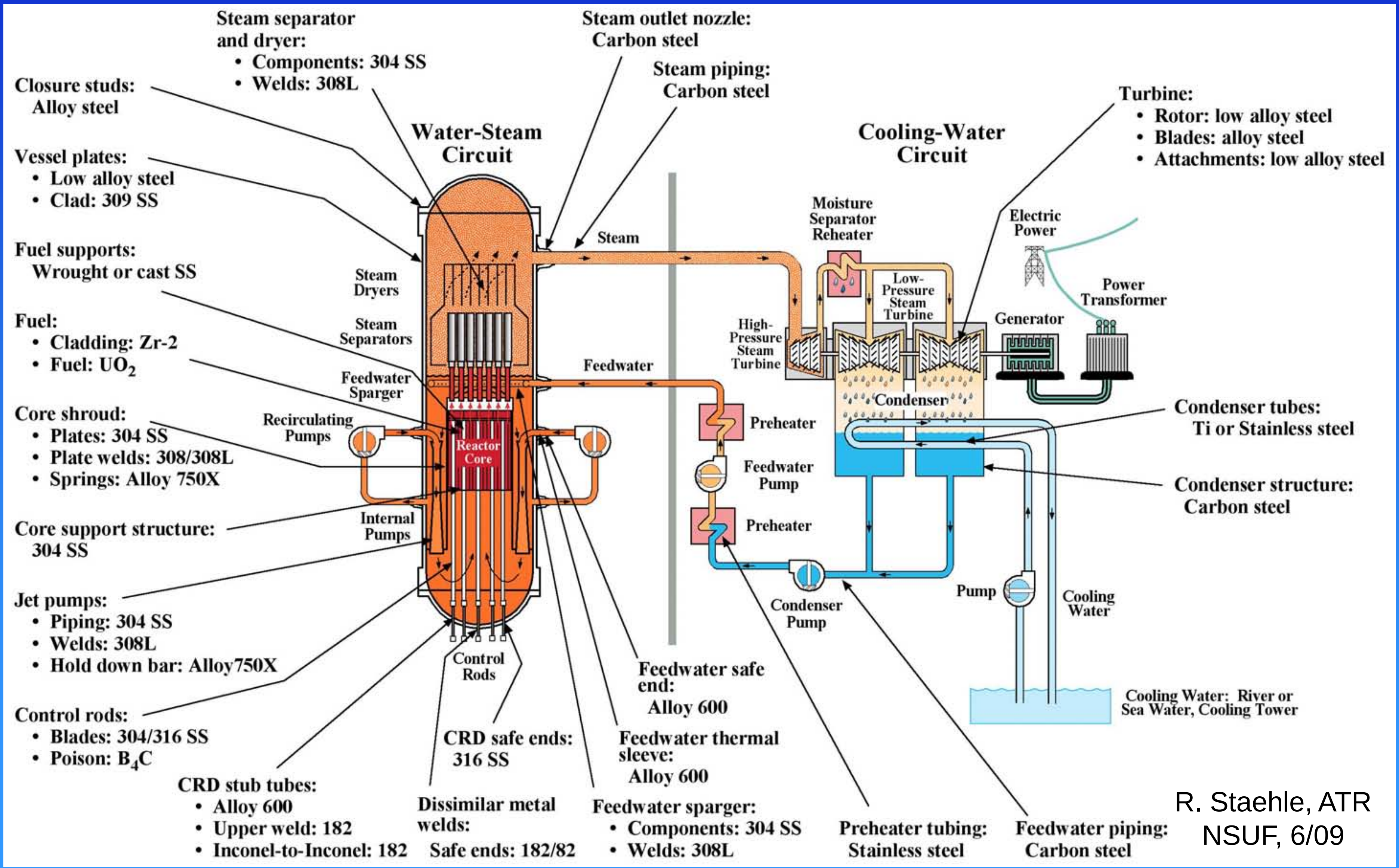
PWR Materials and Components



R. Staehle, ATR NSUF, 6/09

Structural Integrity Associates

BWR Materials and Components



R. Staehle, ATR NSUF, 6/09

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Chemical Compositions of Typical LWR Fe-base Alloys (w%)

	Alloy	C max	Cr	Ni	Mo	Other
CS	A106B	0.3				
	A333 Gr 3	0.19		3.5		
LAS	508-2	0.27	0.25-0.45	0.5-0.9	0.55-0.70	
	533-B	0.25		0.4-0.7	0.45-0.60	
SS	304/304L	0.08/0.03	18-20	8-12		
	316/316L	0.08/0.03	16-18	10-14	2-3	
	316NG	0.020	16-18	10-14	2-3	0.06-0.10 N
	321	0.08	17-19	9-12		0.7 Ti
	347	0.08	17-19	9-13		Nb +Ta
	XM-19	0.06	20.5-23.5	11.5-13.5	1.5-3.0	4-6 Mn
	CF-8/CF-3	0.08/0.03	18-21	8-12		
	410	0.15	11.5-13.5	0.75		
	A286	0.08	13.5-16	24-27	1.0-1.5	Ti + V + Al
	17-4 PH	0.07	15.5-17.5	3-5		3-5 Cu

Carbon Steels

- Carbon steel (a.k.a. plain carbon steel) is iron (Fe) mainly alloyed with carbon (C)
- AISI* definition: "Steel is considered to be carbon steel when no minimum content is specified or required for Cr, Co, Nb, Mo, Ni, Ti, W, V or Zr, or any other element to be added to obtain a desired alloying effect; when the specified minimum for Cu does not exceed 0.40%; or when the maximum content specified for any of the following elements does not exceed the percentages noted: Mn 1.65, Si 0.60 and Cu 0.60"

*American Iron and Steel Institute

Carbon Steel LWR Alloys

- SA333-6 and SA671-Grade CC70 piping, SA516 plate, SA350-Grade LF2, SA508 Class 1 or SA105 forgings and SA352-Grade LCB or SA216 WCB castings and SA420 Grade WPL-6 fittings
- Susceptible to FAC, but resistant to SCC
- Usually clad with austenitic SS weld metal (e.g., Type 308) for improved general corrosion or pitting resistance during low temperature shutdown

Low Alloy Steel

- Low alloy steel is carbon steel alloyed with other alloying elements (4 and 8%) to improve its mechanical properties
  - ♦ Greater strength, hardness, wear resistance, hardenability or toughness compared to carbon steel
- May require heat treatment to achieve such properties
- Common alloying elements are Mo, Mn, Ni, Cr, V, Si and B

Low Alloy Steel LWR Alloys

- LAS used in RPVs and nozzles
- Combination of high strength and fracture toughness properties for design of the vessels at operating conditions
- LWR vessels fabricated from ASTM A-302 and SA-533, Grade B, Class 1 LAS plate
- Nozzles are typically SA-508, Class 2
- Usually clad with austenitic SS weld metal (e.g., Type 308) for improved general corrosion or pitting resistance during low temperature shutdown plus allow for welding of attachments without the requirement for post weld heat treatment (PWHT)

1915 "Discovery" of Stainless Steel

A NON-RUSTING STEEL.

Sheffield Invention Especially Good for Table Cutlery.

According to Consul John M. Savage, who is stationed at Sheffield, England, a firm in that city has introduced a stainless steel, which is claimed to be non-rusting, unstainable, and untarishable. This steel is said to be especially adaptable for table cutlery, as the original polish is maintained after use, even when brought in contact with the most acid foods, and it requires only ordinary washing to cleanse.

Marketed as "Staybrite" by Firth Vickers

New York Times, 1/31/15

Stainless Steels

- Stains less
- Fe-base alloys containing 10.5%< Cr <30%
- “Stainless” because of the formation of an invisible and adherent Cr-rich passive oxide surface film
- Surface oxide heals itself in the presence of oxygen
- ~150 grades commonly divided into five or six groups:
  - ♦ Austenitic stainless steels
  - ♦ Martensitic stainless steels
  - ♦ Ferritic stainless steels
  - ♦ Duplex (ferritic-austenitic) stainless steels
  - ♦ Precipitation-hardening stainless steels
  - ♦ “Super” stainless steels

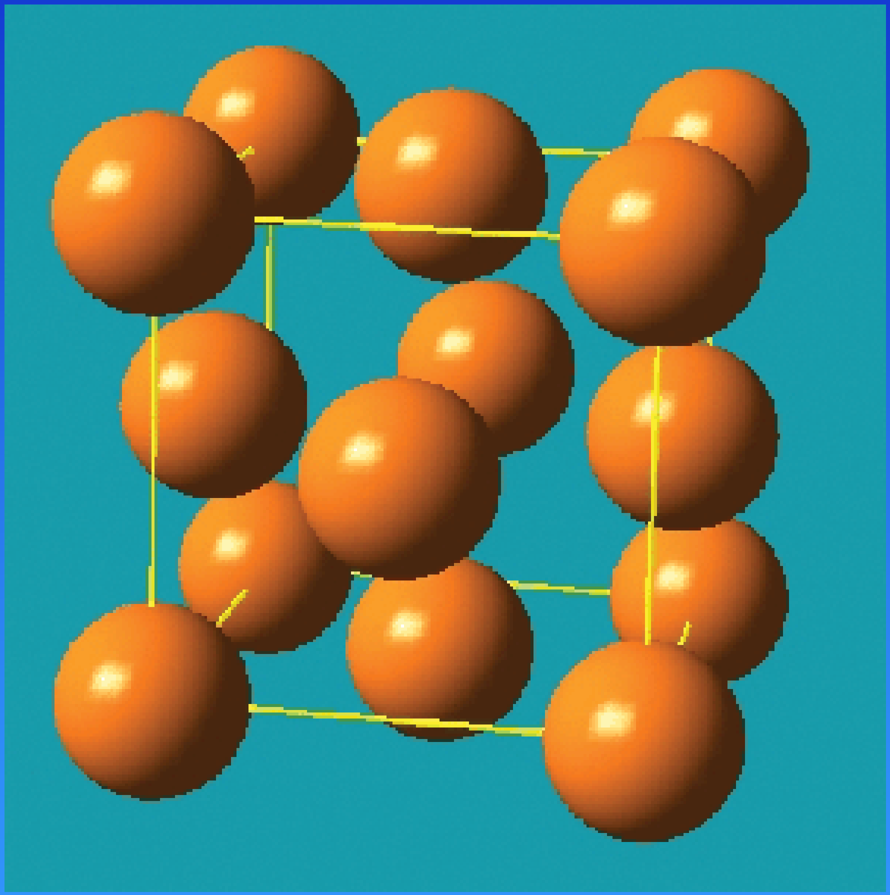
Classified by their crystal structure

Austenitic Stainless Steels

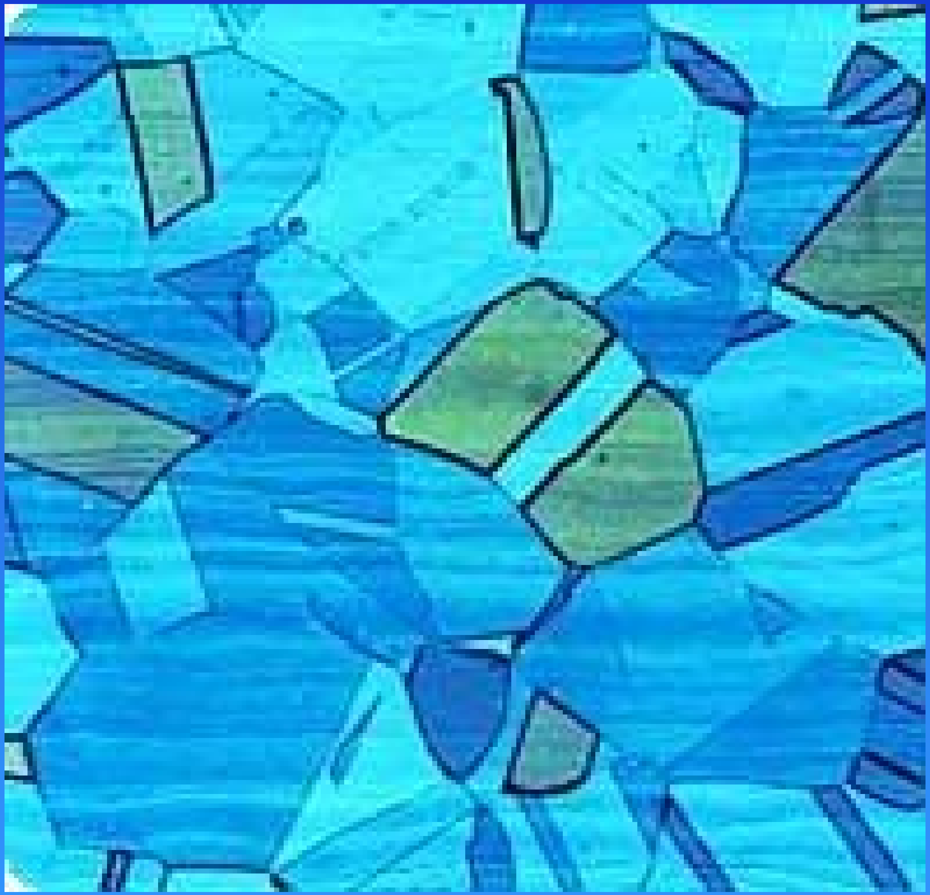
- Austenite that was named after William Chandler Roberts-Austen (1843-1902)
- Face centered cubic (FCC) crystal structure
- Austenite symbol: γ (gamma)
- γ SS is formed through additions of γ stabilizing elements Ni, C, Co, Mn, Cu and N
- γ SS are effectively nonmagnetic in the annealed condition and can be hardened only by cold working
- Cr 16 to 26%; Ni < 35%
- 300 commercial series numbers
  - LWR examples: 304/L/NG, 316/L/NG, 321, 347

WC Roberts-Austen

Austenitic Stainless Steel



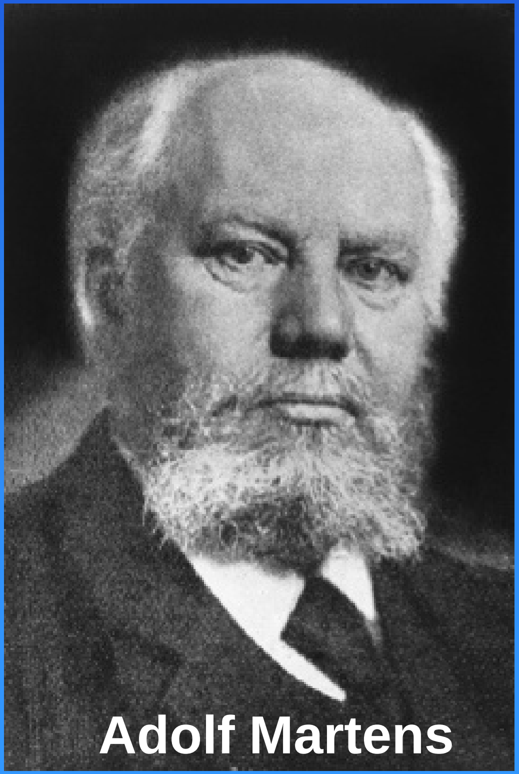
FCC Crystal Structure



Photomicrograph

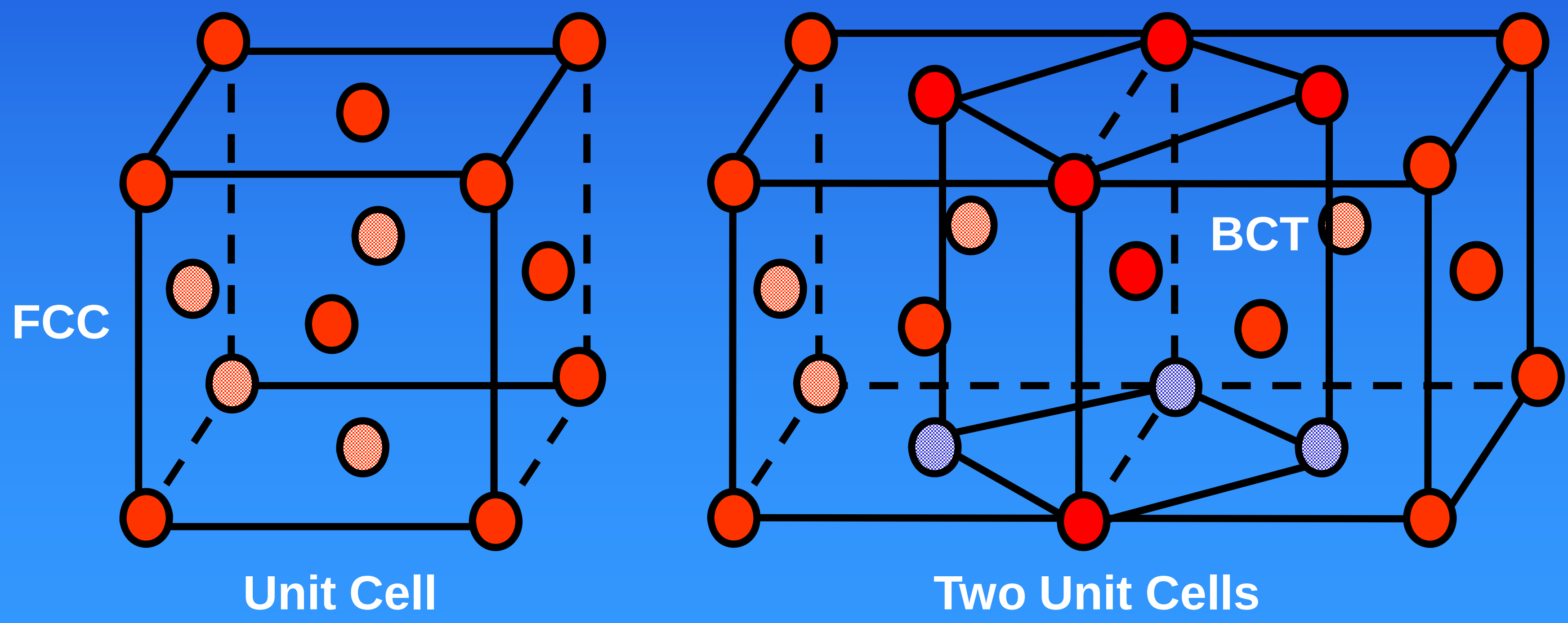
Martensitic Stainless Steels

- Martensite named after Adolf Martens (1850-1914)
- Martensite symbol: α’ (alpha prime)
- Alloys of Fe, Cr and C with a body centered tetragonal (BCT) crystal structure in the hardened condition
- Ferromagnetic
- Hardenable by heat treatments
- Lower corrosion resistance
- Cr <18%, while C may >1.0 %
- Cr and C are adjusted to ensure a α’ structure after hardening
- 400 commercial series numbers
  - LWR Examples: 410, 416, 420, 422



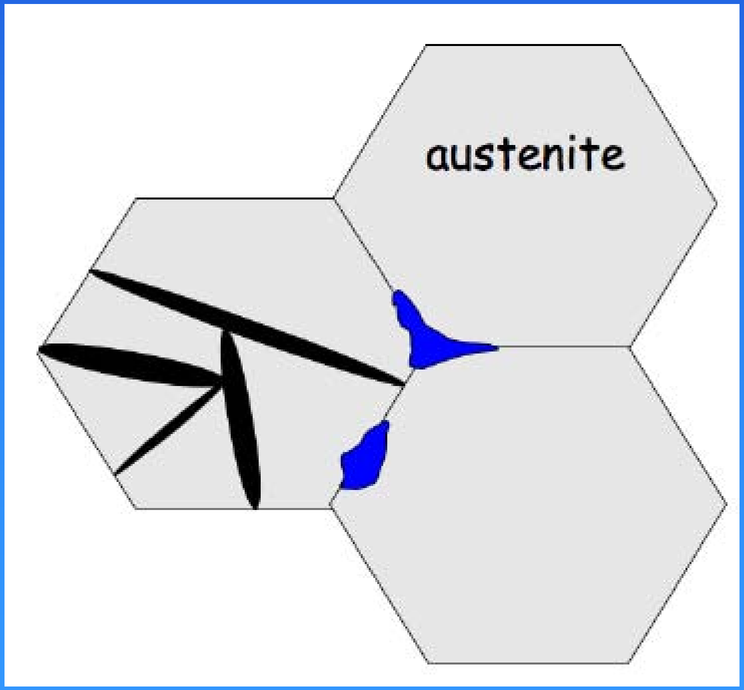
What is Martensite?

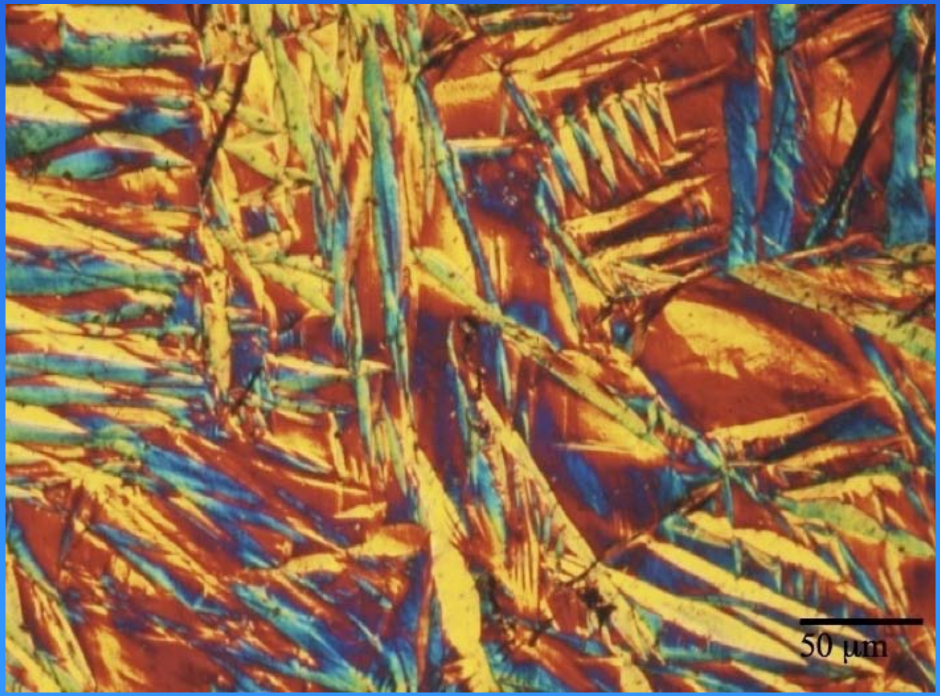
- Metastable BCT martensite (α’) is produced in γ SS by a strain induced, i.e., cold work, structural/diffusionless transformation



Properties of Martensite

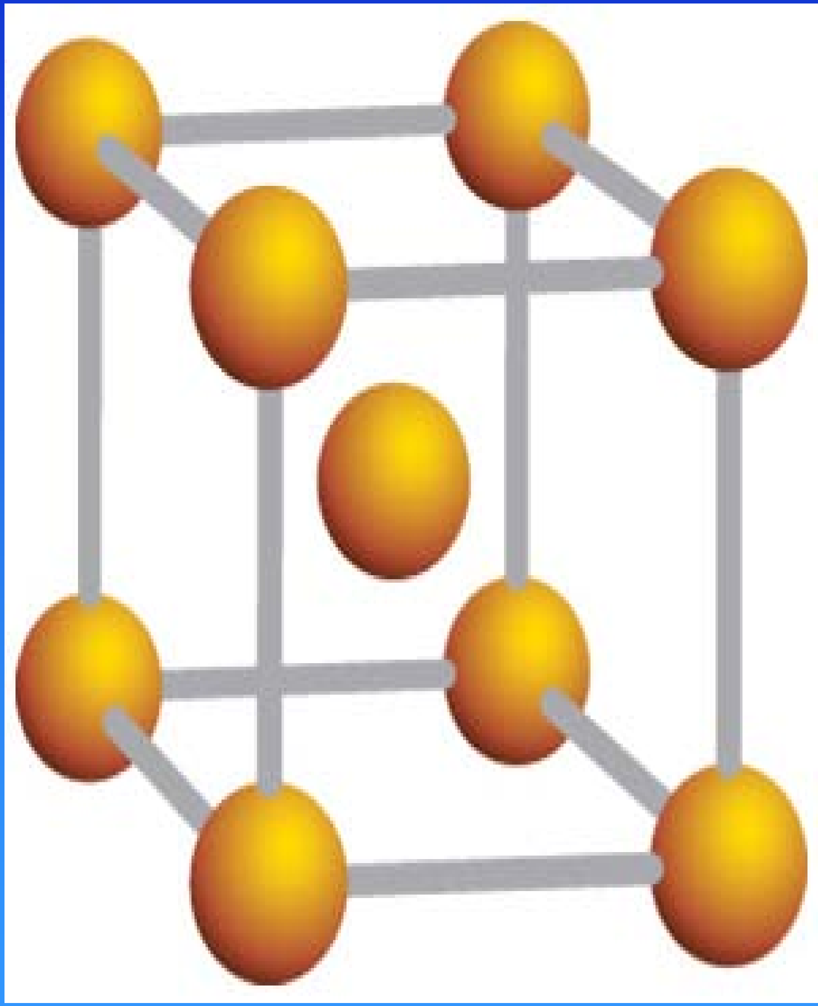
- Cr and C diffuse more rapidly in α' and sensitization occurs more rapidly
- Solubility of C in α' is also lower, therefore more C for sensitization



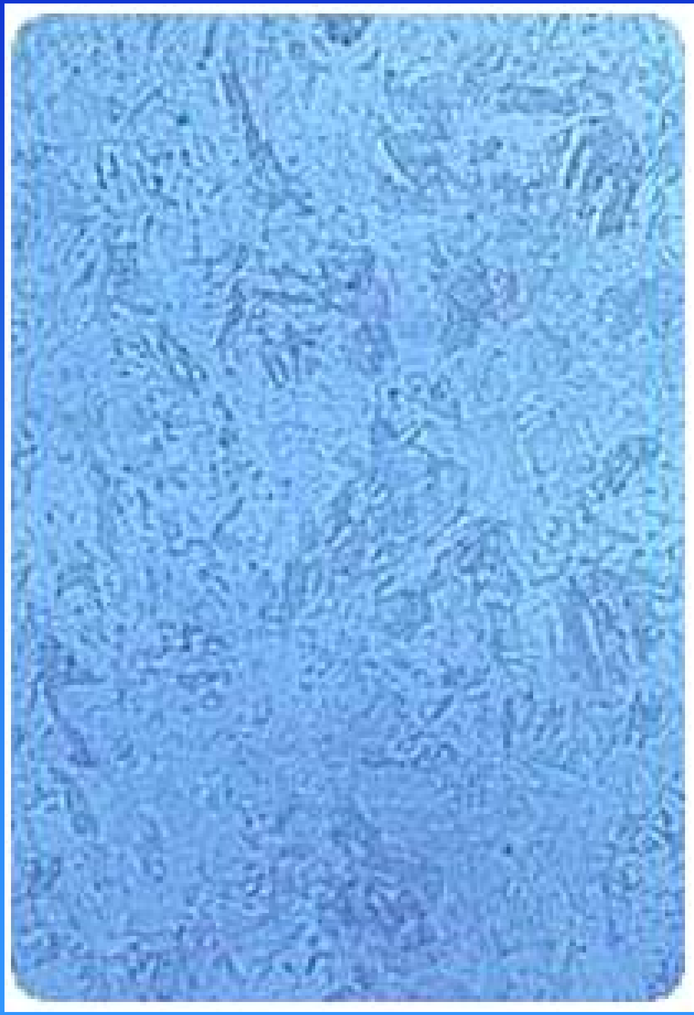


H. Bhadeshia, Cambridge

Martensitic Stainless Steel



BCT Crystal Structure



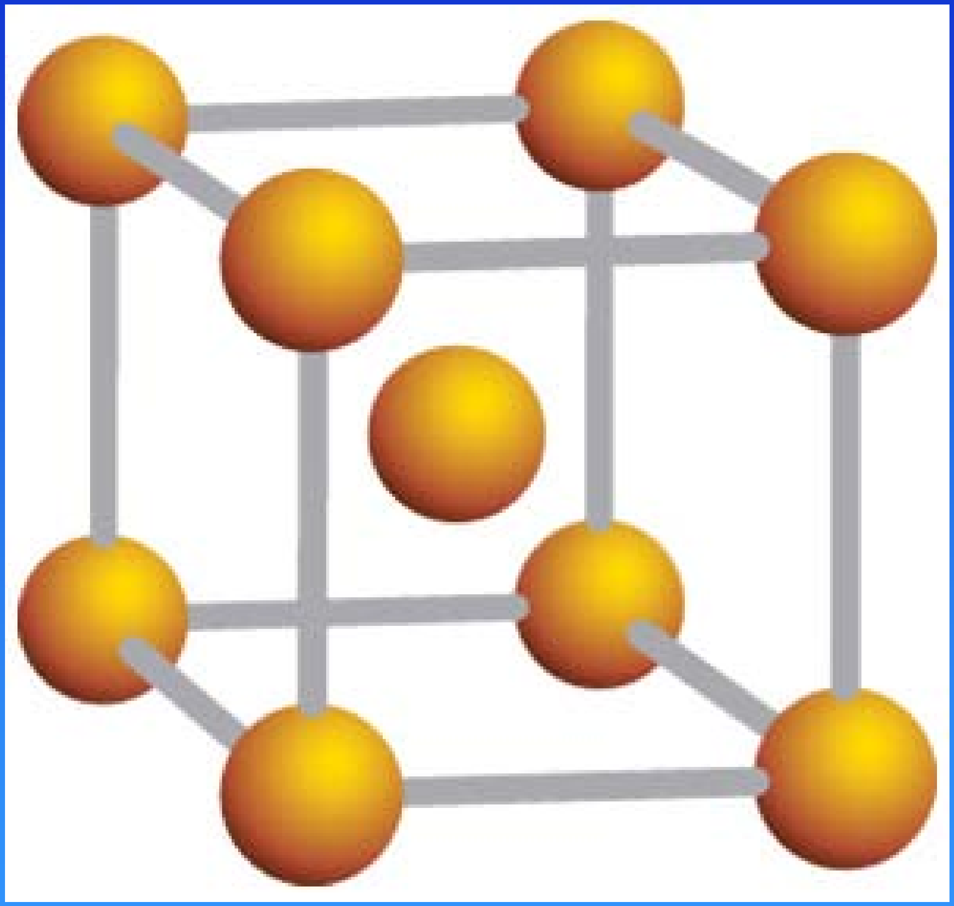
Photomicrograph

Ferritic Stainless Steels

- Body centered cubic (BCC) crystal structure
- Alpha ferrite symbol: α
- α SS is formed through additions of α stabilizing elements Cr, Mo, Si, Nb, Ti, Al, V and W
- Fe – Cr SSs with Cr <30%, non-hardenable
- α stainless steels are ferromagnetic
- Less formable and weldable than γ SSs
- Toughness decreases rapidly <0ºC (<32ºF)
- Good resistance to Cl^- SCC
- Also 400 commercial series numbers
  - LWR Examples: 409, 430, 444

Structural Integrity Associates

Ferritic Stainless Steel



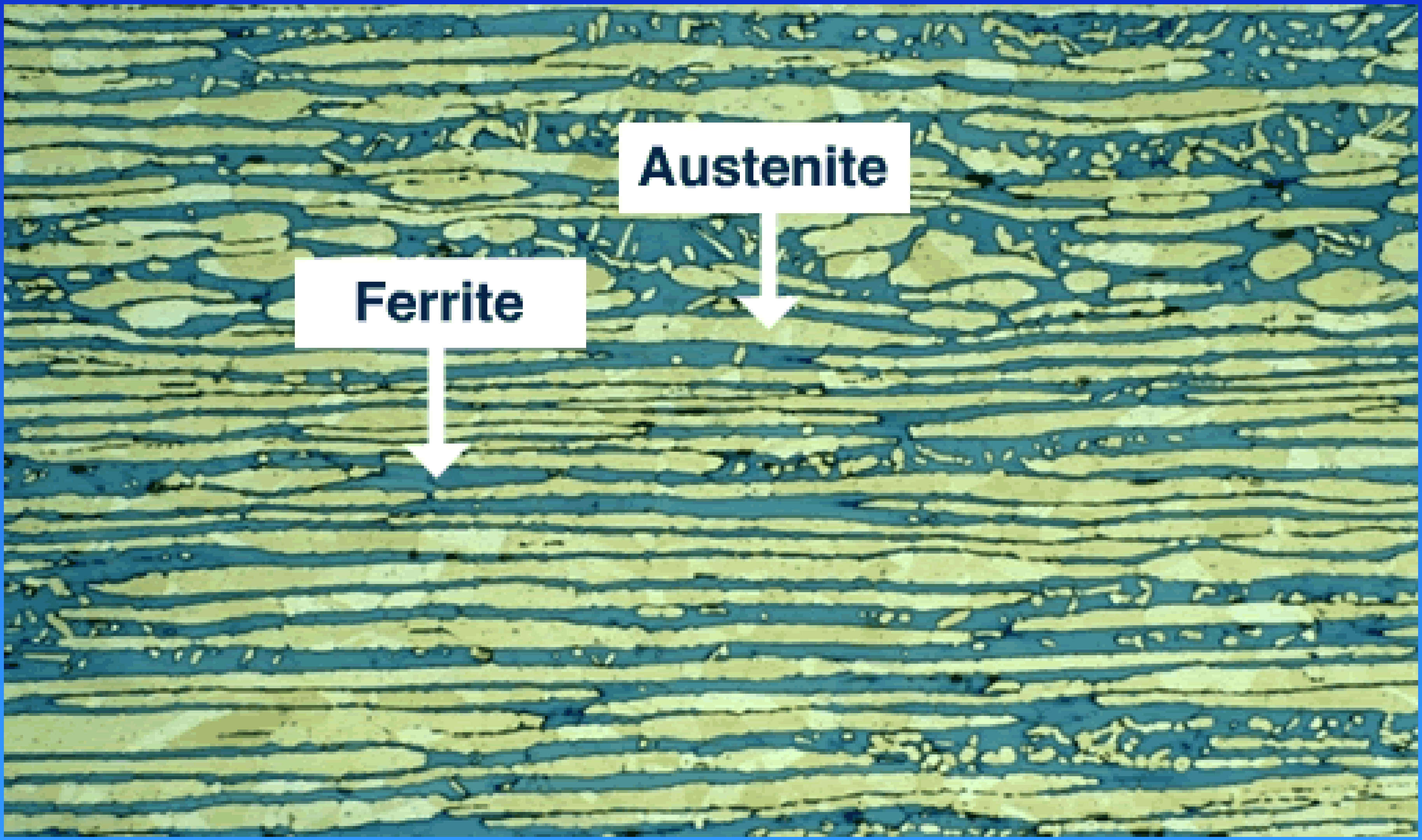
BCC Crystal Structure

Photomicrograph

Duplex Stainless Steels

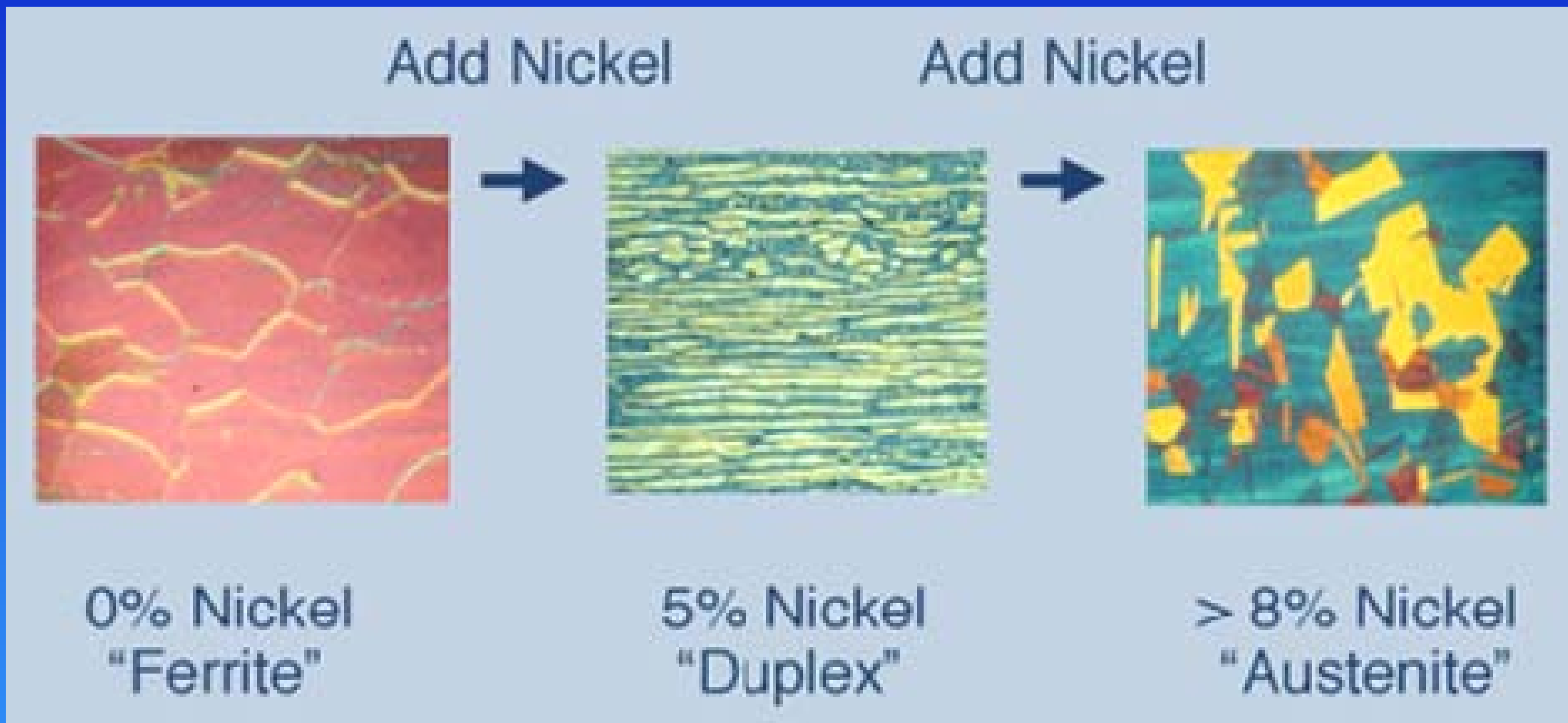
- Mixture of BCC delta ferrite (δ) and FCC austenite structures
  - Typically % ferrite = % austenite in annealed condition
  - LWRs ~2 to 20% δ ferrite
  - Phase % f(composition and heat treatment)
- Primary alloying elements are Cr and Ni
- Duplex SS generally have similar corrosion resistance to γ SS except have better SCC resistance
- Duplex SS also generally have greater tensile and yield strengths, but poorer toughness than γ SS
- LWR examples: CF3, CF8M, 308, 309 weld metals

Duplex Stainless Steel

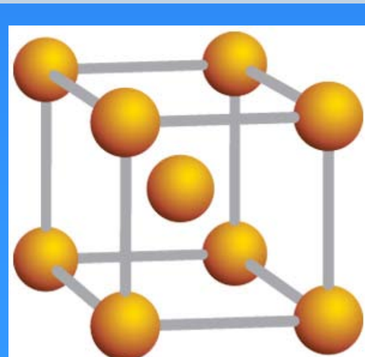


IMOA

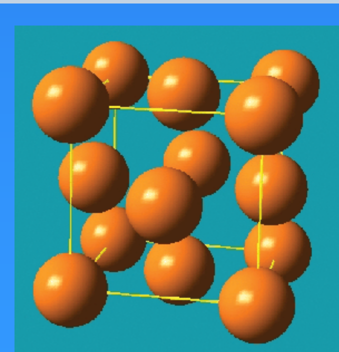
Ferritic to Duplex to Austenitic SS



BCC



Add Ni →



FCC

Nickel Institute 2007

Precipitation Hardening Stainless Steels

- Precipitation-hardening (PH) stainless steels may be either austenitic or martensitic in the annealed condition
- In most cases, precipitation hardening stainless steels attain high strength by precipitation hardening of the martensitic structure
- Usually with PH in commercial name
- LWR alloys: 17-4 PH, 17-7 PH, PH 13-8, A286

"Super" Stainless Steels

- Super austenitic stainless steels have higher corrosion resistance
  - Higher contents of Cr, Ni, Mo and N

ASTM	C	N	Cr	Ni	Mo	Others/ Comment
S31726	0.02	0.14	18	13	4.1	
N08904	0.01	-	20	25	4.3	1.5 Cu
S31254	0.01	0.20	20	18	6.1	0.5-1 Cu
N08926	0.01	0.20	20	25	6.5	0.5-1.5 Cu
S34565	0.02	0.45	24	17	4.5	5.5 Mn
S32205	0.02	0.17	22	5.7	3.1	Duplex
S32750	0.02	0.27	25	7.0	4.0	Duplex

Chemical Compositions of Typical LWR Ni-base Alloys (w%)

Alloy	C max	Cr	Fe	Mo	Other
600	0.15	14-17	6-11		
690	0.04	28-31	7-11		
625	0.10	20-23	5	8-10	3.1-4.1 Nb + Ta
X-750	0.08	14-17	5-9		1.0 Nb + 2.5 Ti + 0.7 Al
718	0.045	17-21	21 (bal.)	2.8-3.3	4.9-5.2 (Nb + Ti) + 0.5 Al
182	0.10	13-17	10		5.0-9.5 Mn, 1.0-2.5 Nb+Ta
82 / 82H	0.10 / 0.03-0.10	18-22	3	0.050	2.5-3.5 Mn / 2.0-3.0 Nb+Ta
52 / 52M	0.04	28-31.5	7-11	0.050	0.1 Nb / 0.5-1.0 Nb, Zr, B
152 / 152M	0.05	28-31.5	7-12	0.050	5 Mn / 5 Mn, Zr, B
132	0.08	13-17	<11.5		1.5-2.5 Nb

Alloy 600

- UNS N06600 (Unified Numbering System)
- Alloy 600 is an austenitic alloy containing ~72% Ni
- Standard material for applications that require resistance to corrosion and high temperatures
- Not precipitation hardenable; it is hardened and strengthened only by cold work
- Good general corrosion resistance in high purity high temperature water
- Excellent mechanical properties and presents the desirable combination of high strength and good workability

Alloy X-750

- UNS: N07750
- Age-hardenable, nickel-base “superalloy” that is nearly compositionally equivalent to Alloy 600
- Very good strength at high temperatures up to ~870°C (~1600°F)
- High tensile and creep-rupture properties at temperatures to 700°C (1300°F)
- Although much of the effect of precipitation hardening is lost with increasing temperature over 700°C (1300°F), heat-treated material has useful strength up to 982°C (1800°F)
- Excellent relaxation resistance is useful for high temperature springs and bolts
  - Fuel spacer springs in BWRs

Alloy 718

- UNS: N07180
- Age-hardenable, nickel-base “superalloy”
- Sluggish age-hardening response permits annealing and welding without spontaneous hardening during heating and cooling
- Exceptionally high yield, tensile and creep-rupture properties at temperatures up to 700°C (1300°F)
- Used for jet engine and high-speed airframe parts such as wheels, buckets, spacers and high temperature bolts and fasteners
- Fuel grids in PWRs

Bottom Line on Materials

When in doubt

Make it stout

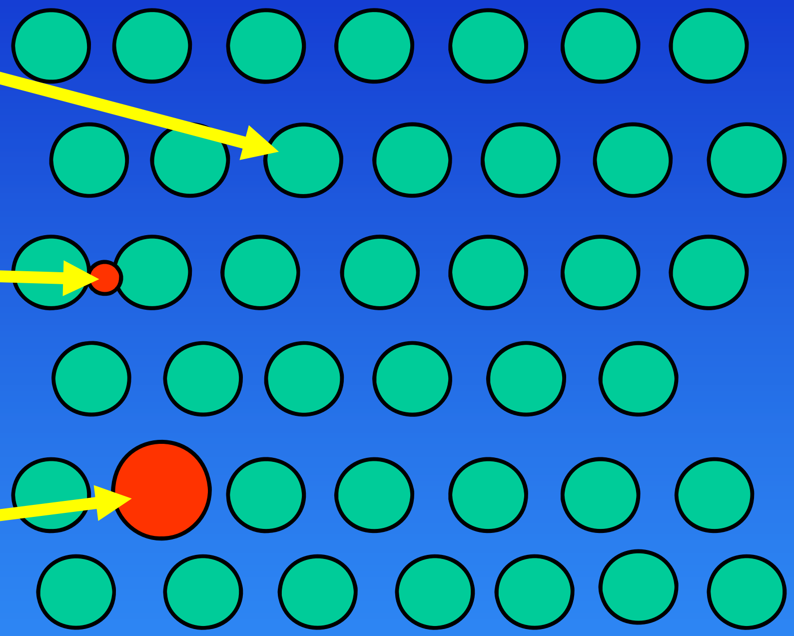
Out of materials

You know about!

Defects in Materials

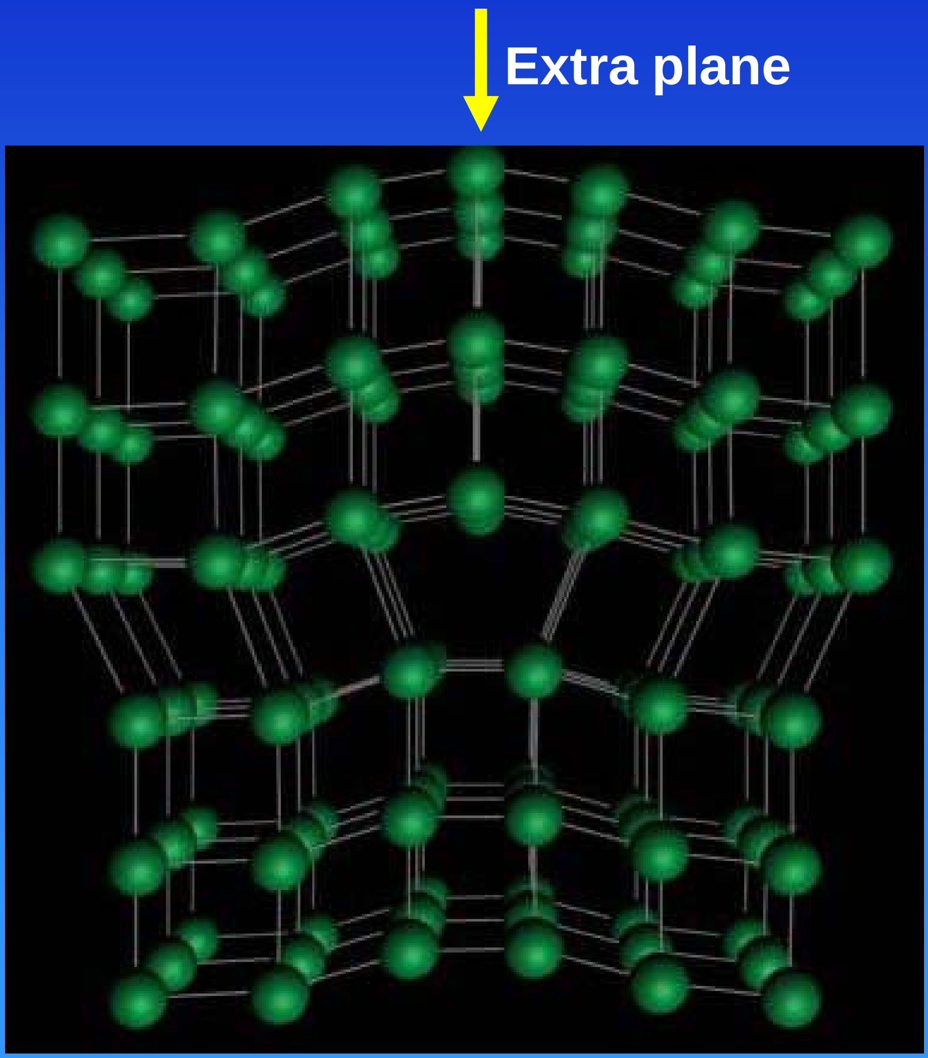
Point Defects Tutorial

- **Vacancies – missing atoms**
- **Interstitials – atoms between lattice sites**
- **Substitutional atoms – replacing an atom that should occupy a lattice site with a different atom**

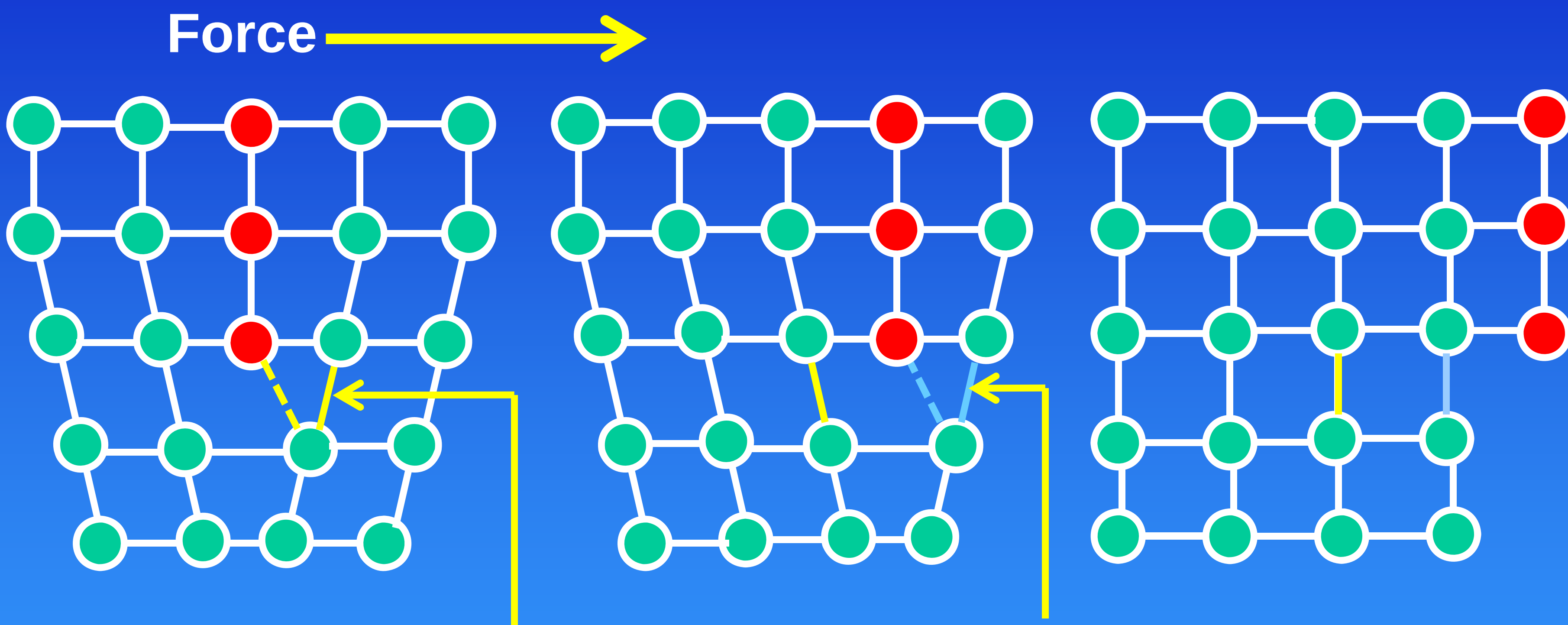


Planar Defects

- Dislocations are linear defects inside a crystal lattice
- Extra lattice planes inserted in the crystal like a single playing card inserted halfway into a deck of cards
- Plastic deformation is due to the motion of a large number of dislocations. The motion is called slip.
- Edge dislocations allow slip to occur and slip provides ductility in metals
  - Affect all mechanical phenomena: strain hardening, yield point, creep, fatigue and brittle fracture



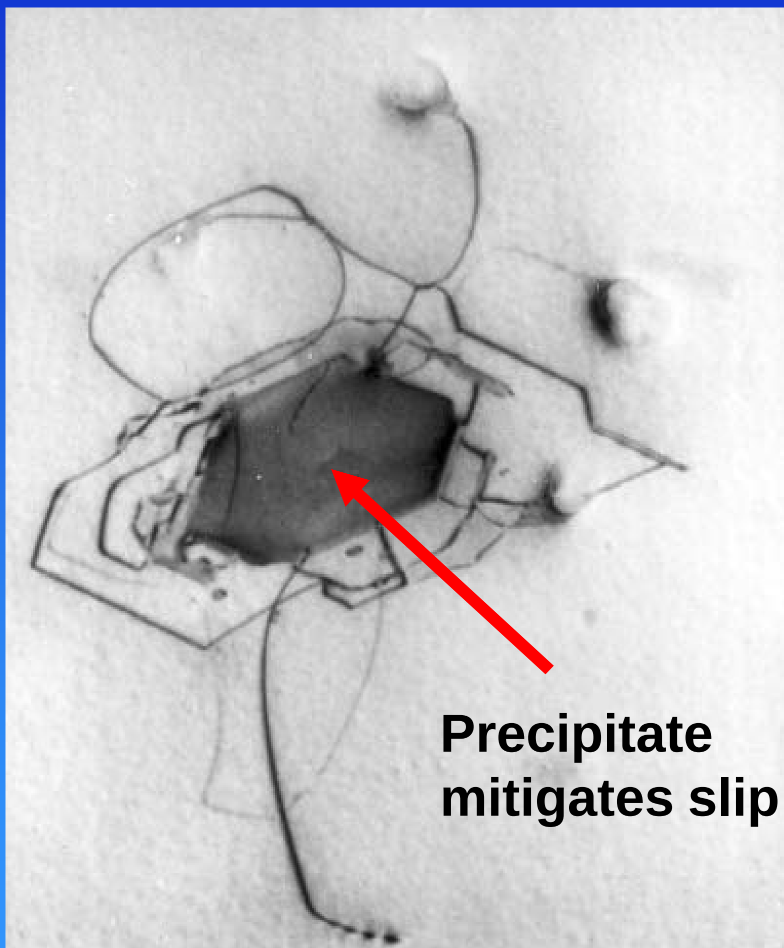
Movement of an Edge Dislocation through a Crystal

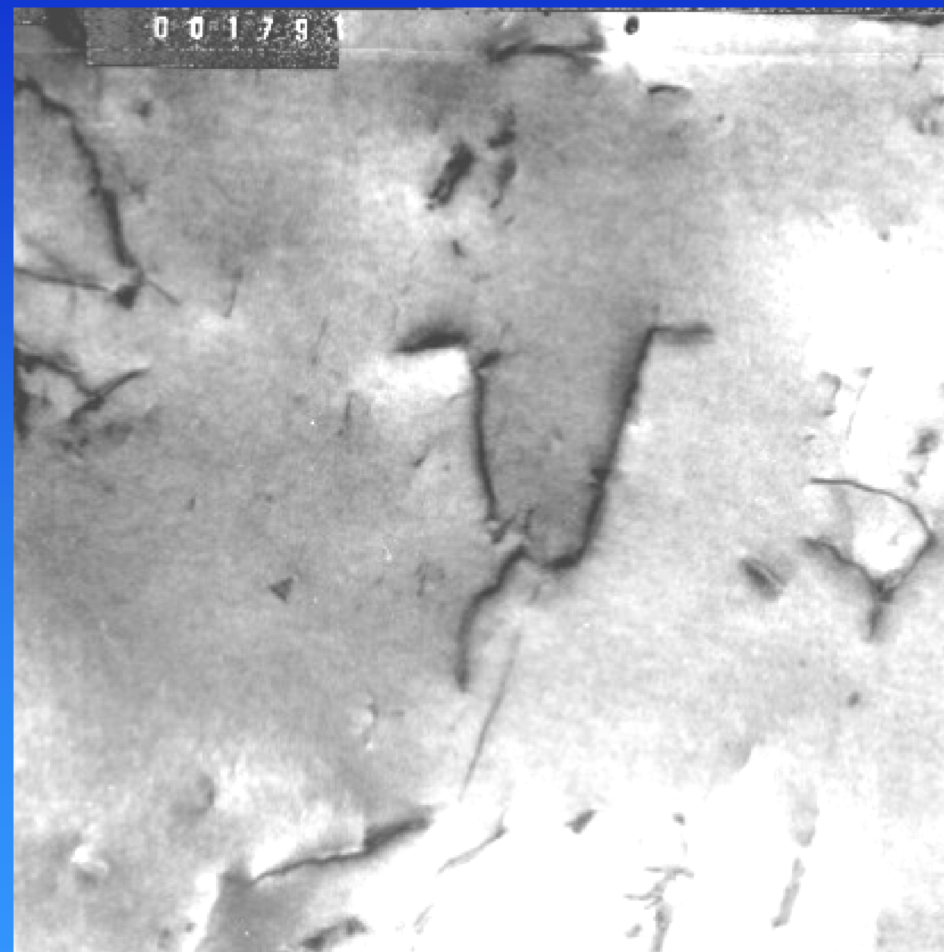


This row of bonds will break and reattach itself to a different row of atoms

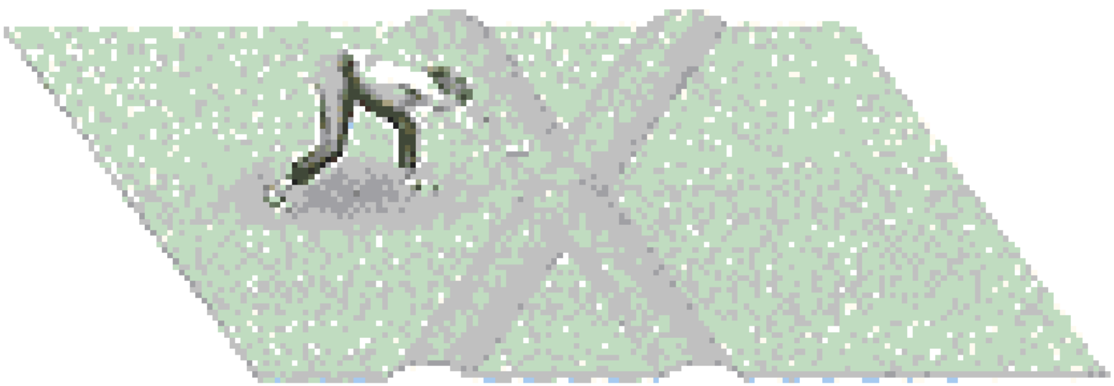
It is much easier for only one row of bonds to break and reform than for an entire plane of bonds

Dislocations



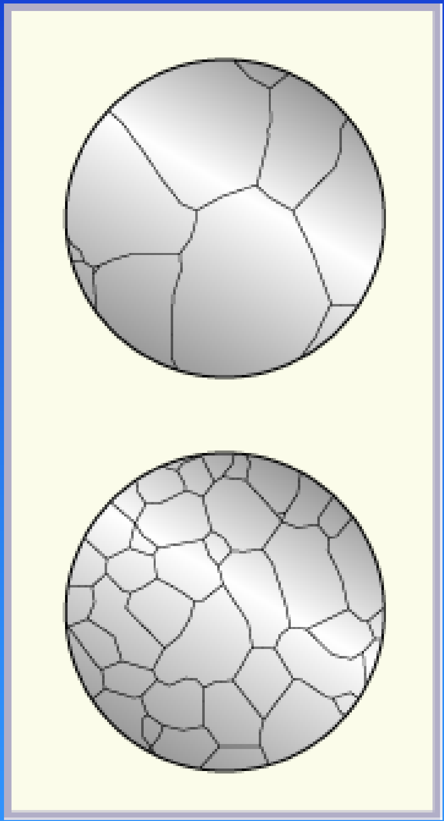


Dislocations and Work Hardening



Grain Boundaries (gbs)

- gbs are interfaces where crystals of different orientations meet
- gbs contain atoms that have been perturbed from their original lattice sites, dislocations and impurities that have migrated to the lower energy gb
- gbs disrupt the motion of dislocations through a material, i.e., dislocation propagation is impeded due to the stress field of the gb defect region
- Reducing grain size is a common way to improve strength because the smaller grains create more obstacles per unit area



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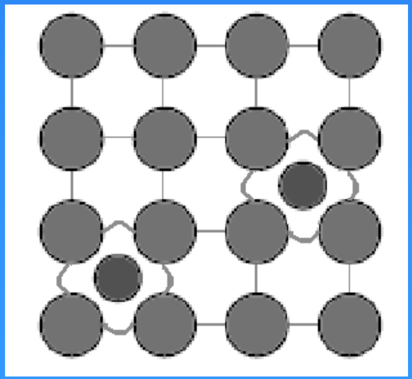
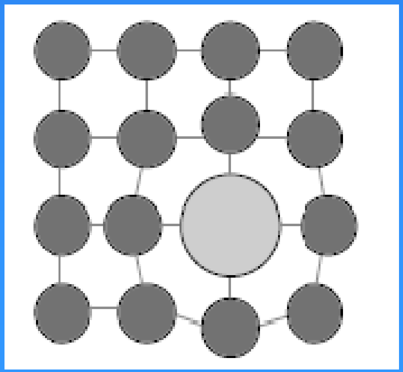
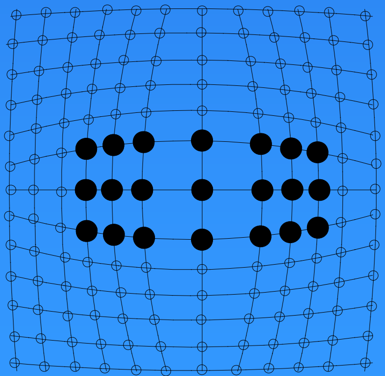
Strengthening Mechanisms

- Strength (resistance to deformation) can be improved by installing obstacles to slip
  - Grain boundaries
  - Cold working - dislocations
  - Solid-Solution Strengthening
    - Adding another element that goes into interstitial or substitutional positions increases strength. These atoms cause lattice strain that "anchors" dislocations.
  - Precipitation Hardening (age hardening)
    - Caused by the precipitation of a coherent structure from a supersaturated solid solution


Fe-C

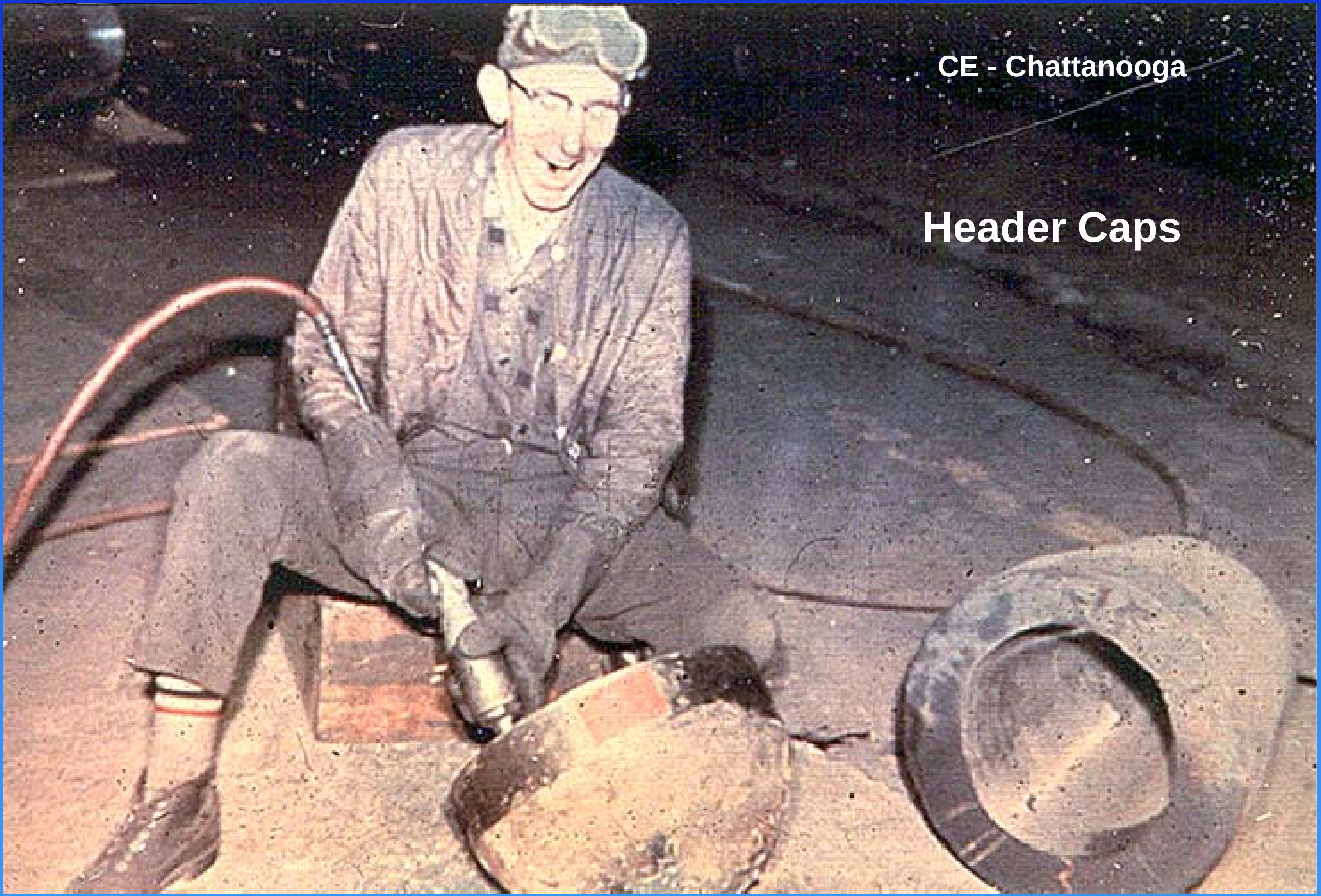

Fe-Ni


Fe-Cu-Nb

Cold Work

Not This……

But this…….



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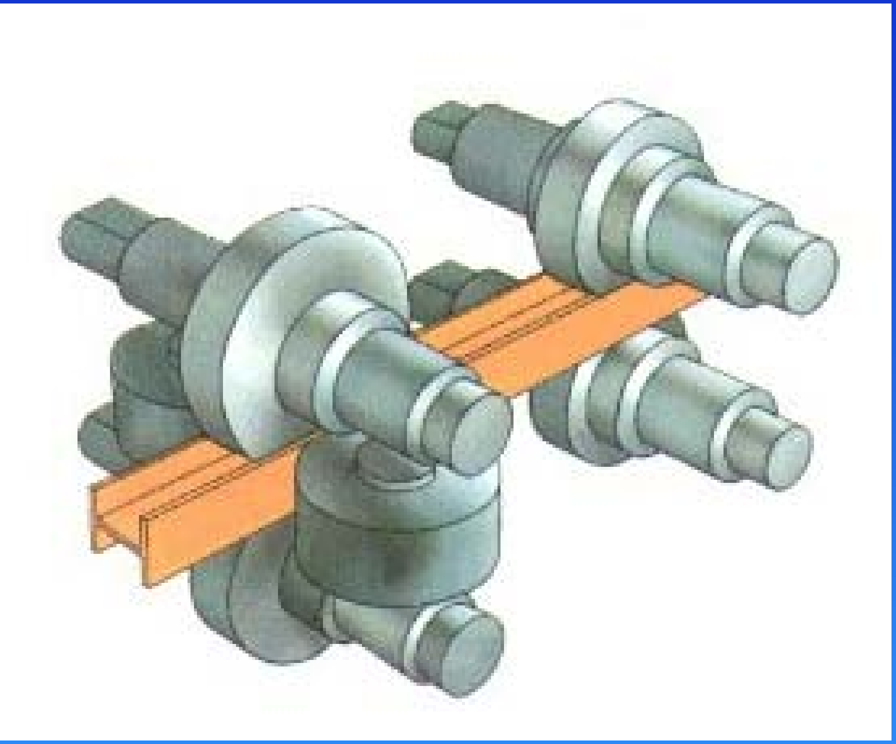
Or this……..

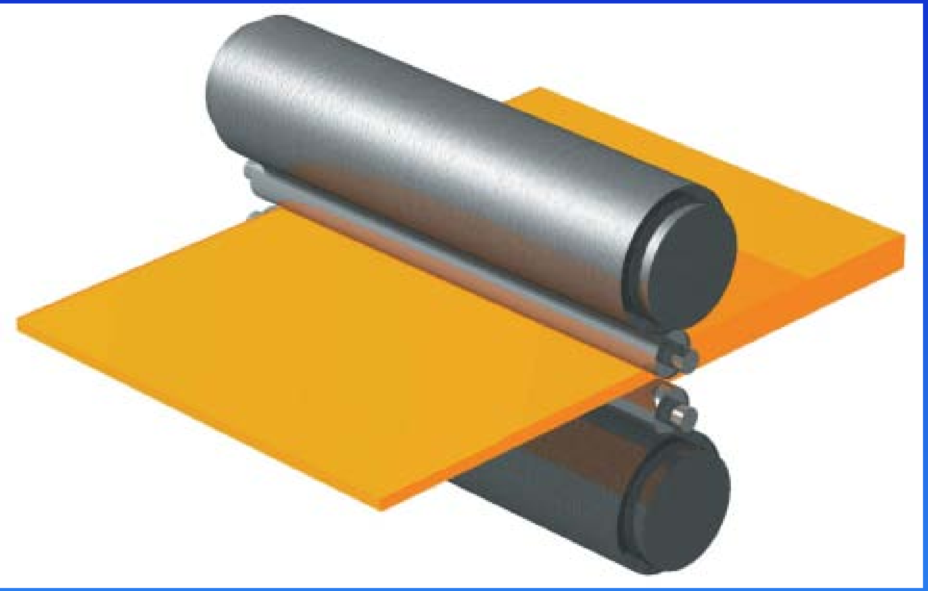
What is Cold Work?

- Plastic deformation that is performed at a temperature and over a time period where strain hardening is not relieved is "cold work"
- Increases internal stored energy due to an increased defect structure
- In the fabrication of LWRs (or anything else), cold work can occur due to:

Cutting	Grinding	Machining	Shearing
Boring	Sawing	Broaching	Honing
Drilling	Stamping	Bending	Dropping
	Turning	Hammering	

Cold Work Examples





- Cold working to increase yield strength (e.g., rolling steel, Al, etc.)
- Cold rolling is the most widely used method of shaping metals

E. Jacobs and T. Mazurkiewicz, U of Wisconsin

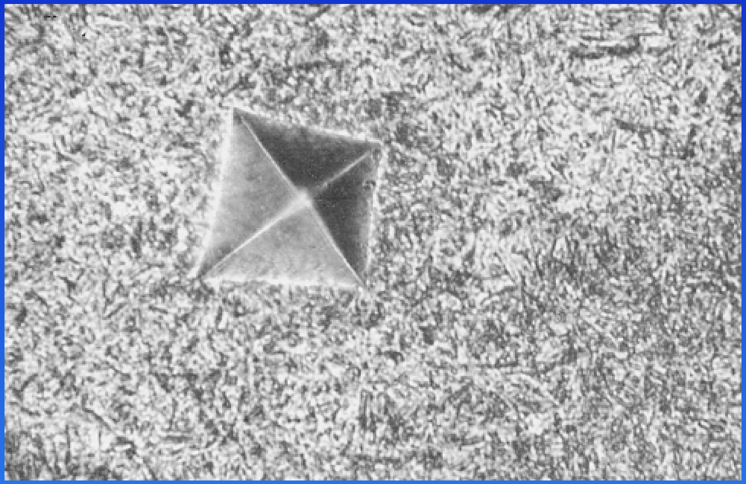
Cold Work's Effect on Mechanical Properties

- Cold work has a dramatic effect on the mechanical properties of materials since it increases the number of line defects (dislocations) from $10^6 - 10^8$ to 10^{12} per cm^3
- Therefore, cold work:
  - Increases hardness
  - Increases yield strength
  - Increases ultimate tensile strength
  - Decreases ductility
- Cold work can produce BCT martensite

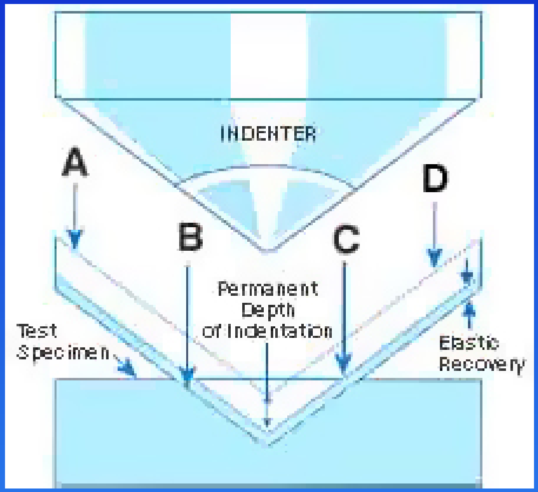
Hardness

- Resistance to plastic deformation, usually measured by indentation
- Hardness measurement: macro-, micro- or nano- scale based on forces applied and displacements obtained
- Measurement of the macro-hardness is a quick and simple method of obtaining mechanical property data for the bulk material from a small sample
- For fine microstructures, multi-phases, non-homogeneous or prone to cracking microstructures, macro-hardness measurements will be highly variable and will not identify individual surface features
  - Need to use micro-hardness measurements

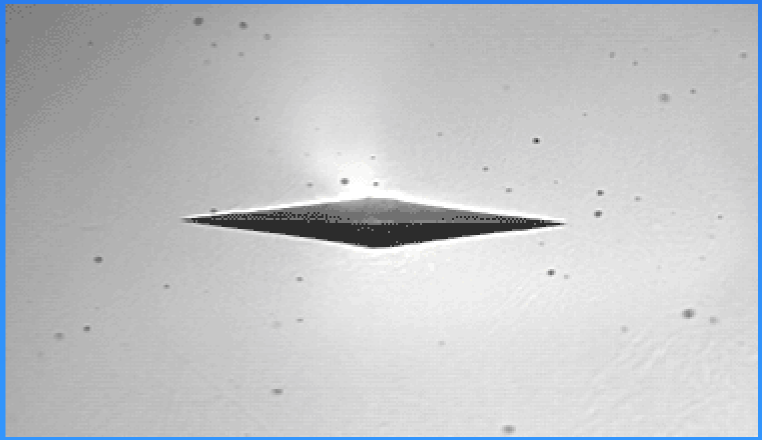
Hardness Testing Techniques



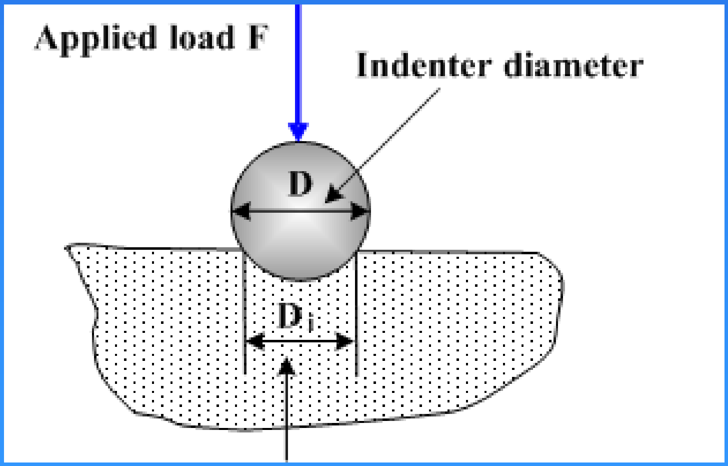
Vickers - Pyramid Indenter



Rockwell - Cone or Ball Indenter



Knoop - Elongated Diamond Pyramid



Brinell - Ball Indenter

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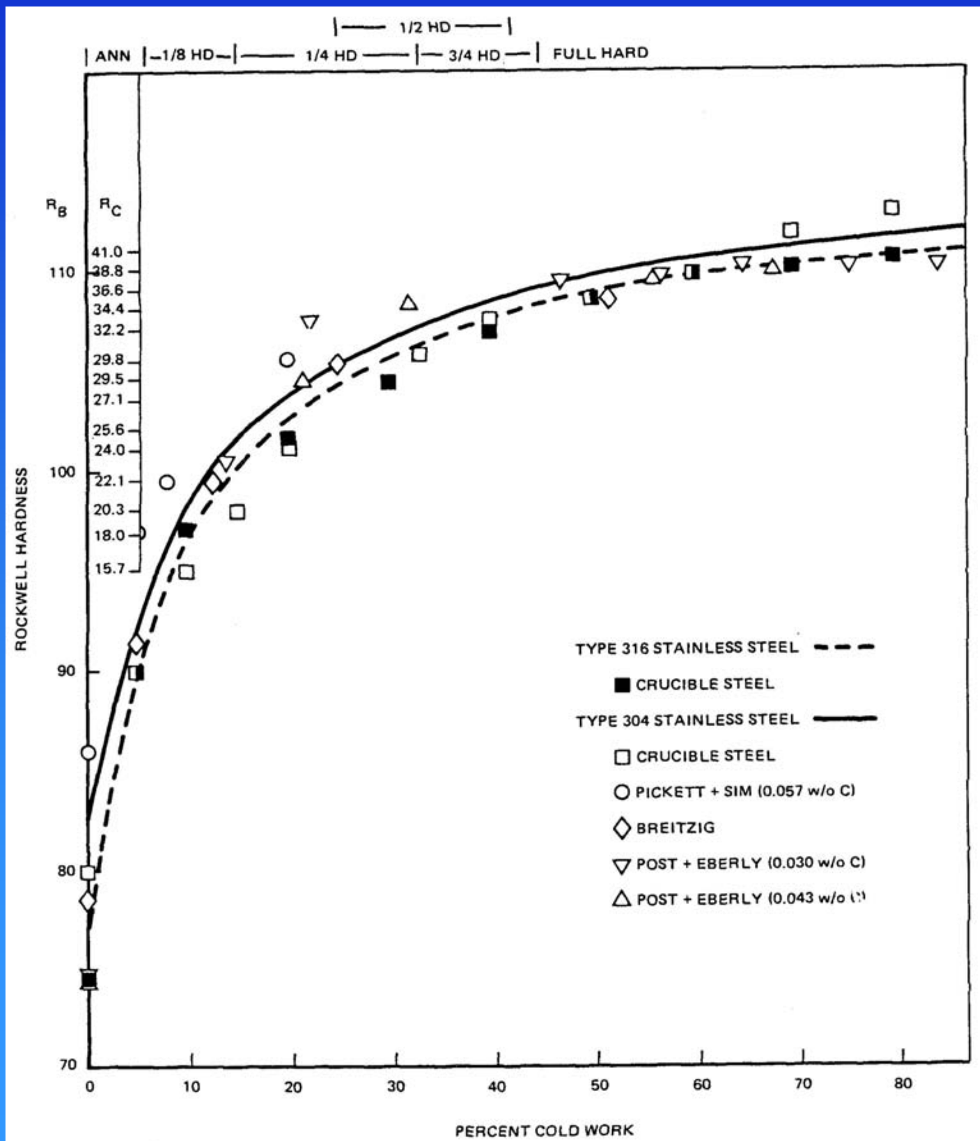
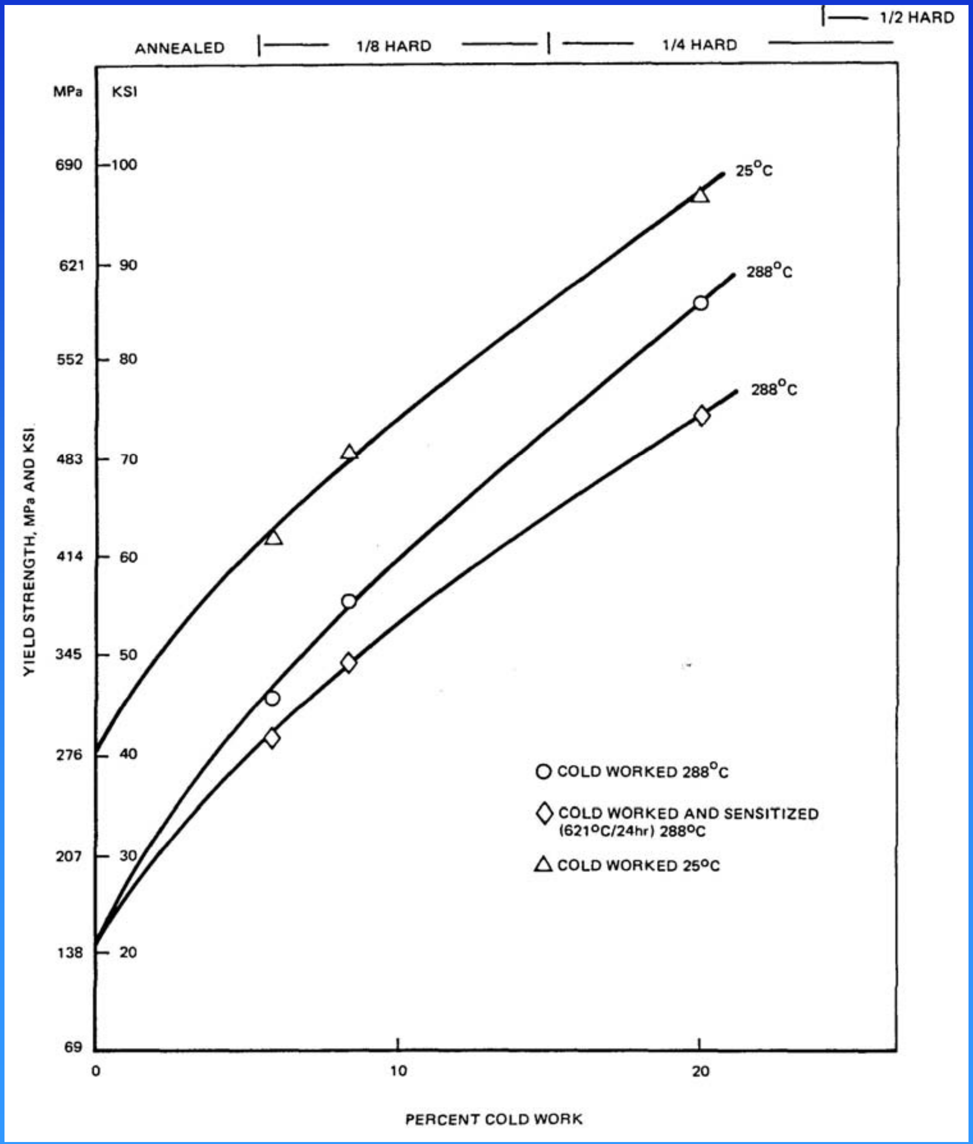
Effect of Cold Work on the Hardness of Types 304 and 316 Stainless Steel



Hardness increases with cold work

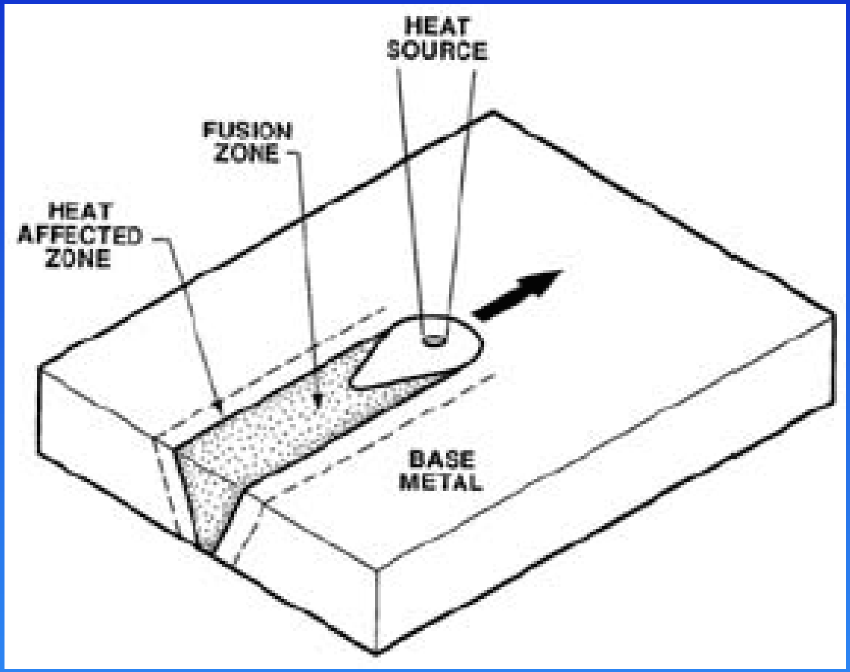
Effect of Cold Work on the Yield Stress of Type 304 Stainless Steel



Yield stress increases with cold work

Welding

Welding



As heat source interacts with the material, the severity of thermal changes experienced by the material varies from region to region, resulting in three distinct regions in the weldment:

1. **Fusion zone (FZ), a.k.a. weld metal**
2. **Heat affected zone (HAZ)**
3. **Unaffected base metal (BM)**

S. David, et al., JOM, 6/03

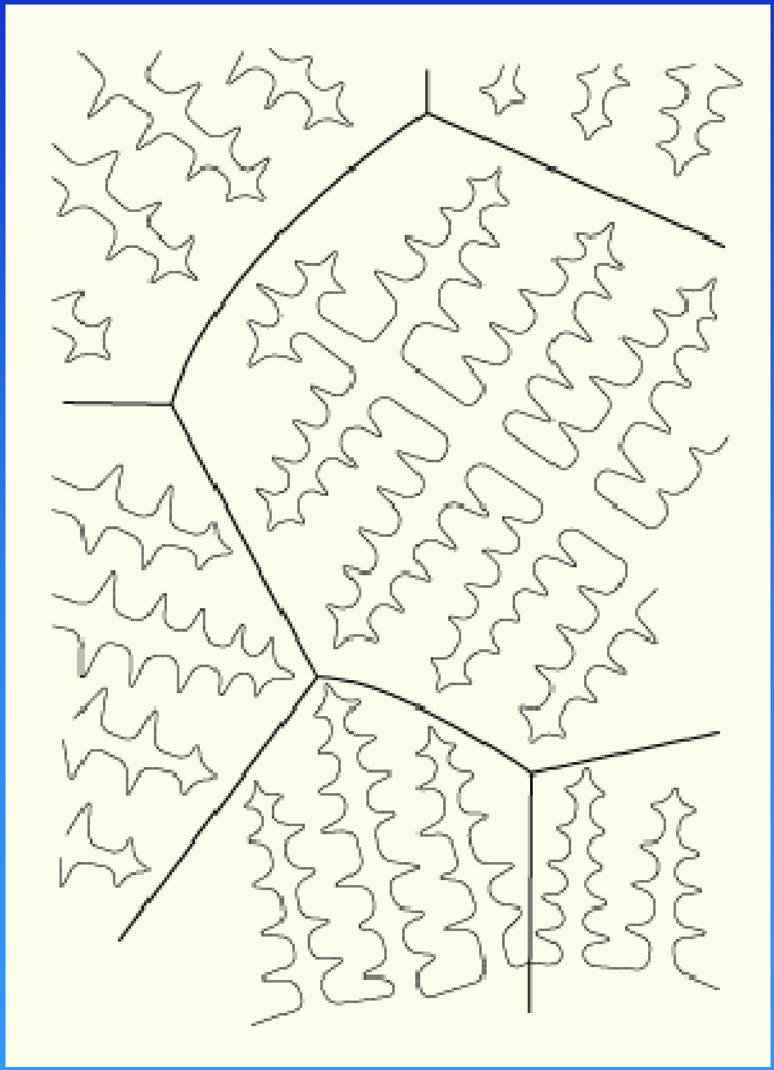
Weld Metal Microstructure

- Microstructure of weld metal depends on the solidification behavior of the weld pool
- Principles of solidification control the size and shape of the grains, segregation, distribution of inclusions and porosity
- Parameters important in determining microstructures are growth rate, temperature gradient, undercooling and alloy composition

S. David, et al., JOM, 6/03

Weld Metal and Dendrites

- **Weld metal forms by solidification that leads to the formation of dendrites growing in the direction of the heat flow, i.e., perpendicular to the solid material on which the weld is deposited**
- **Strong pattern of columnar grains formed by dendrites - pattern persists through many weld passes**
- **From Greek "dendron" – tree**



Multipass Weld

Similar Metal Welds

- Butt welding of similar metals/alloys with the heat source placed symmetrical about the centerline on the top would usually lead to microstructural features that are well understood
- Weld pool solidification takes place by continuous growth of base metal grains leading to columnar grains with a weld-centerline or equiaxed grains at the center of the weld
- The shape of the weld pool is symmetric about the centerline

Dissimilar Metal Welds

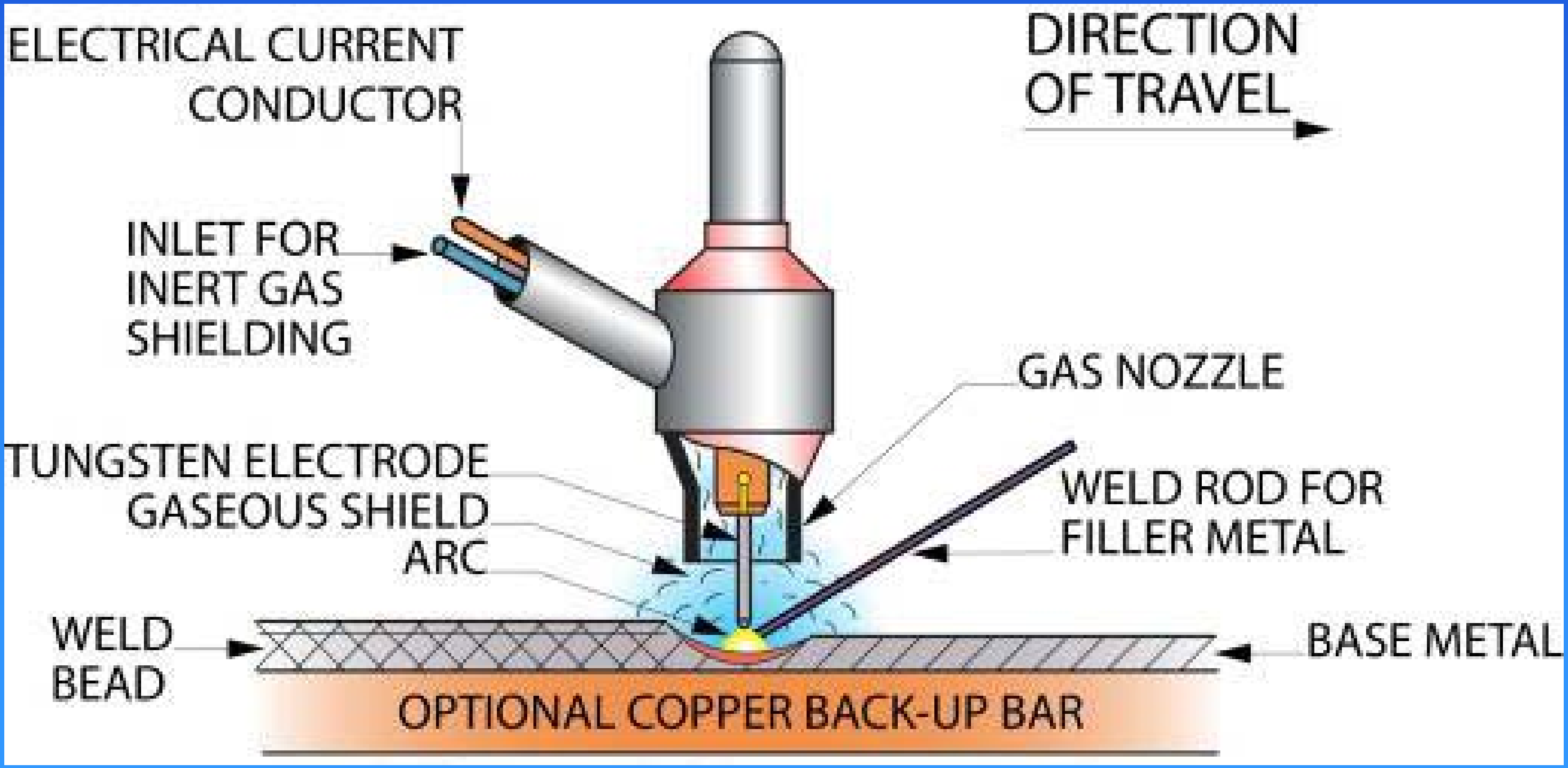
- Weld between two materials that are significantly different in chemical composition (e.g., SS to CS or LAS) or a weld between similar materials using a filler material with significantly different chemical composition (e.g., SS welded with Ni-base filler)
- There are many features that are not completely understood during welding of dissimilar metals
- Physical properties of the two metals being very different from each other lead to complexities in:
  - weld pool shape
  - solidification microstructure
  - segregation patterns

Gas Tungsten Arc Welding (GTAW)

- GTAW (1941), aka tungsten inert gas (TIG) welding, is an arc welding process that uses a non-consumable tungsten electrode
- Weld area is protected from atmospheric contamination by a shielding gas (e.g., Ar)
- Bare wire filler metal is normally used, though some welds (autogenous welds) do not use filler metal
- Constant-current welding power supply produces energy that is conducted across the arc through a column of highly ionized gas and metal vapors, i.e., a plasma
- Very clean process with few inclusions or oxides

Gas Tungsten Arc Welding (GTAW)

- **An arc welding process that uses a non-consumable tungsten electrode to produce the arc. The weld area is protected from atmospheric contamination by a shielding gas (usually an inert gas such as argon)**

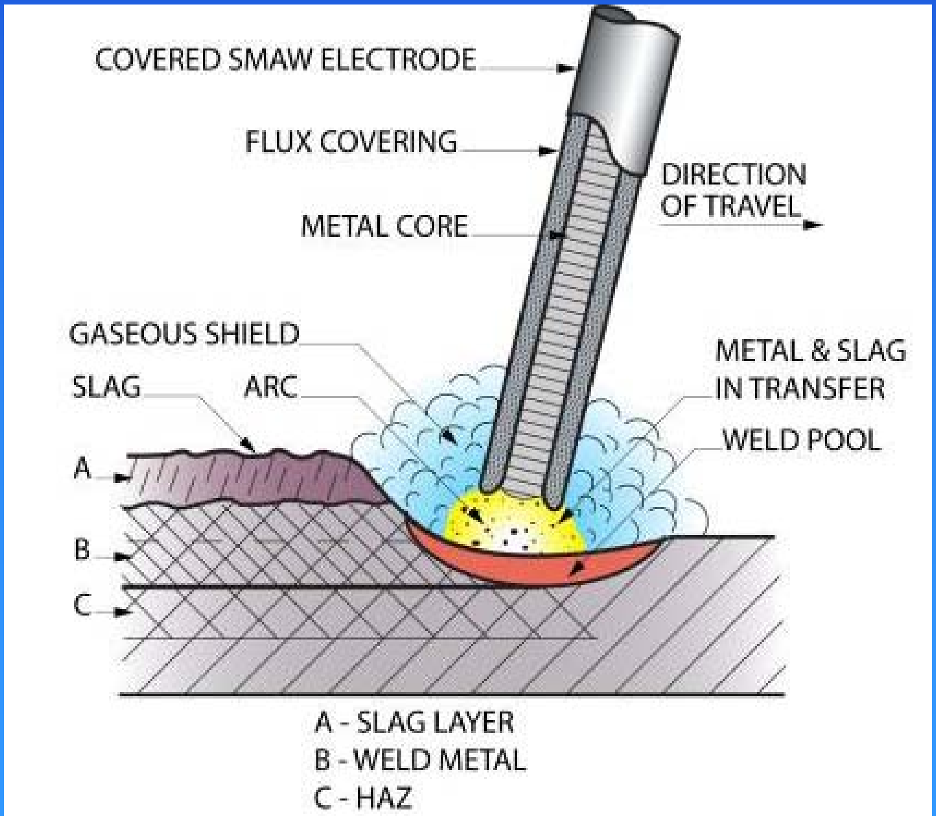


GTAW Advantages and Disadvantages

- **Advantages of GTAW:**
  - Manual, machine, automatic
  - Concentrated arc, resulting in a narrow heat-affected zone
  - No Slag
  - Limited Sparks or Spatter
  - Little Smoke or Fumes
  - Compatible with most structural metals and metal alloys
  - Can be automated with a high degree of control
  - Good control of shielding gas composition
  - Less starts and stops (machine)
- **Disadvantages of GTAW:**
  - Slower travel speeds than other processes
  - Lower filler metal deposition rates
  - Brighter UV rays
  - Equipment costs can be high
  - Concentration of shielding gas in confined areas
  - Requires a higher degree of training

Shielded Metal Arc Welding (SMAW)

- **A manual arc welding process that uses a consumable electrode coated in flux to deposit a weld. The filler metal is transferred across an electric arc between the electrode and work piece**



SMAW Advantages and Disadvantages

- **Advantages of SMAW:**
  - Manual
  - Low initial cost
  - Portable
  - Easy to use outdoors or indoors
  - All position capabilities
  - Easy to change among many base materials
  - Less susceptible to defects caused by impurities in base metal
- **Disadvantages of SMAW:**
  - Lower consumable utilization
  - Difficult to weld very thin materials
  - Frequent starts and stops
  - Higher degree of operator dexterity required
  - Increased fume generation
  - Possibility for entrapment of slag or porosity

Alloy 182

- UNS W86182
- Alloy 182 welding electrode is used for SMAW of Alloy 600 and other nickel-base and stainless steel alloys and carbon steels
- Excellent high temperature strength and oxidation resistance
- Electrodes provide excellent operability for groove and fillet welding in the downhand position
- Smaller diameter electrodes are suitable for all position welding

Alloys 82/132

- **Alloy 82 - UNS N06082**
  - ♦ **Filler metal is used GTAW of Alloy 600 and other Ni-base and stainless steels**
  - ♦ **Used for surfacing steel**
  - ♦ **Excellent high temperature strength, creep rupture strength and oxidation resistance**

- **Alloy 132 - UNS W86132**
  - ♦ **Filler metal is used for SMAW of Alloy 600 and other nickel-base and stainless steels**
  - ♦ **Not used in BWRs**
  - ♦ **Used with Alloys 182 and 82 in some PWRs (mainly in Japan)**

Alloys 52/52M and152/152M

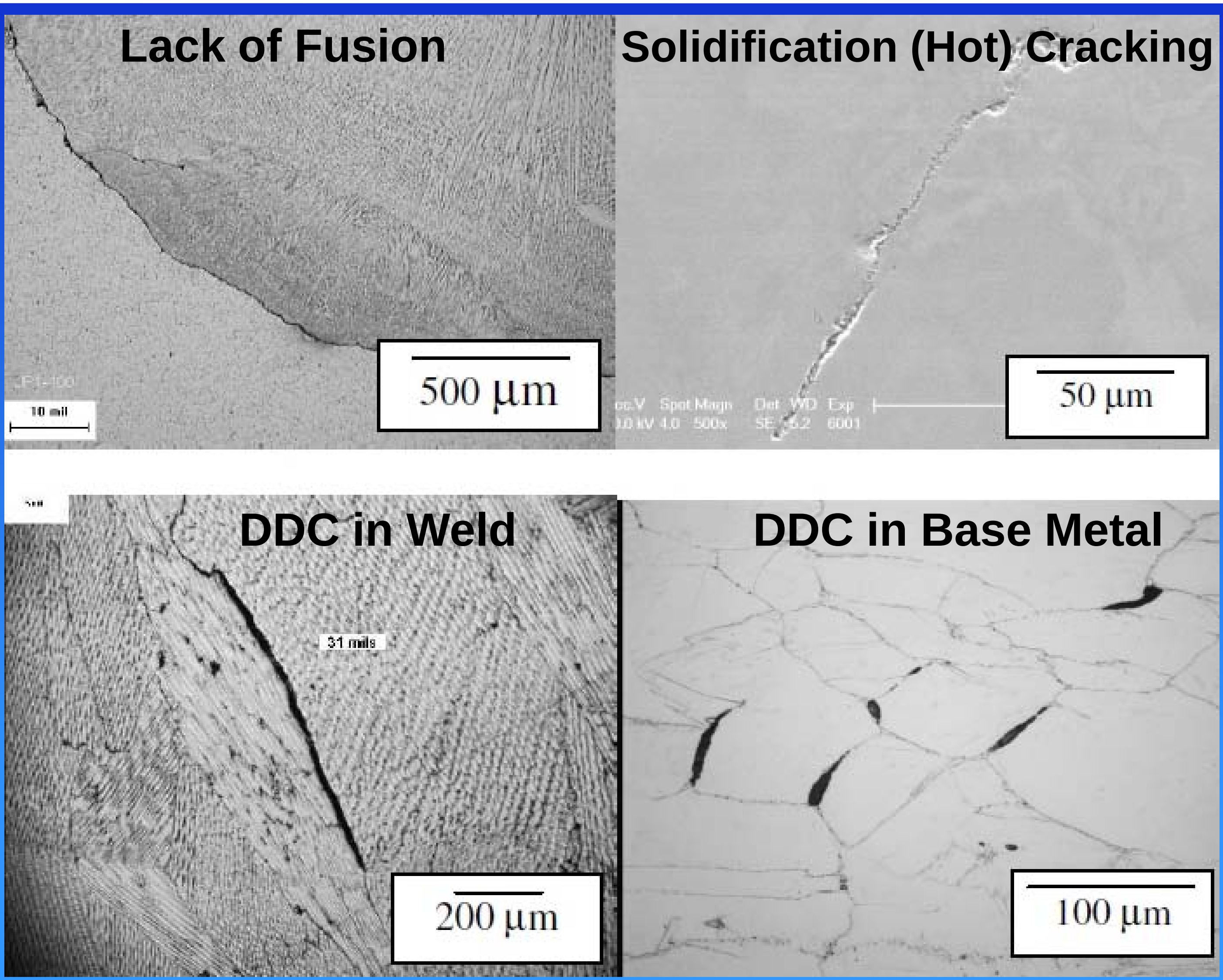
- **Alloy 52 - UNS N06052**
  - **Filler metal is used for GTAW of Alloy 600 and other Ni-base, stainless steels, low alloy steels and carbon steels**
  - **Developed for LWR industry**
  - **Alloy 52M with higher Nb (0.5-1.0) + Zr + B to mitigate ductility dip cracking**

- **Alloy 152 - UNS W86152**
  - **Filler metal is used for SMAW of Alloy 600 and other NI-base stainless steels, low alloy steels and carbon steels**
  - **Developed for LWR industry**
  - **Alloy 152M with Zr + B to mitigate ductility dip cracking**

Alloy 52 and 52M DDC and Hot Cracking

- **Alloy 52 and 52M are susceptible to ductility-dip cracking (DDC) and hot cracking that can be mistaken for PWSCC and/or potentiality act as PWSCC initiation sites**
  - ♦ **DDC is an intermediate temperature solid-state intergranular cracking that occurs during high temperature processing in highly restrained welds**
  - ♦ **Hot cracks appear near the end of the solidification process in the fusion zone due to the incapacity of the molten and semi-solid material to absorb the thermal shrinkage strains due to weld solidification and cooling without tearing**
- **Industry is developing improved filler metals (e. g., 52MSS and 52i) to minimize DDC and hot cracking**

Types of Weld Defects in Alloy 52



L. Paul and G. Young, Corrosion 2011

Nominal Alloy 52/82 Compositions

	52i	52MMS	52M	52	82
Cr	27.0	30.0	30.0	29.0	19.8
Fe	2.5	8.3	8.2	9.0	1.0
C	0.030	0.025	0.02	0.020	0.035
Al	<0.10	0.14	0.11	0.55	0.06
Ti	0.3	0.19	0.22	0.55	0.27
Nb	2.5	2.5	0.80	<0.01	2.6
Mn	3.0	0.50	0.80	0.22	3.2
B			0.1	0.001	0.001
Zr			0.1	0.001	0.001
Mo	0.01	3.9	0.01	0.01	0.01
N	0.020			0.01	0.014
Si	0.05	0.16	0.09	0.15	0.12

Chemical Compositions of Other LWR Alloys (w%)

- Admiralty brass: 72 Cu – 26 Zn – 0.04 As - 1.2 Sn
- Al bronze: 91 Cu – 7 Al – 2 Fe
- 90-10 Cu-Ni: 88.7 Cu – 1.3 Fe – 10 Ni
- 70-30 Cu-Ni: 70 Cu – 30 Ni
- Muntz Metal: 60 Cu – 40 Zn
- Ti Gr. 2: Ti – 0.3 Fe – 0.25 O
- Stellite 6™: Co – 1.2 C – 29 Cr – 3 Ni – 3 Fe
- Zircaloy 2: Zr – 1.5 Sn – 0.13 Fe – 0.1 Cr – 0.6 Ni
- Zircaloy 4: Zr – 1.5 Sn – 0.21 Fe – 0.1 Cr
- ZIRLO™: Zr – 1.0 Sn – 0.1 Fe – 1.0 Nb

General Corrosion vs. Localized Corrosion

Two Overall Forms of Corrosion

- General or Uniform Corrosion
  - Switching anodes and cathodes
  - Weight loss very useful information
  - Non-passive alloys
- Localized Corrosion
  - Stationary “locked” electrodes, i.e., all of the dissolution occurs in one location
  - Weight loss not useful information
  - Local penetration and leakage may be failure
  - May or may not jeopardize structural integrity
  - Passive alloys
  - Autocatalytic
  - Insidious

Specific Forms of Corrosion

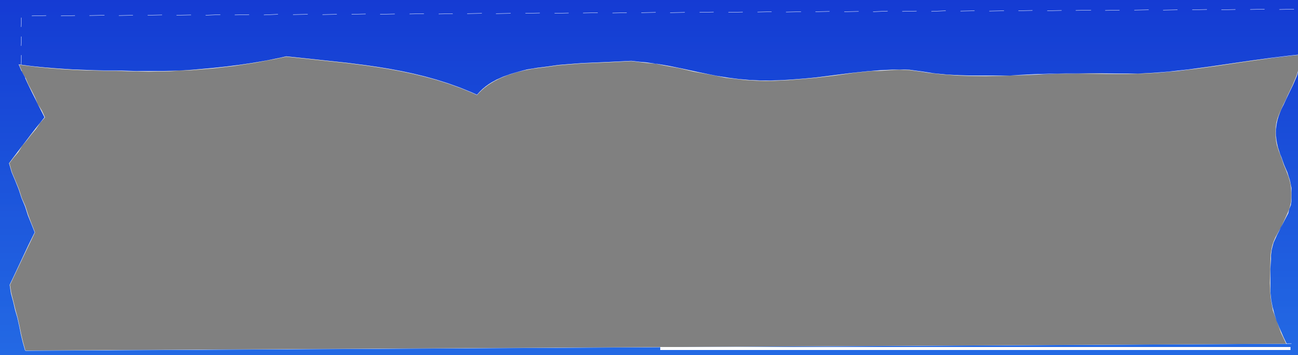
1. General or uniform corrosion
2. Galvanic corrosion
3. De-alloying corrosion
4. Velocity phenomena - erosion corrosion, cavitation, impingement, fretting and FAC
5. Crevice corrosion
6. Pitting corrosion
7. Intergranular corrosion
8. Corrosion fatigue
9. Stress corrosion cracking

Macro Localized Corrosion (items 2–5)

Micro Localized Corrosion (items 6–9)

Microbiological activity can affect all of the above

General Corrosion



- **Mechanism**
- **LWR Case Study Examples:**
  - ♦ **LWR decontamination solutions**
  - ♦ **LWR containment corrosion**
  - ♦ **PWR boric acid corrosion**
  - ♦ **BWR Alloy X-750 corrosion**
  - ♦ **LWR Zr fuel cladding corrosion**

General Corrosion Mechanism

General Corrosion

- Least "dangerous" form of corrosion because it is:
  - ♦ Measurable
  - ♦ Predictable
  - ♦ Can be considered in design, i.e., basis for corrosion allowance
- General corrosion rate tables exist for many alloys in many environments

Example of Corrosion Table

Sandvik Corrosion Table
HCl + $CuCl_2$

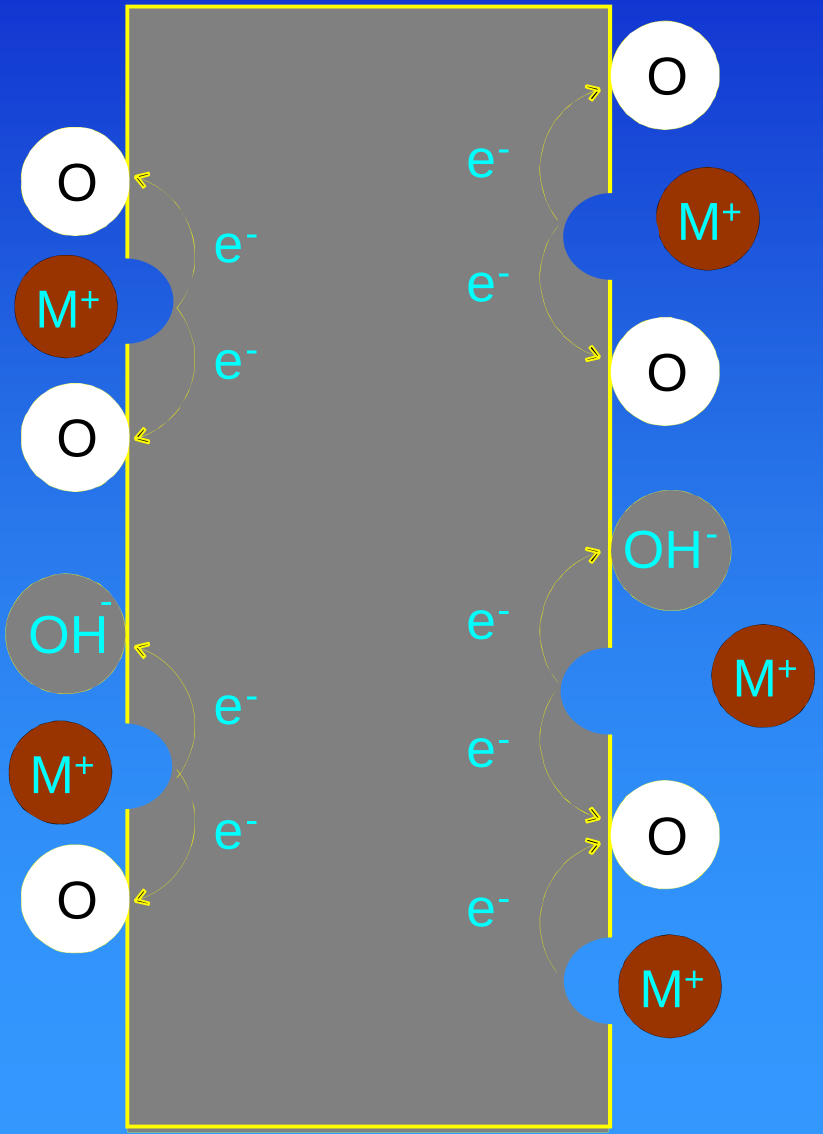
Conc. HCl %	**10**	**10**	**25**	**25**	**37**
Conc. $CuCl_2$ %	**0.05**	**1.5**	**0.05**	**0.05**	**0.05**
Temp. °C	**80**	**Bp**	**25**	**50**	**25**
Carbon Steel	2	2	2	2	2
13% Cr-Steel	2	2	2	2	2
18-2	2	2	2	2	2
18-13-3	2	2	2	2	2
17-14-4	2	2	2	2	2
654 SMO	2	2		1	
Ti	0	0	0	0	2

Symbol	Description
0 =	Corrosion rate less than 0.1 mm/year. The material is corrosion proof.
1 =	Corrosion rate 0.1 – 1.0 mm/year. The material is not corrosion proof, but useful in certain cases.
2 =	Corrosion rate over 1.0 mm/year. Serious corrosion. The material is not usable.
p, P =	Risk (Severe risk) of pitting and crevice corrosion.
c, C =	Risk (Severe risk) of crevice corrosion. Used when there is a risk of localized corrosion only if crevices are present. Under more severe conditions, when there is also a risk of pitting corrosion, the symbols p or P are used instead.
s, S =	Risk (Severe risk) of stress corrosion cracking.
ig =	Risk of intergranular corrosion.
BP =	Boiling solution.
ND =	No data. (Used only where there are no actual data to estimate the risk of localized corrosion instead of p or s).

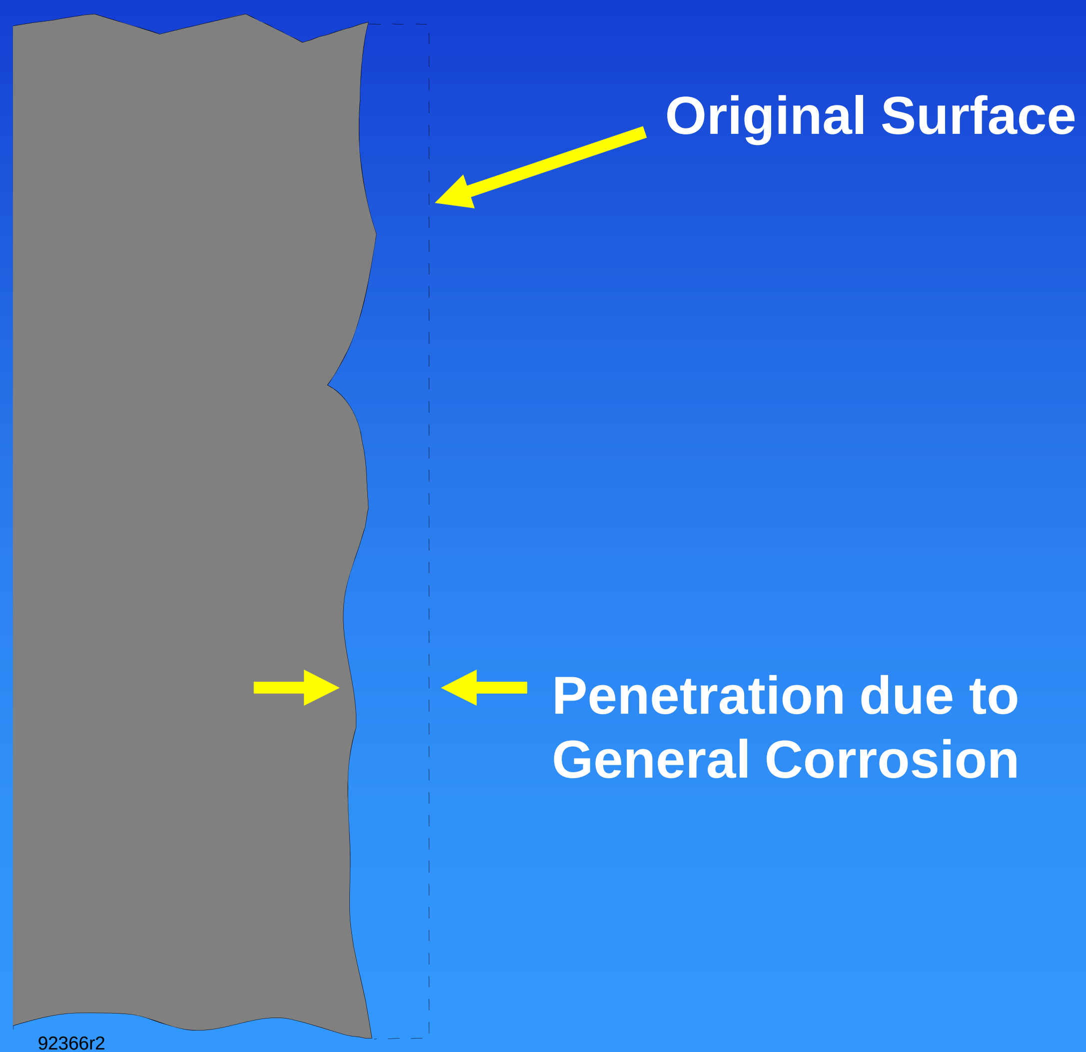
General Corrosion

- Movement (nearly continuous movement) of anodes and cathodes (salt drop experiment – early stage)
- ~ Uniform thinning – but not really on a microscopic scale
- Weight loss or gain per unit area with time and change in thickness with time are measured

General Corrosion - Schematic



General Corrosion Surface Penetration

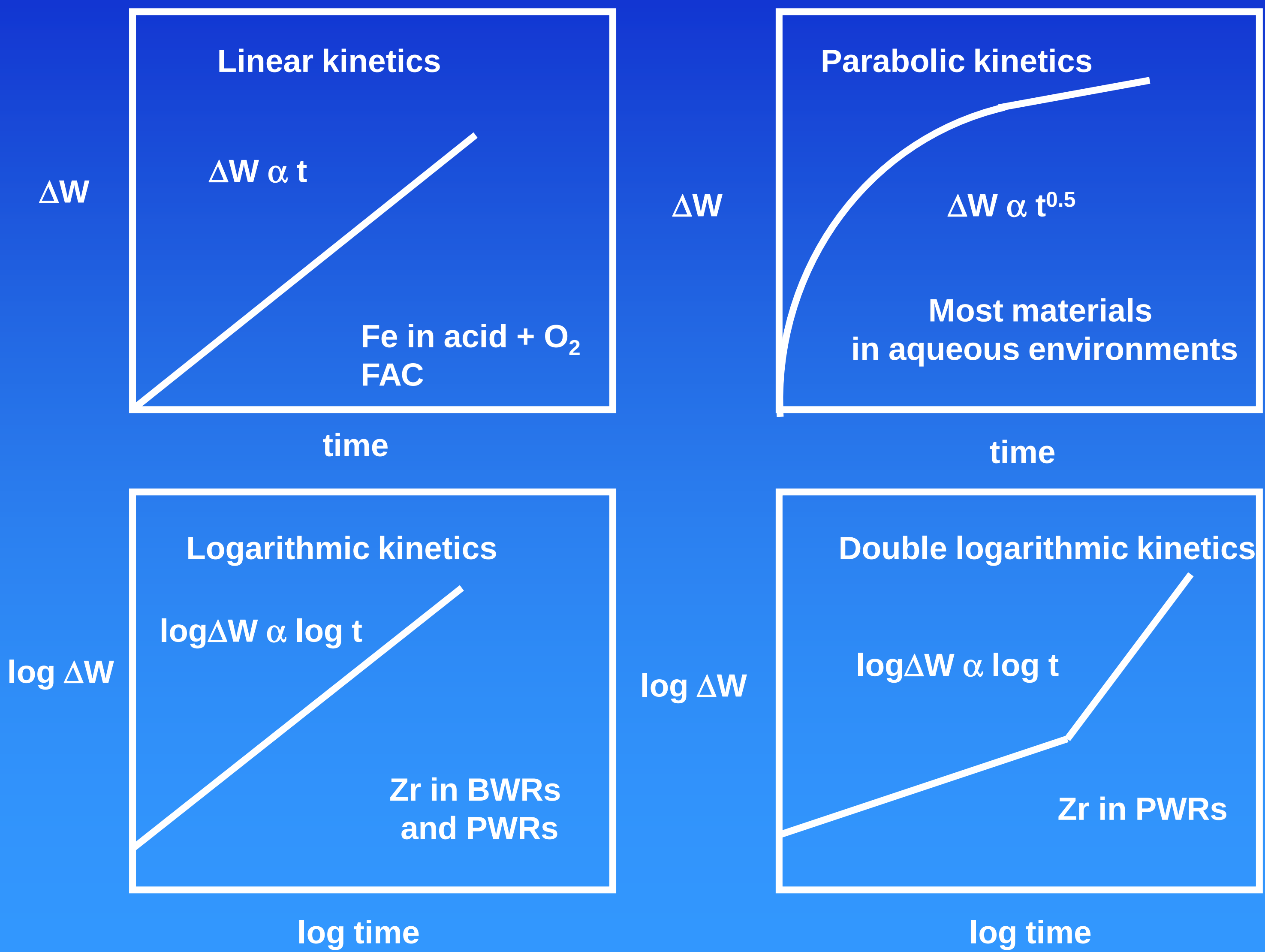


Sheet Metal (Steel) Roof

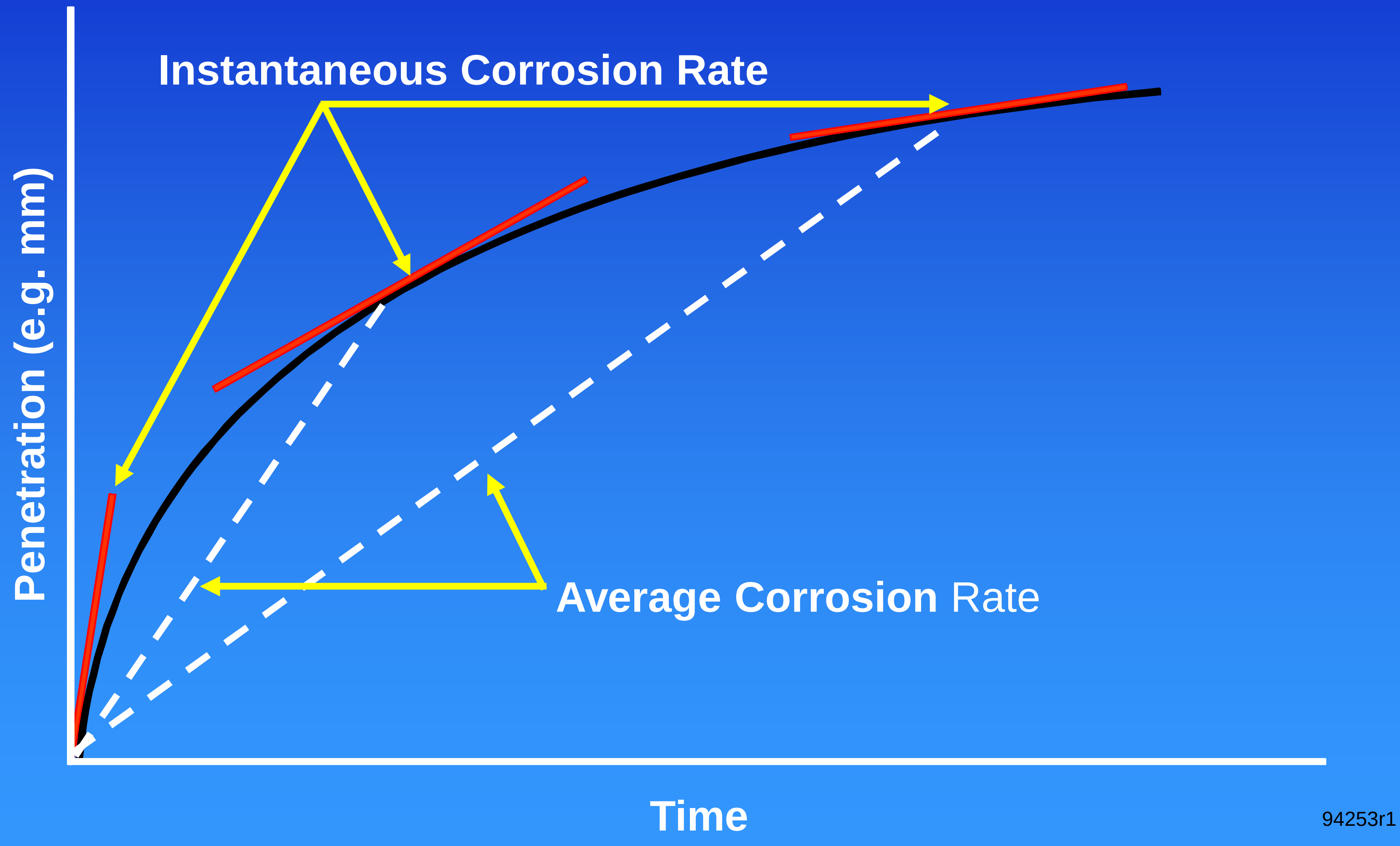
Drill Bits - Midway Island

Atmospheric Corrosion of Corten™ in San José, CA

General Corrosion Kinetics



Instantaneous vs. Average General Corrosion Rate



Structural Integrity Associates

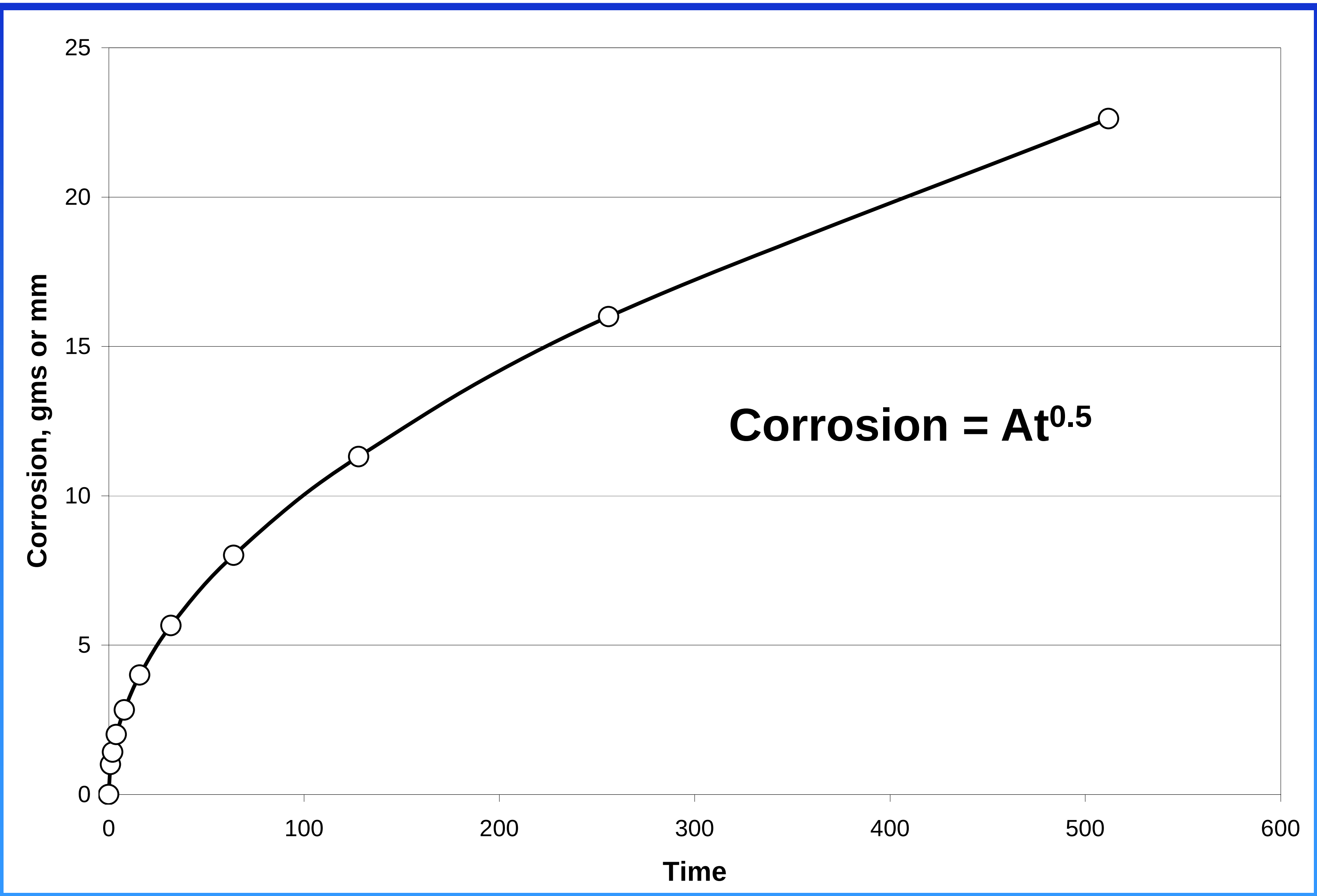
Example of the Dangers of Short-term General Corrosion Testing

Weight Change Data for A533-Gr. B Tested at High Temperature and Pressure in a Room Temperature-Saturated Boric Acid Solution (9090-wppm B) under Hydrogen Cover Gas

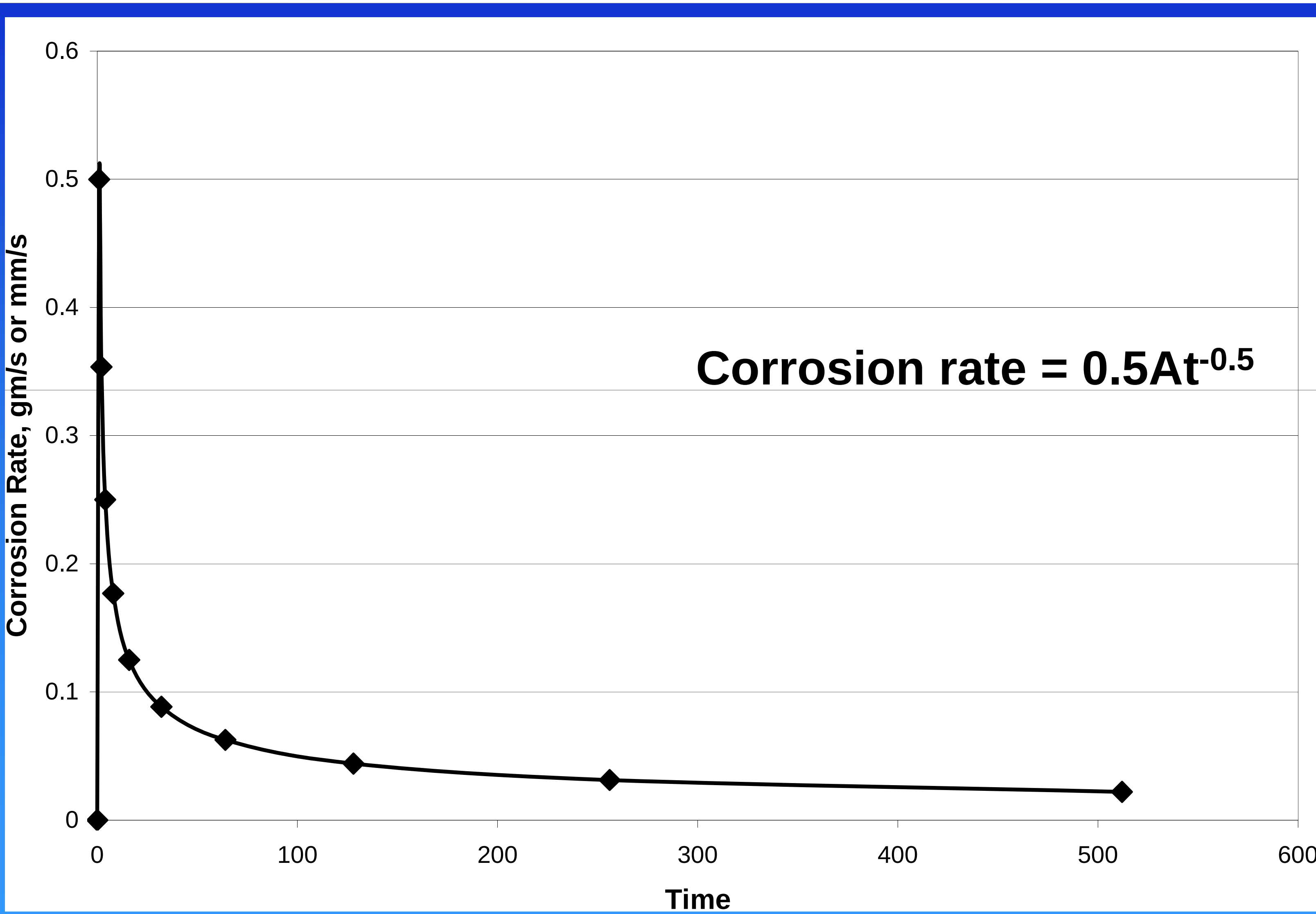
Temperature, Time	Sample Code	Wi (g)	Wf (g)	ΔW (g) = (Wi-Wf)	CR (mm/y)	Average CR (mm/y)
316°C, 24 h	LAS-1	0.27147	0.27128	0.00019	0.112	0.12
	LAS-2	0.26854	0.26834	0.00020	0.118	
	LAS-3	0.27466	0.27444	0.00022	0.129	
	LAS-4	0.27178	0.27158	0.00020	0.118	
316°C, 91 h	LAS-5	0.27667	0.27649	0.00018	0.0279	0.04
	LAS-6	0.27212	0.27181	0.00031	0.0481	
	LAS-7	0.26586	0.26554	0.00032	0.0497	
	LAS-8	0.27800	0.27780	0.00020	0.0310	
288°C, 24 h	LAS-9	0.27531	0.27485	0.00046	0.271	0.41
	LAS-10	0.30749	0.30668	0.00081	0.477	
	LAS-11	0.32178	0.32110	0.00068	0.400	
	LAS-12	0.24150	0.24068	0.00082	0.483	
250°C, 24 h	LAS-13	0.15433	0.15388	0.00045	0.265	0.26
	LAS-14	0.30678	0.30631	0.00047	0.277	
	LAS-15	0.27755	0.27702	0.00053	0.312	
	LAS-16	0.27583	0.27554	0.00029	0.171	

NUREG/CR-6875, 7/05

General Corrosion Following Parabolic Kinetics – Diffusion Contolled



General Corrosion Rate for Parabolic Kinetics



Convenient General Corrosion Conversion Factors

- To obtain mils per year (mpy) from mg/decimeter/day (mdd) multiply mdd by 1.437/ρ (ρ = density in g/cm^3)
- To obtain mdd from mpy multiply mpy by 0.696 x ρ

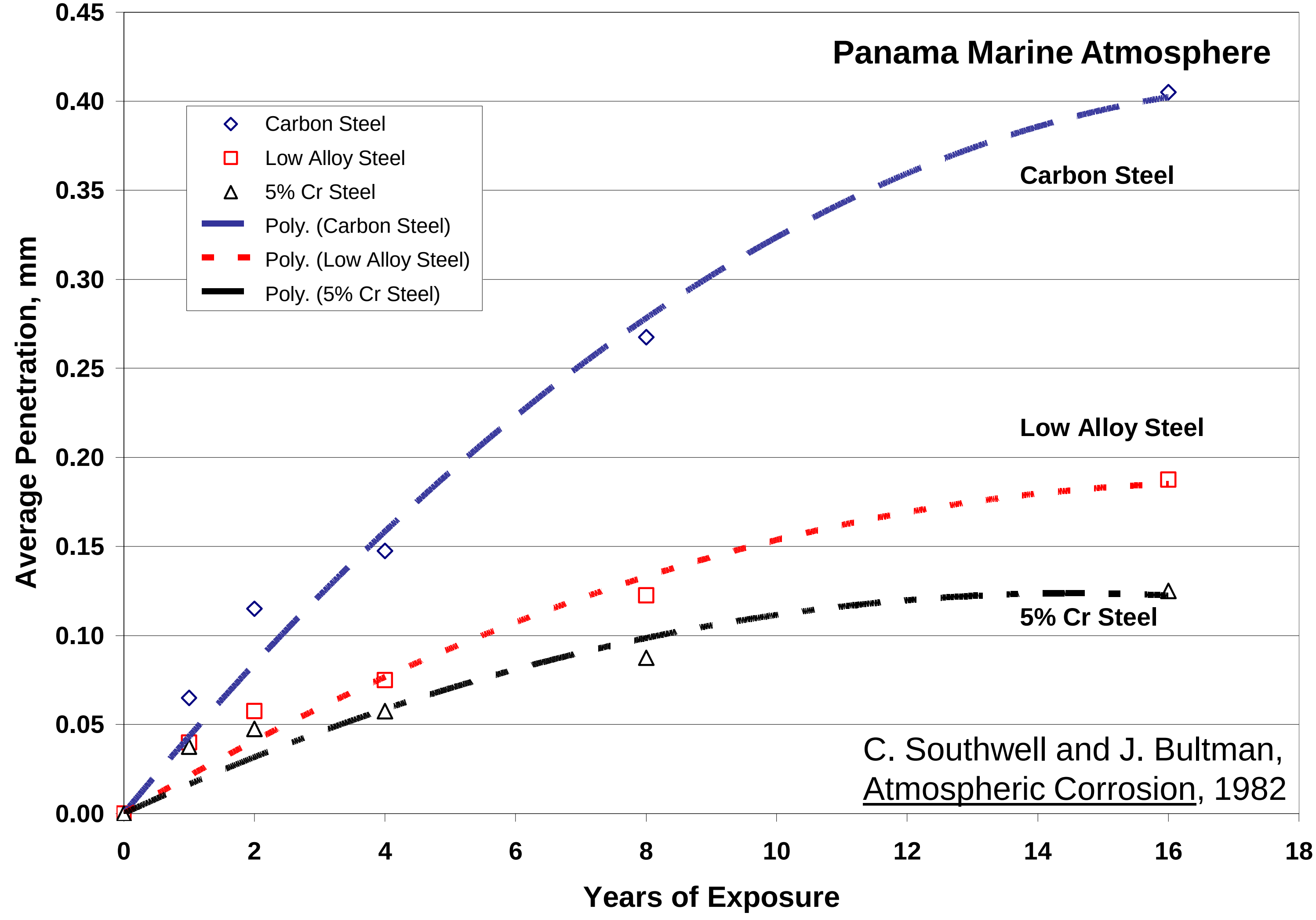
Selected LWR Alloy Densities, g/cm^3

304/L 7.94	LAS 7.85	A600 8.47	A625 8.44
316/L 7.98	CF3/8 8.02	A690 8.19	Zn 7.13
CS 7.86	A800 7.95	X-750 8.28	Zr 2/4 6.55

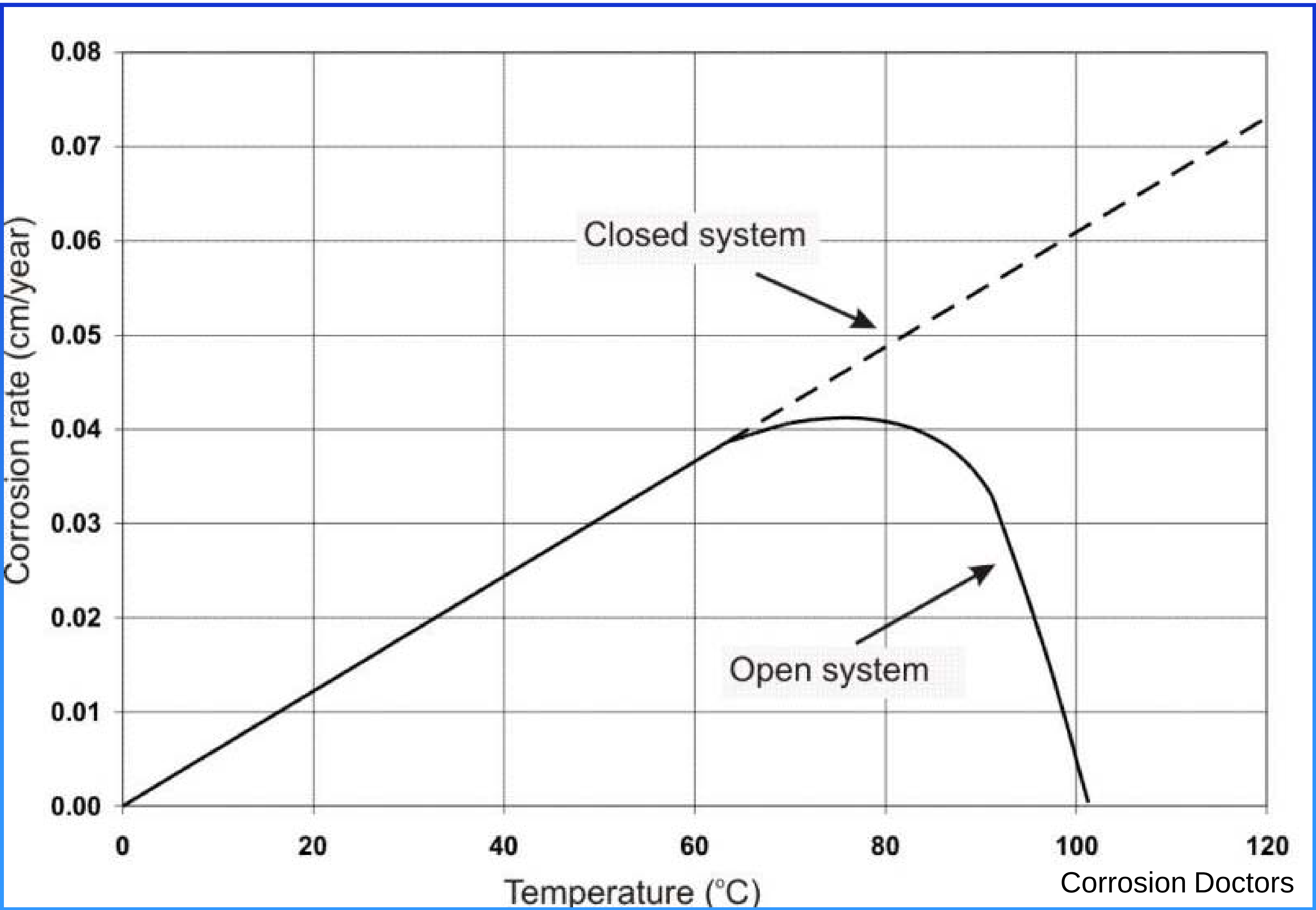
- 1 mm/s = 141.73 in/h
- 1 mpy = 1.14 x 10^{-7} in/h

} Also, used for crack propagation conversions

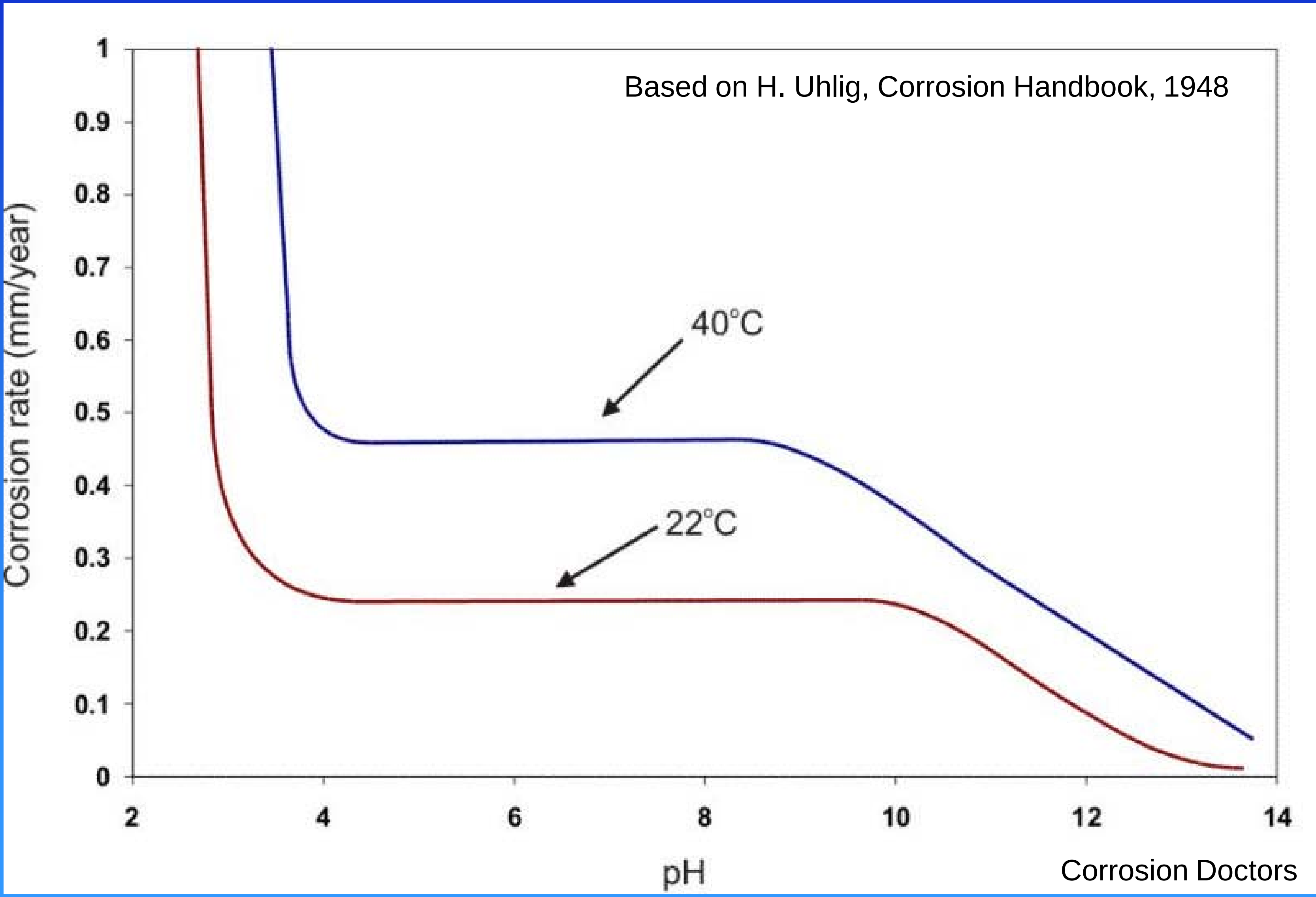
Effect of Alloying Content on General Corrosion Kinetics



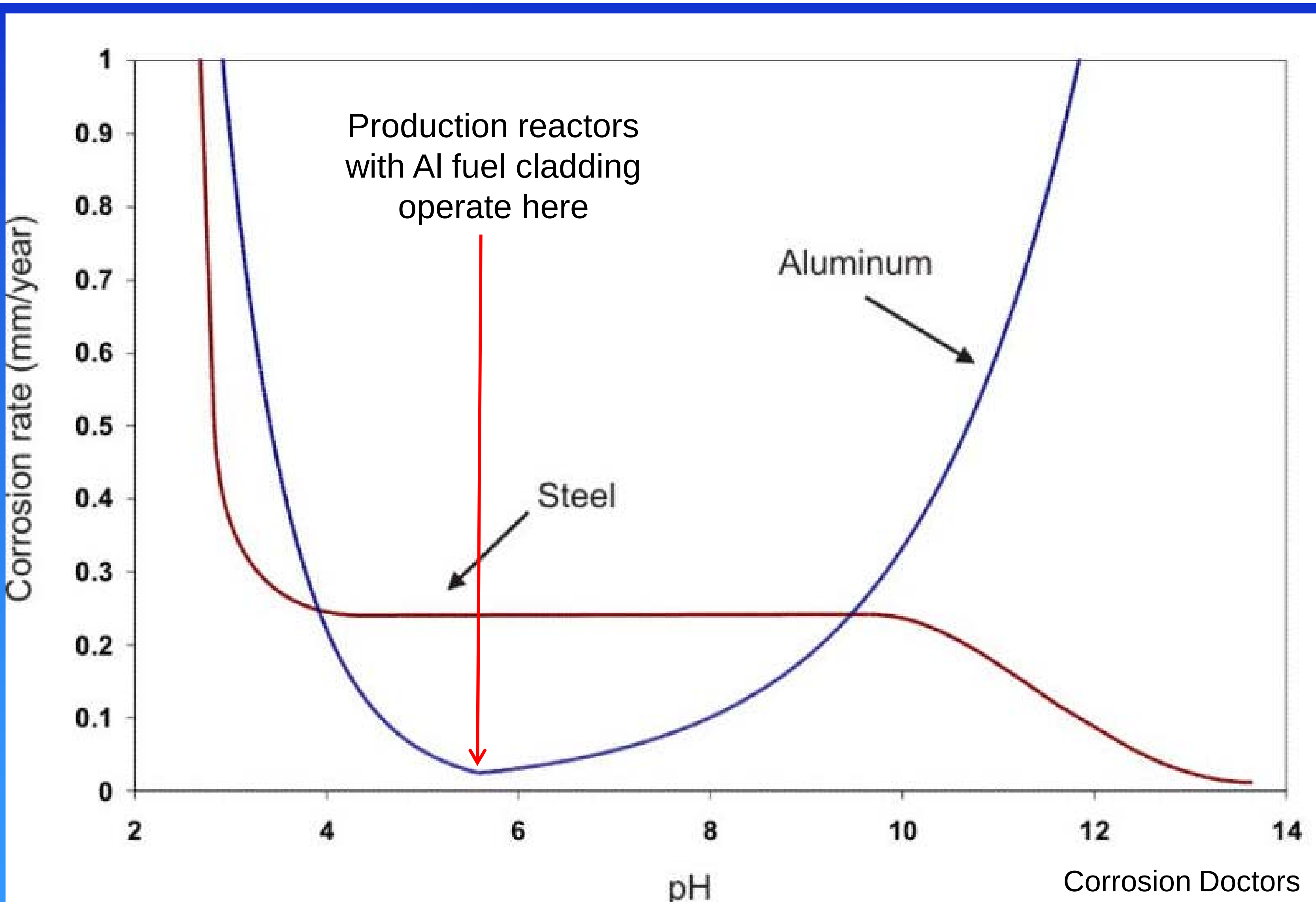
Effect of Temperature on CS General Corrosion Kinetics – Open vs. Closed System



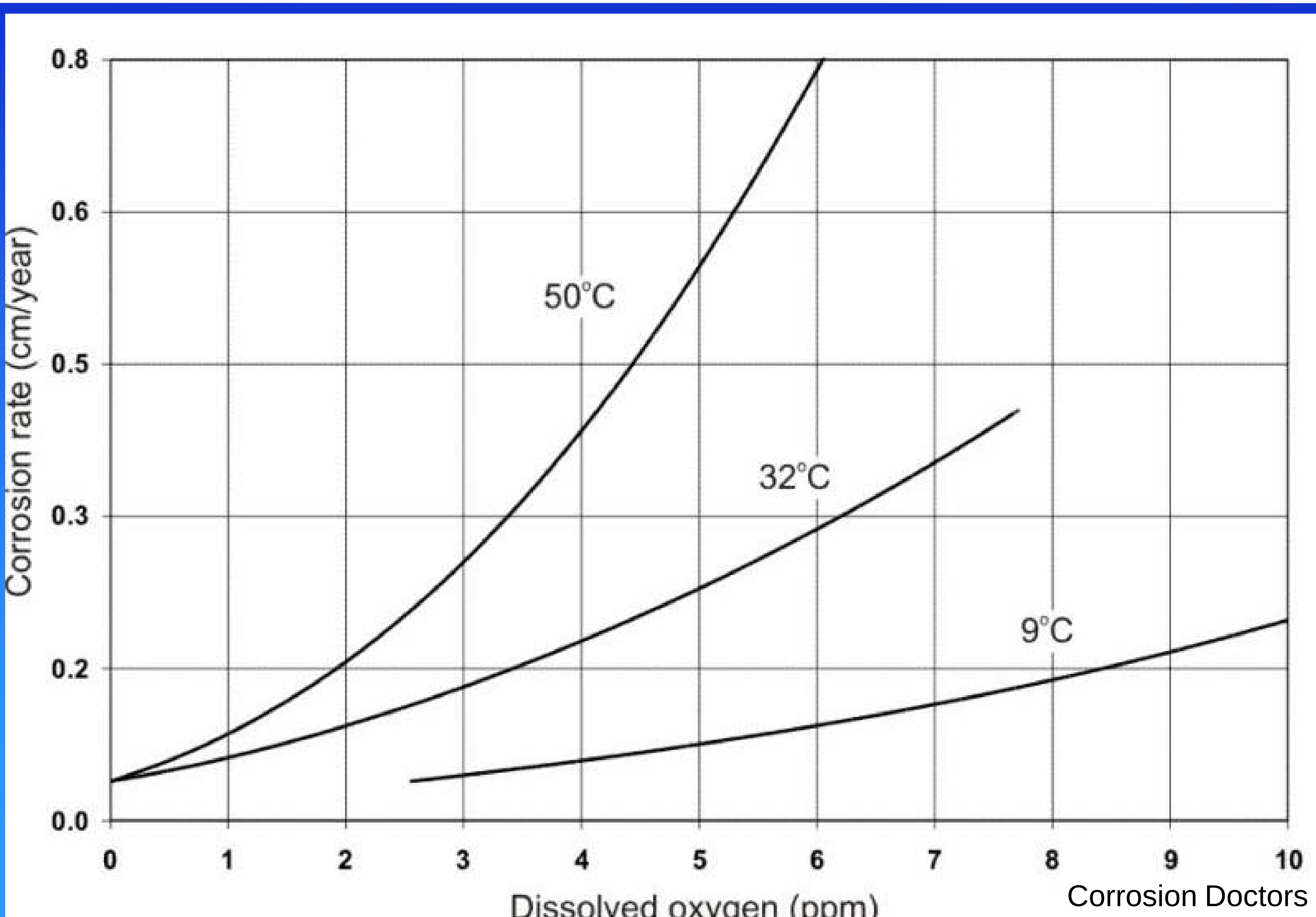
Effect of pH on CS Corrosion in 5 ppm Dissolved Oxygen



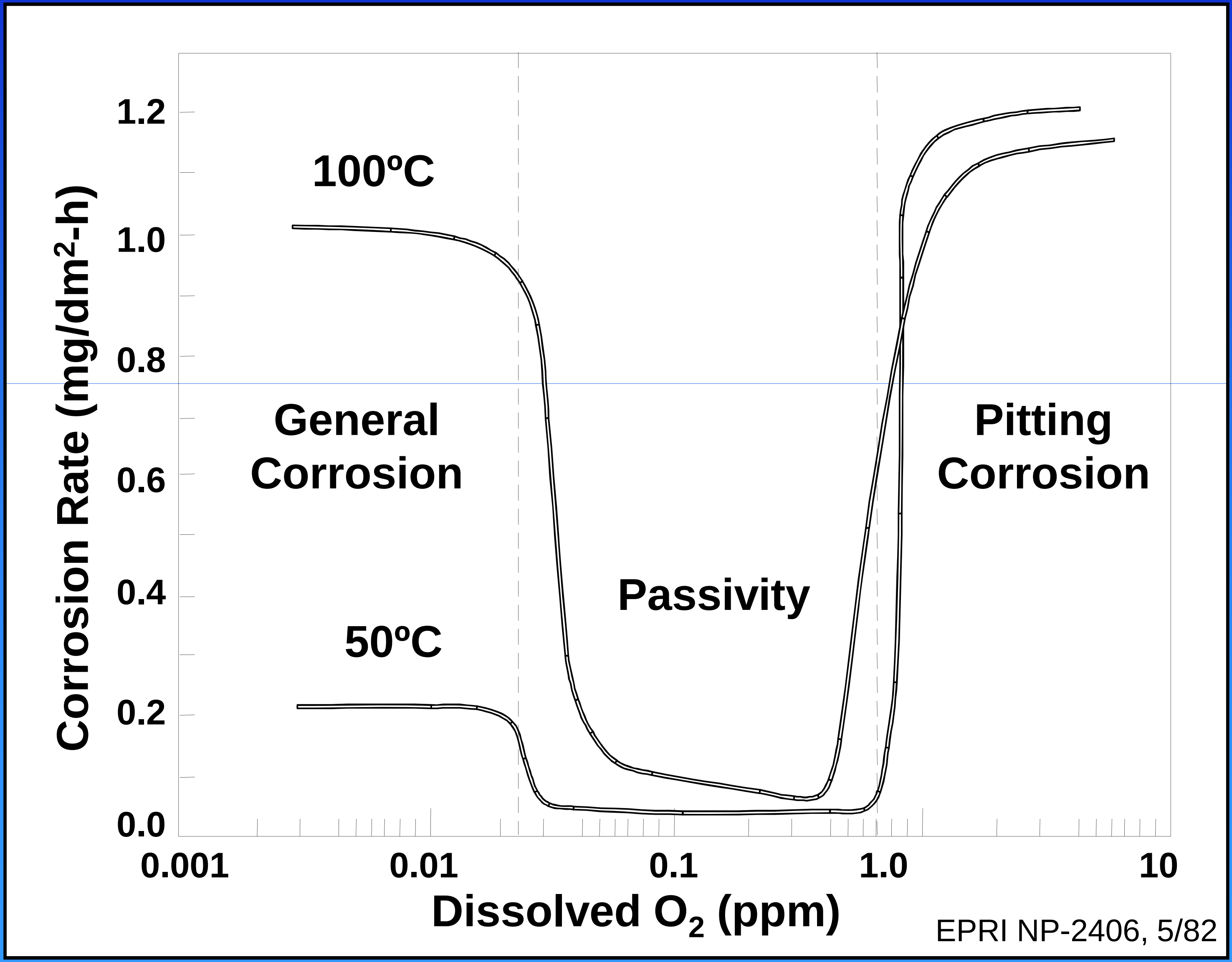
Corrosion of Steel and Al vs. pH at 22ºC



Effect of DO and Temperature on Corrosion of Carbon Steel in Tap Water



Corrosion Rates of Carbon Steel in High Purity Neutral Water at 50 and 100°C



General Corrosion in LWRs Case Studies

Decontamination Solutions

Decontamination Solutions

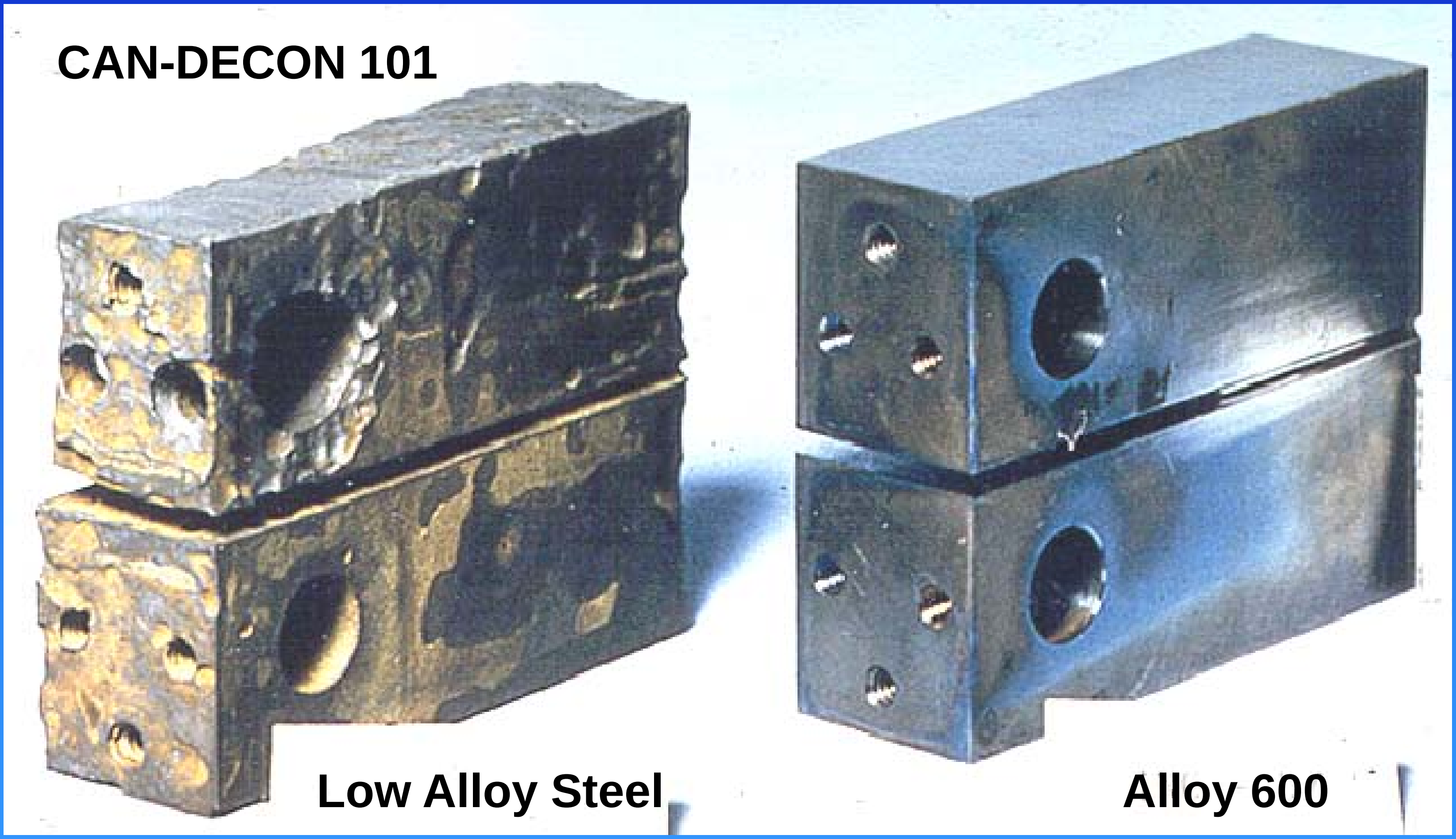
- By definition, all decontamination solutions have to be “corrosive” to be able to remove contaminated oxides from the metal surfaces
- Need to balance corrosion/removal of contaminated, but protective oxides, without affecting the base metal
- Most popular agents are:
  - LOMI – vanadous picolinate
  - CAN-DEREM – organic acids
  - CITROX – citric and oxalic acids
  - CORD – permanganic/oxalic acids

Chris Wood
of LOMI fame

Oxidation Decontamination Processes

- Oxides produced in HWC + Zn BWRs and PWRs are so adherent that special oxidation steps must be taken prior to introduction of the decontamination solution
- Again, need to balance corrosion/removal of contaminated, but protective oxides without affecting the base metal
- Most popular oxidizing agents are:
  - AP – alkaline permanganate (e.g., potassium permanganate and sodium hydroxide)
  - NP – nitric permanganate (e.g., potassium permanganate and nitric acid)

Decontamination Solution Corrosion



Containment Corrosion

Some NRC Containment Corrosion Documents

- BL-80-24 - Prevention of Damage Due to Water Leakage Inside Containment (October 17, 1980 Indian Point 2 Event)
- IN2010-12 - Containment Liner Corrosion
- IN04009 - Corrosion of Steel Containment and Containment Liner
- IN97010 - Liner Plate Corrosion in Concrete Containments
- IN89079S1 - Degraded Coatings and Corrosion of Steel Containment Vessels
- IN89079 - Degraded Coatings and Corrosion of Steel Containment Vessels
- IN88082S1 - Torus Shells with Corrosion and Degraded Coatings in BWR Containments
- IN88082 - Torus Shells with Corrosion and Degraded Coatings in BWR Containments
- IN86099S1 - Degradation of Steel Containments
- IN86099 - Degradation of Steel Containments

Containment Corrosion

- Corrosion in BWR sand cushion and LWR containment floor-containment liner interface
- Revealed by inspections of free standing metallic containment and containment liner plates

Containment Corrosion History

- 1980 – Oyster Creek – Water identified in sand bed drains leads to corrosion of drywell
- 1992 – Robinson 2 – Discoloration of vertical portion of containment liner at an insulation joint
- 1992 – Beaver Valley 1 and Trojan (not operating) – Peeled coating and spots of liner corrosion
- 1993 – Brunswick 1 and 2 – Corrosion of the drywell liner at various spots at the junction of the base floor and the liner
- 1993 – Salem 2 – Minor corrosion of the containment liner
- 1998 – D. C. Cook 1/2 – "pitting" of the containment liner at moisture barrier seal areas

Containment Corrosion History

- 1999 – Brunswick 2 & 3 – through-wall corrosion in drywell liner. One hole due to leather work glove buried in the concrete other two holes were adjacent to wood buried in the concrete
- 2001 – Dresden 2 – corrosion in area of missing coating encircling the drywell shell adjacent to the basement floor
- 2001 – D. C. Cook – Through-wall hole in containment liner plate due to wire brush handle in concrete at the interface with the liner
- 2002 – Sequoyah 2 – Areas of steel containment vessel with degraded coatings and rust

Containment Corrosion History (continued)

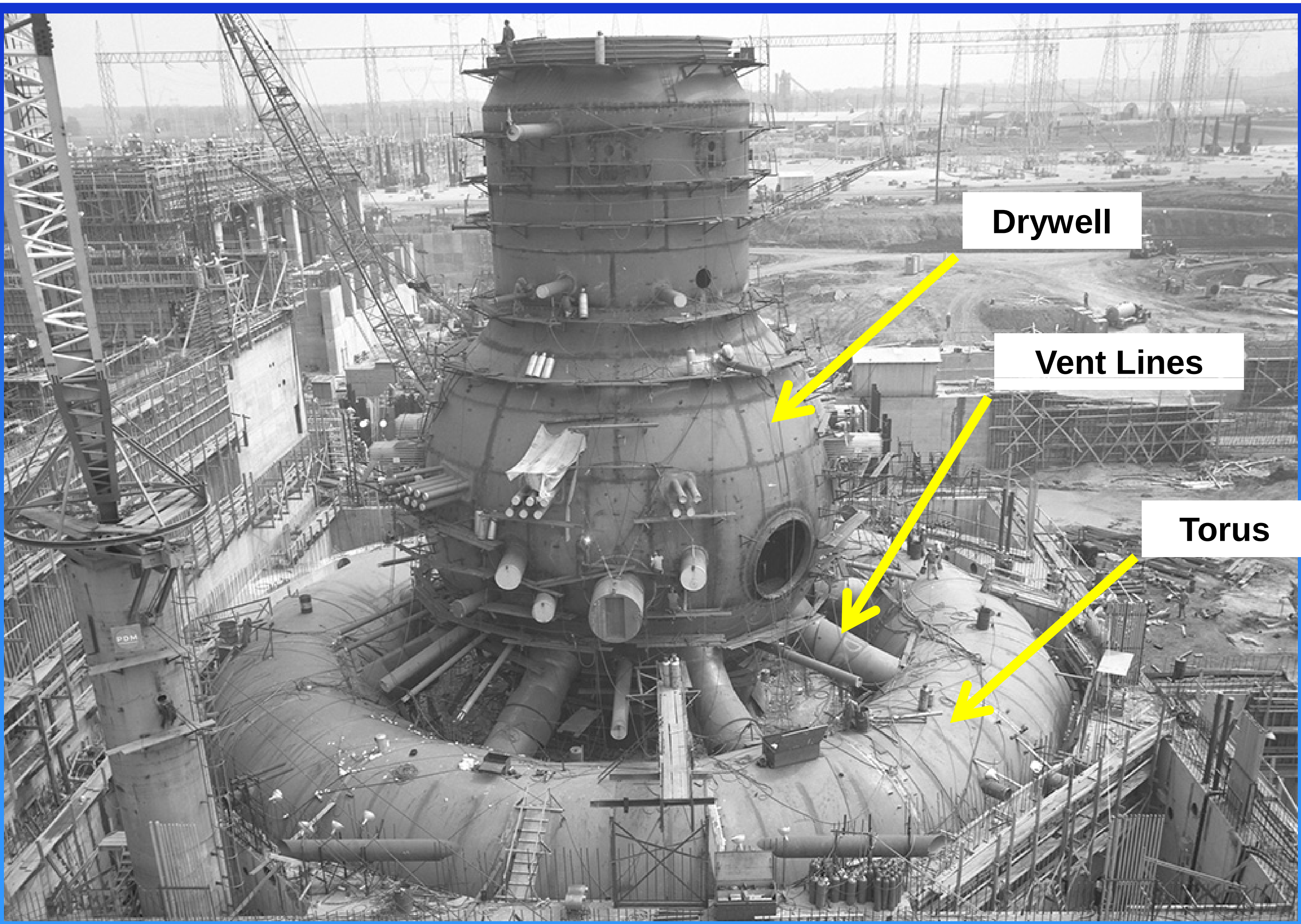
- 2002 – Davis-Besse – Corrosion at containment floor interface
- 2003 – Surry 2 – Degraded coatings and rust on containment liner at junction of metal liner and interior concrete floor
- 2008 – Brunswick 1 – Corrosion under wet felt covering primary containment penetration sleeve
- 2007 – Three Mile Island 1 – Corrosion at defective moisture barrier seal between the containment and concrete floor
- 2009 – Beznau – Corrosion on both sides of steel containment below concrete floor

Containment Corrosion History (continued)

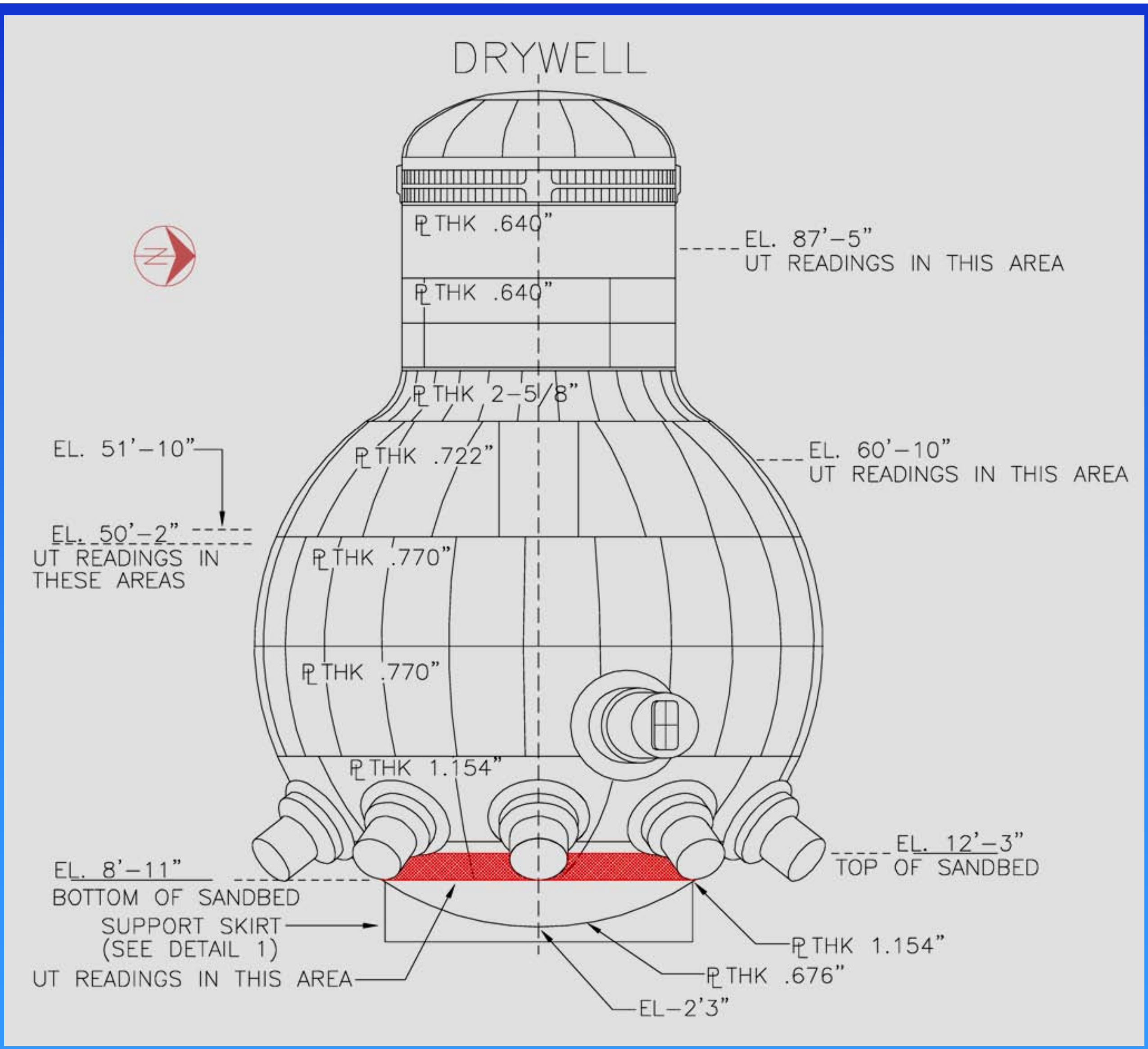
- 2009 – Salem 2 – Corrosion at defective moisture barrier seal between the containment and concrete floor
- 2009 – Beaver Valley 1 – Through-wall containment corrosion under blistered paint and rust due to buried wood in concrete
- 2010 – Turkey Point 3 – Through-wall corrosion of containment sump liner

Oyster Creek Drywell Corrosion

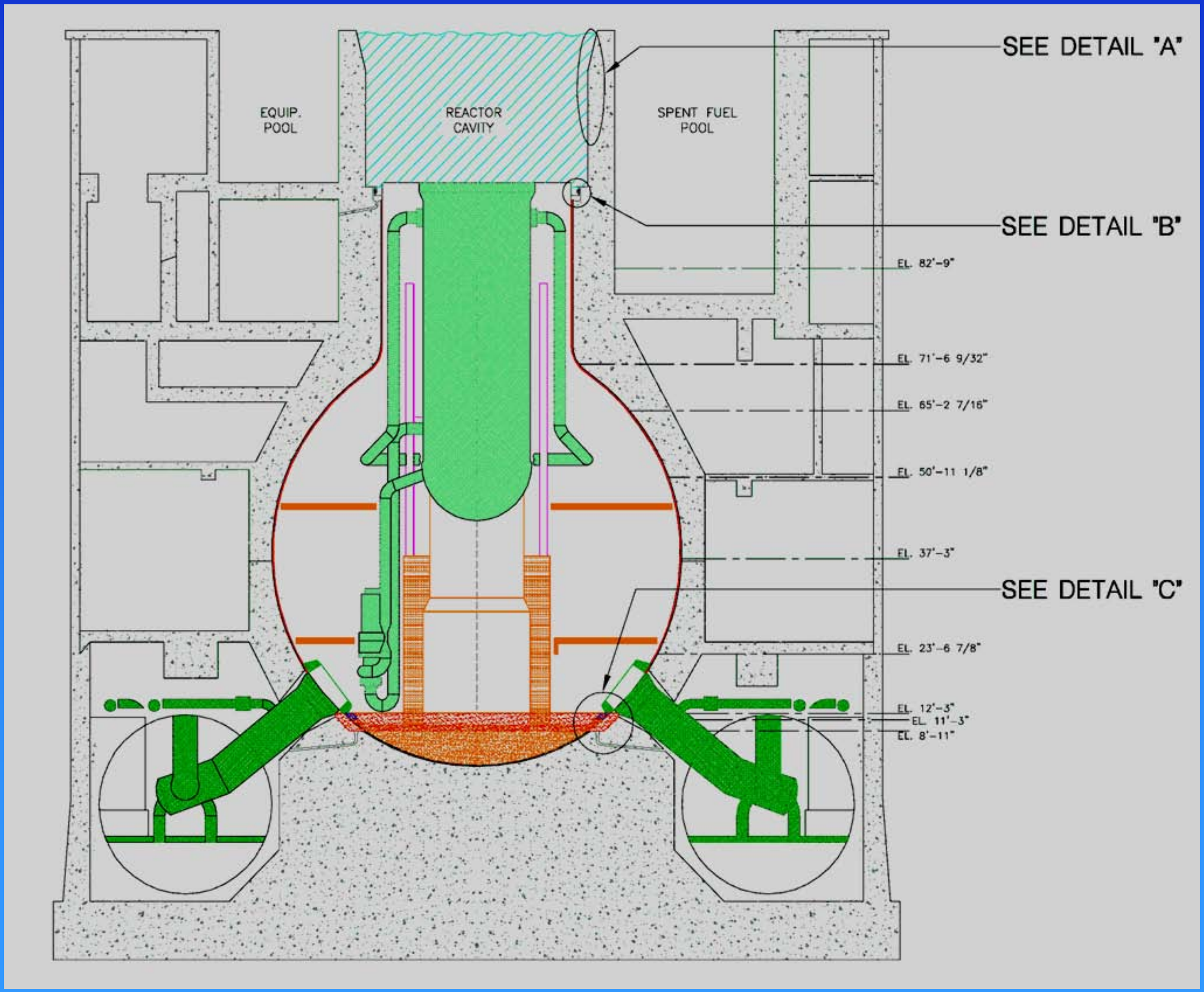
BWR Mark 1 Containment (1966)



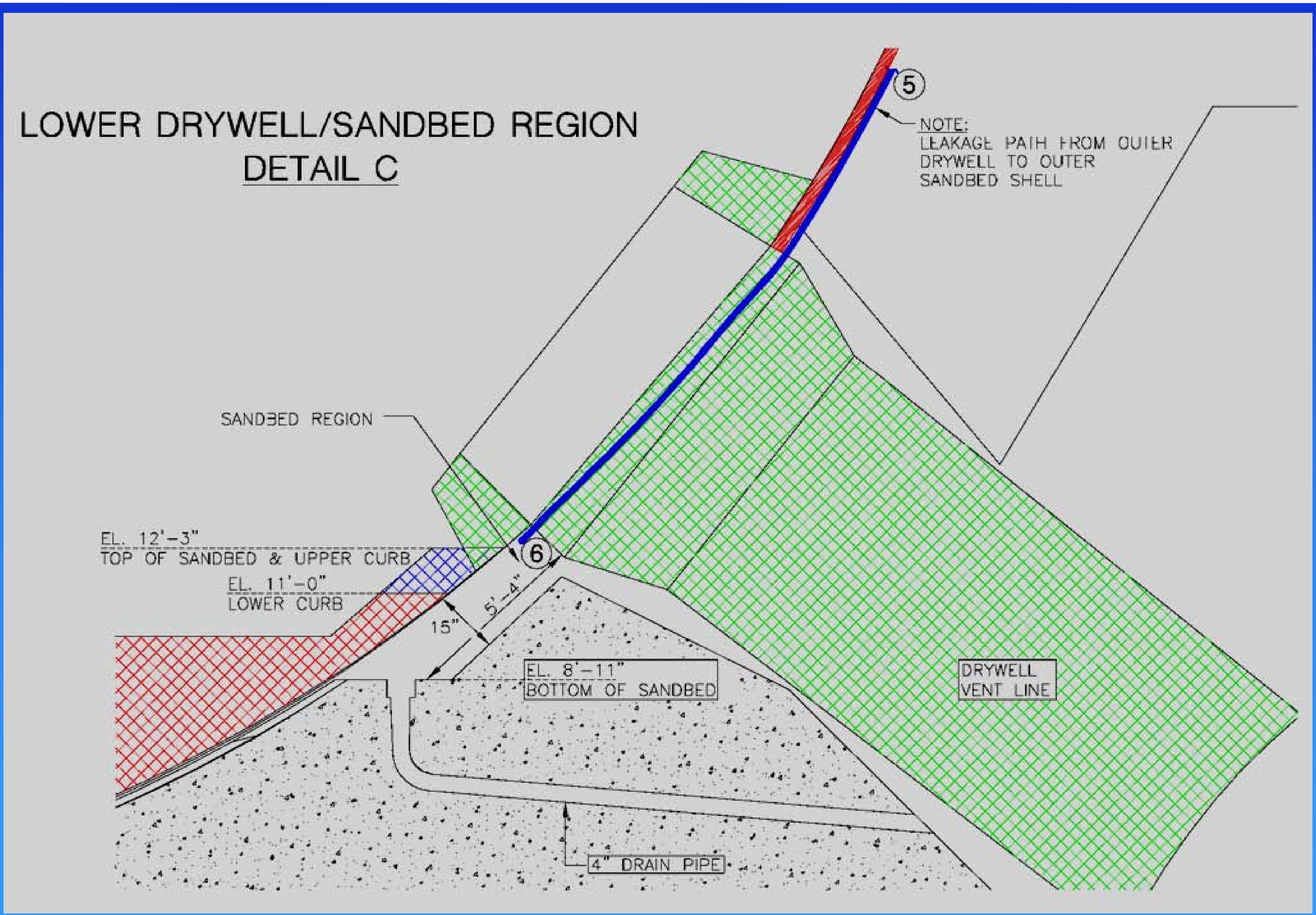
General Corrosion of Oyster Creek Mark 1 Containment Drywell



General Corrosion of Oyster Creek Mark 1 Containment Drywell

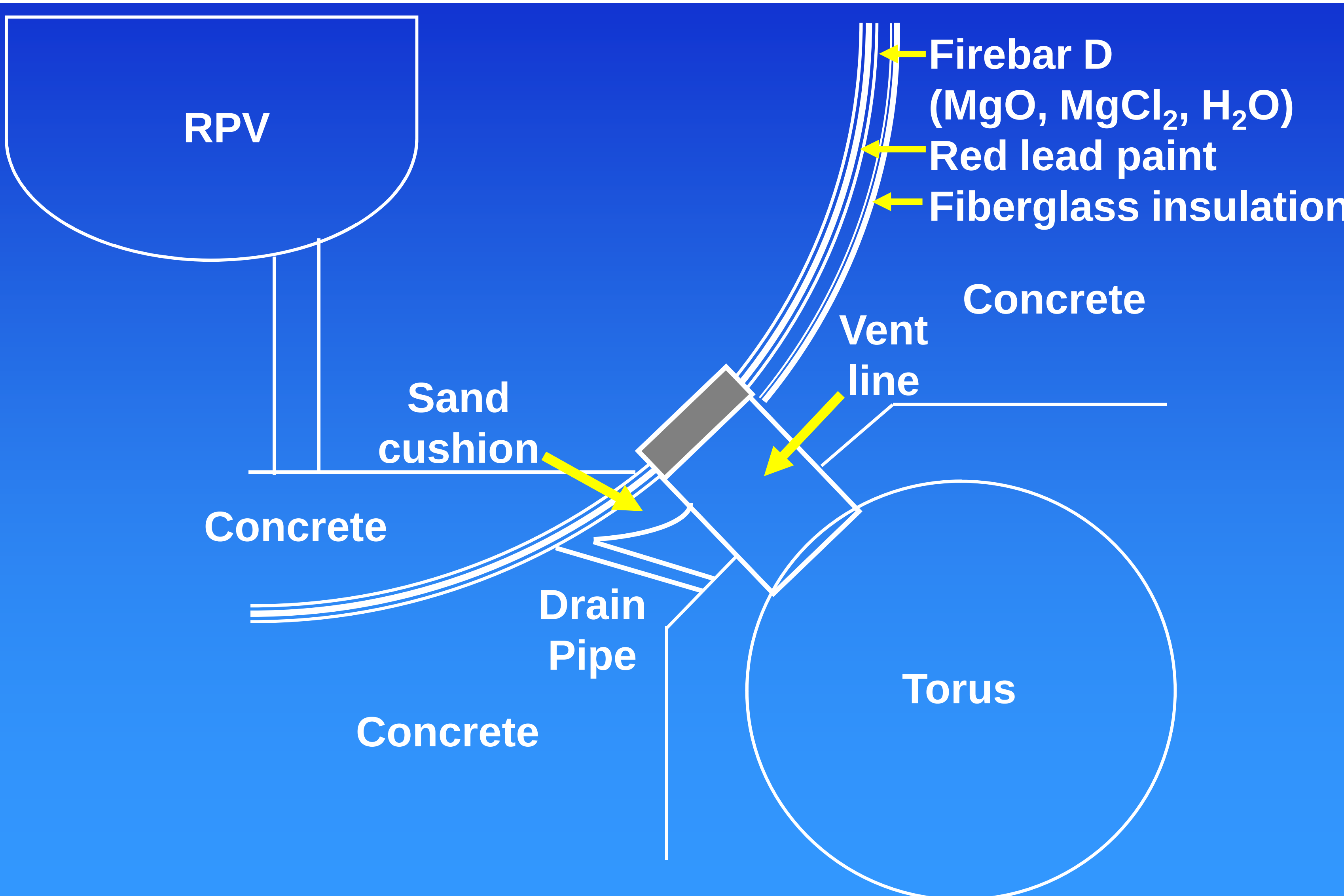


Detail of Oyster Creek Sand Bed

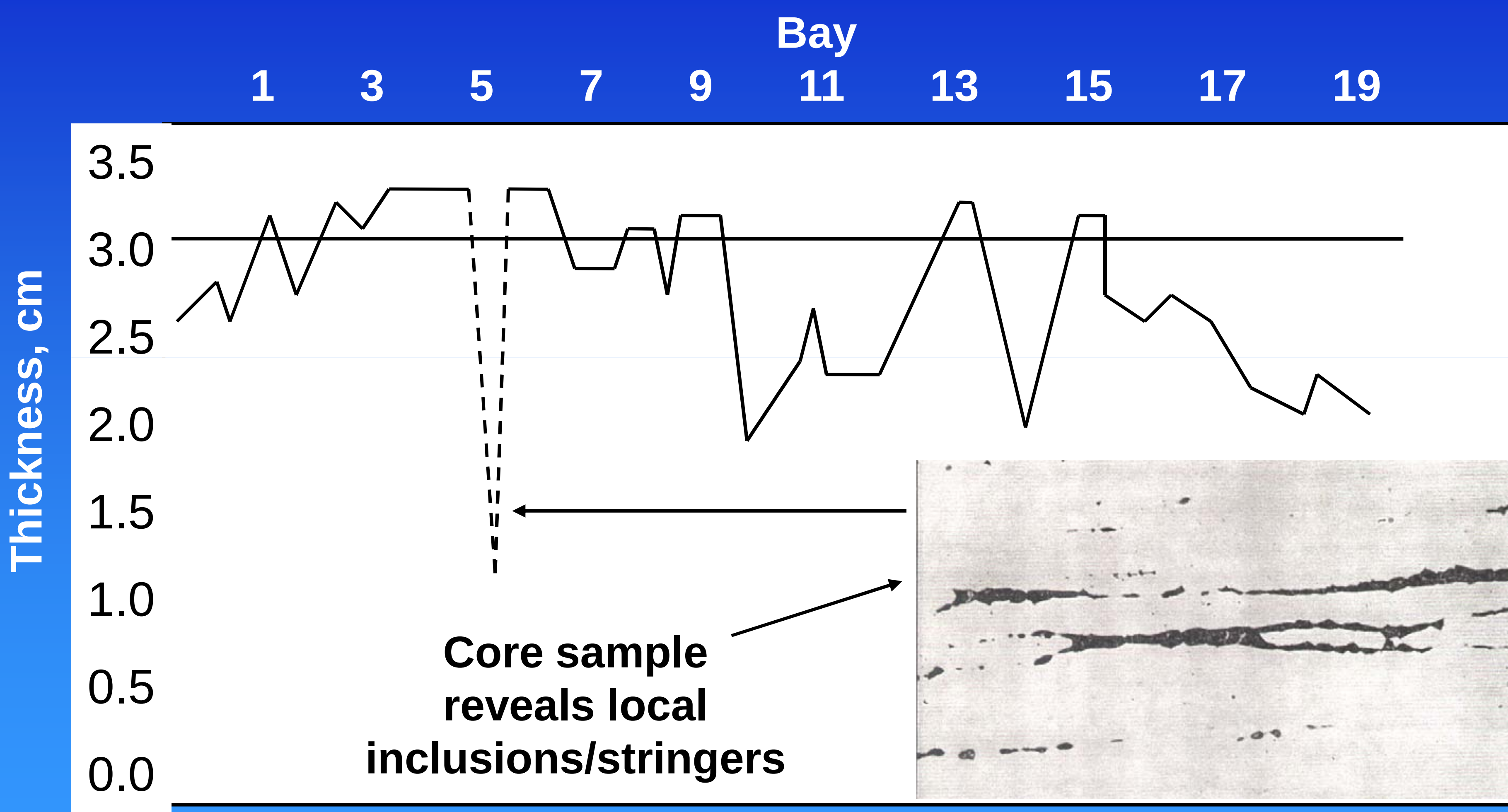


Structural Integrity Associates

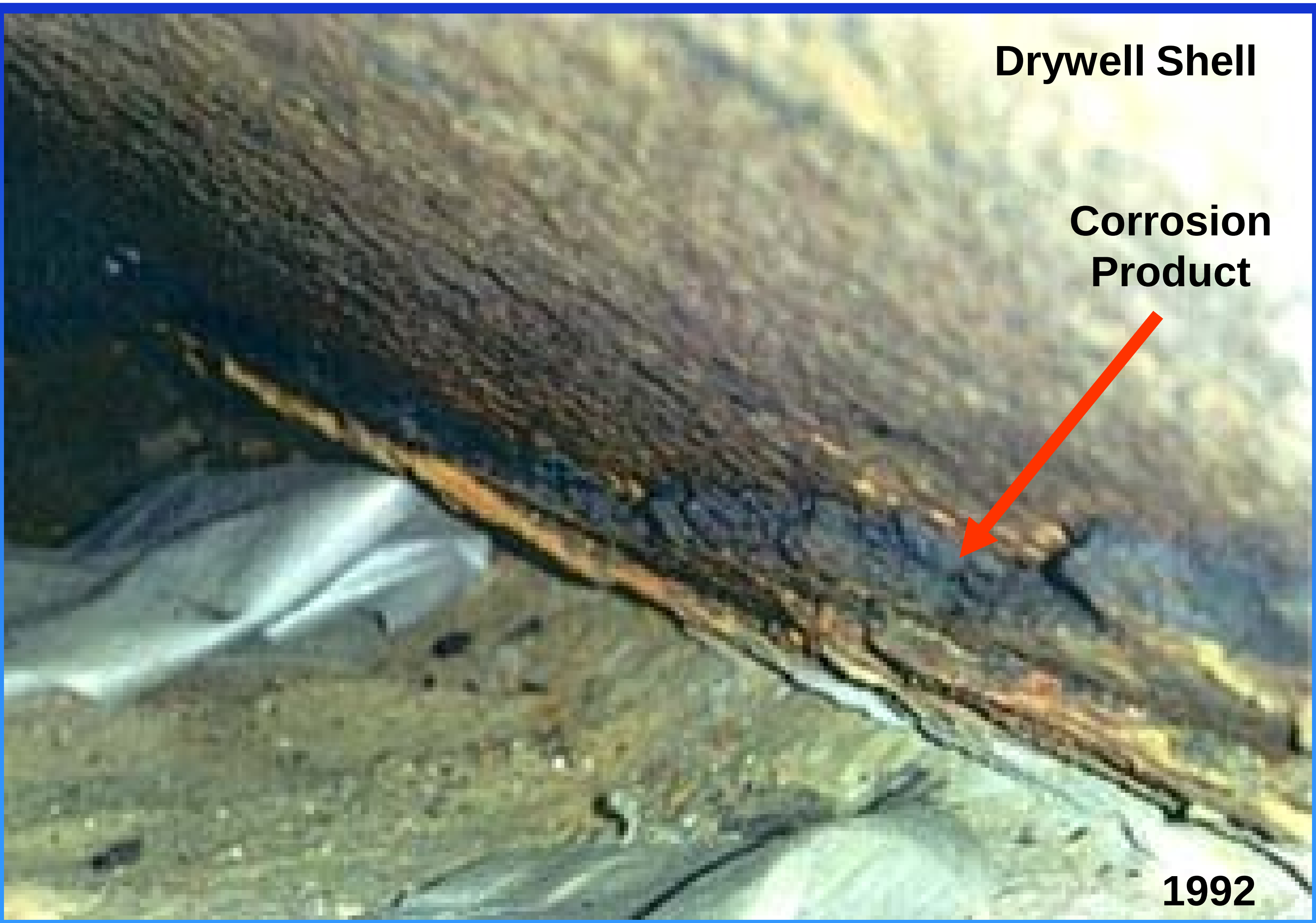
BWR Mark 1 Containment
Sand Cushion at Oyster Creek



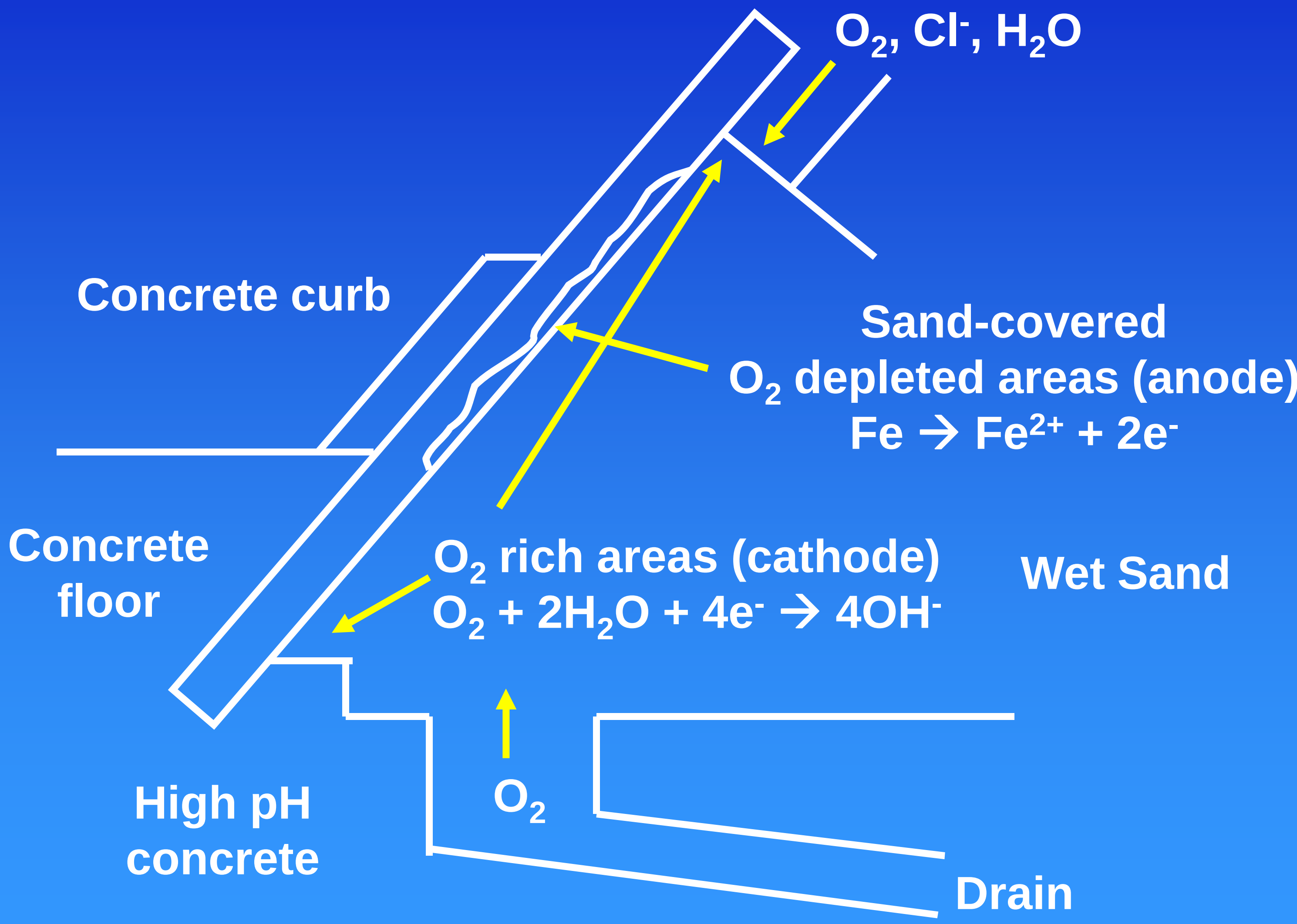
UT Thickness Measurements on Carbon Steel in Sand Region



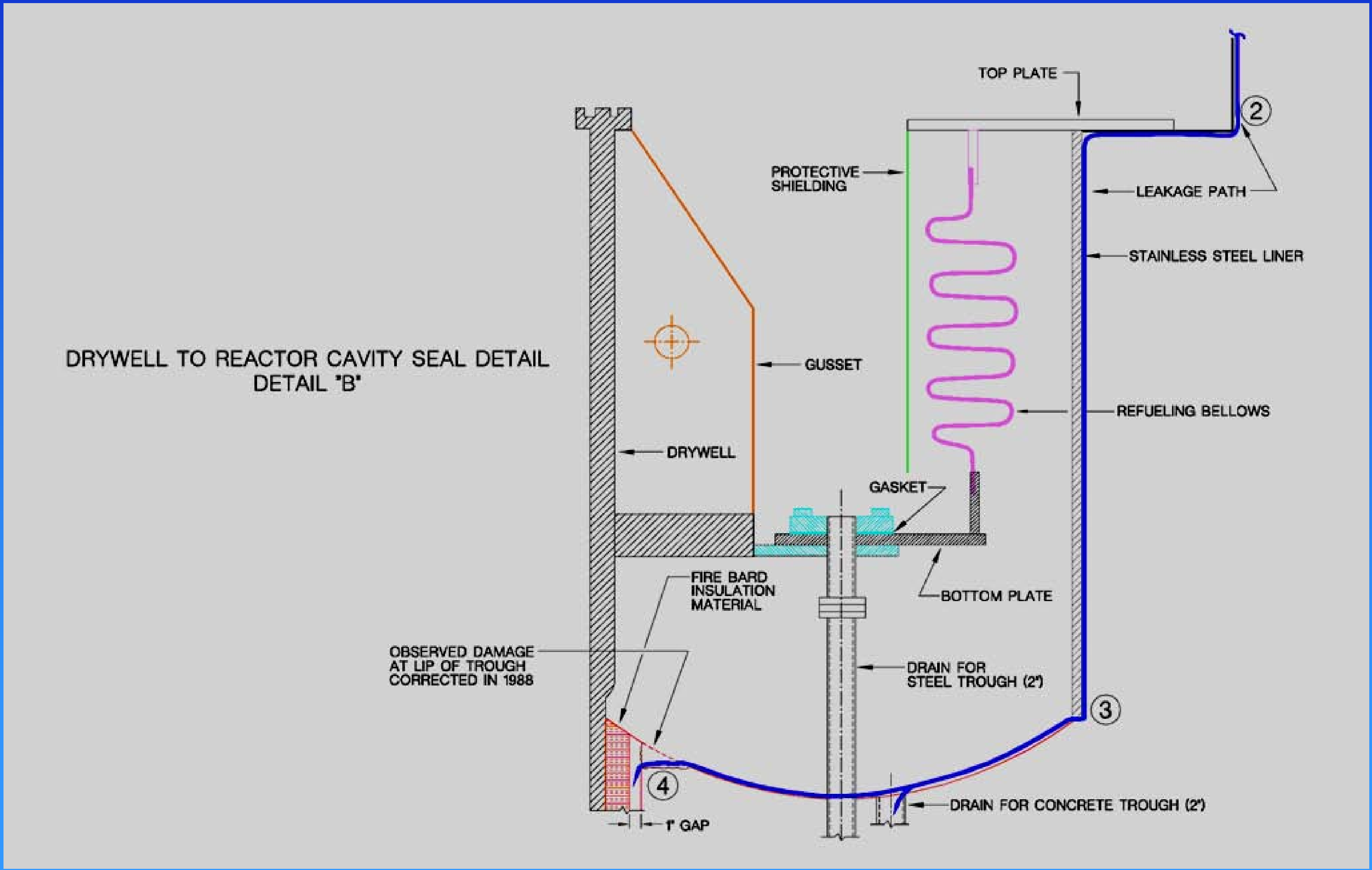
Oyster Creek Sand Bed Region



Corrosion Mechanism of OC Drywell



Oyster Creek – Drywell to Cavity Seal



Corrosion and Corrosion Control in LWRs

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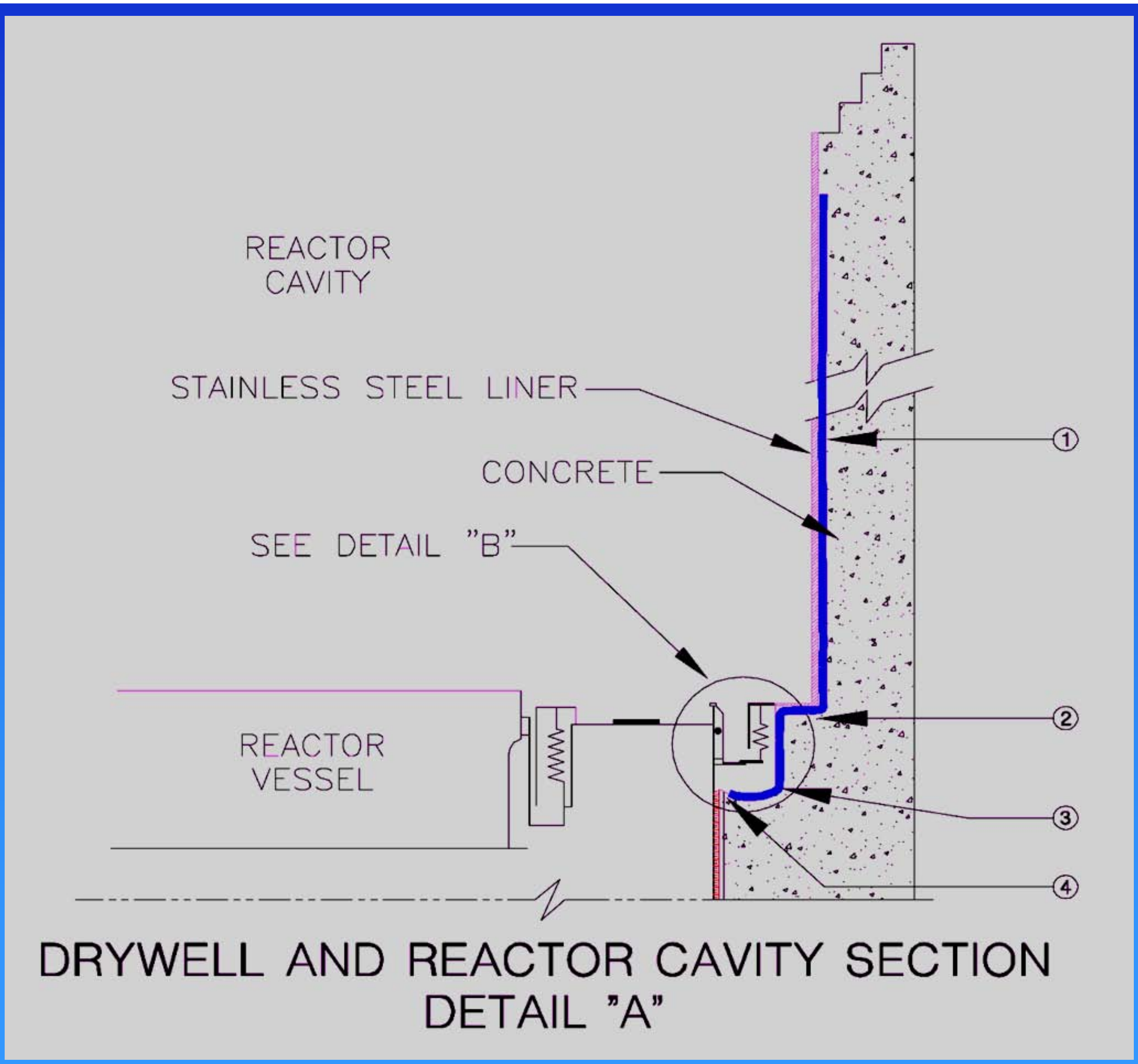
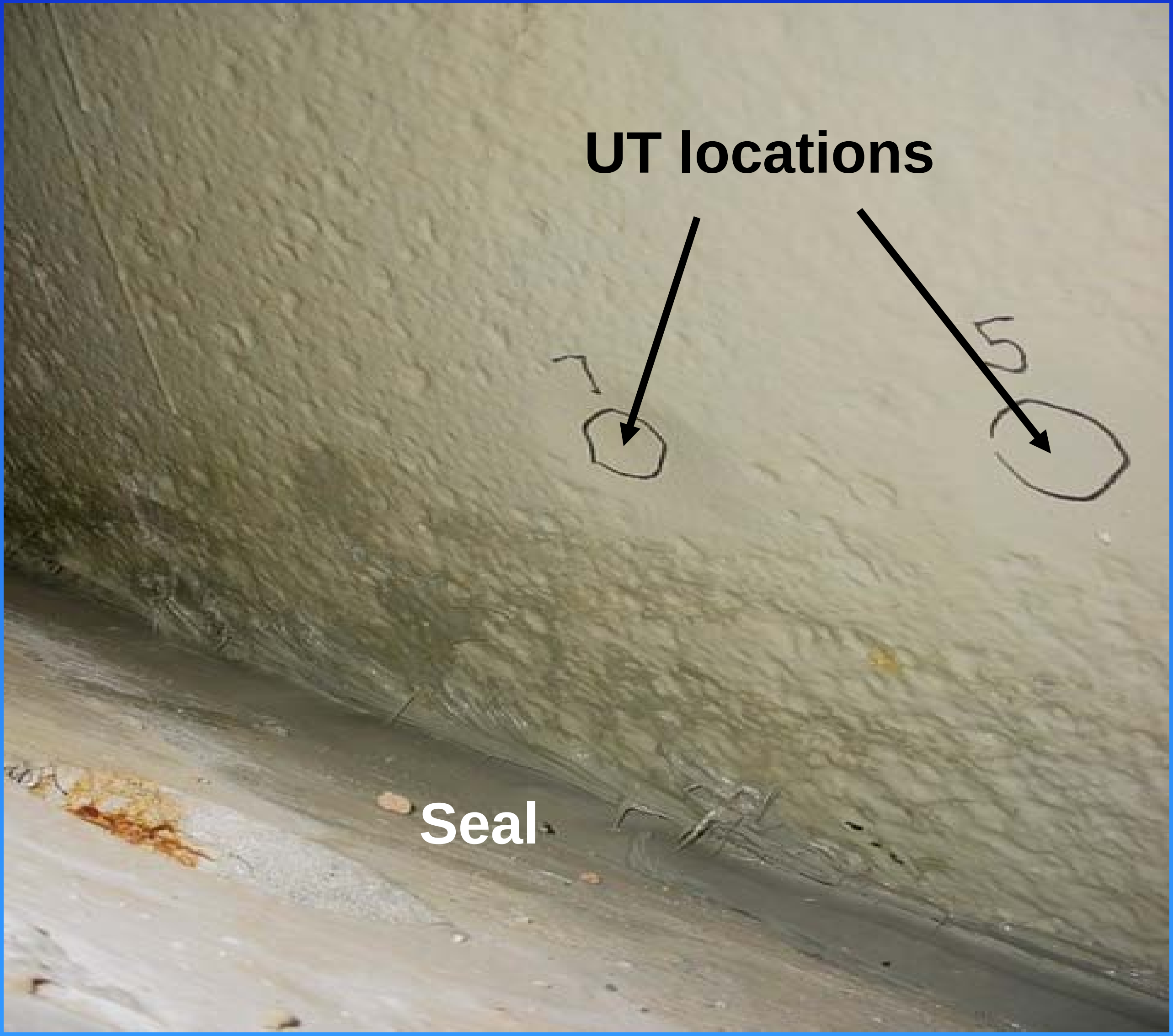
Oyster Creek – Drywell/Reactor Cavity

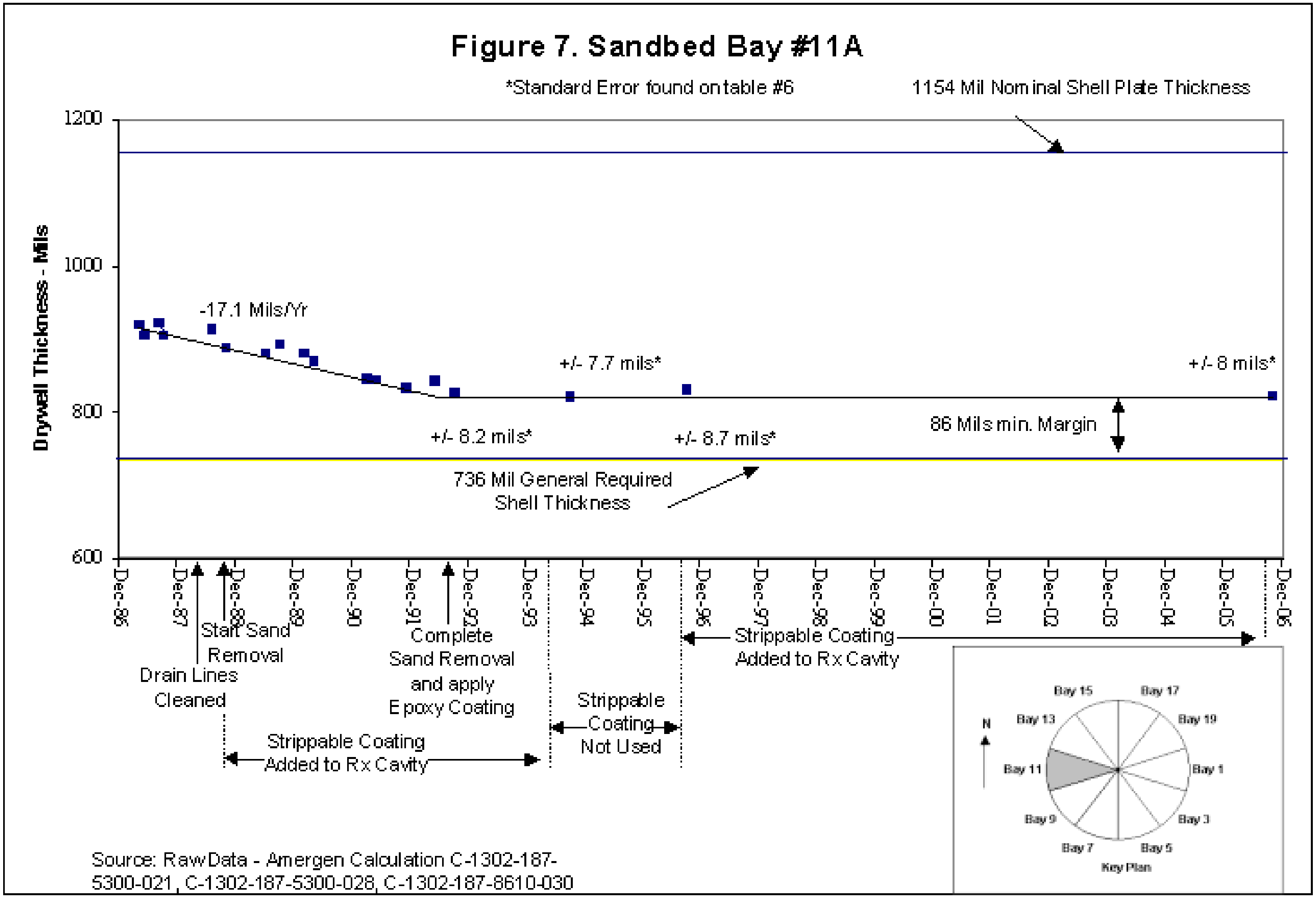


Structural Integrity Associates

Coated Oyster Creek Drywell



OC Thickness Measurements vs. Time



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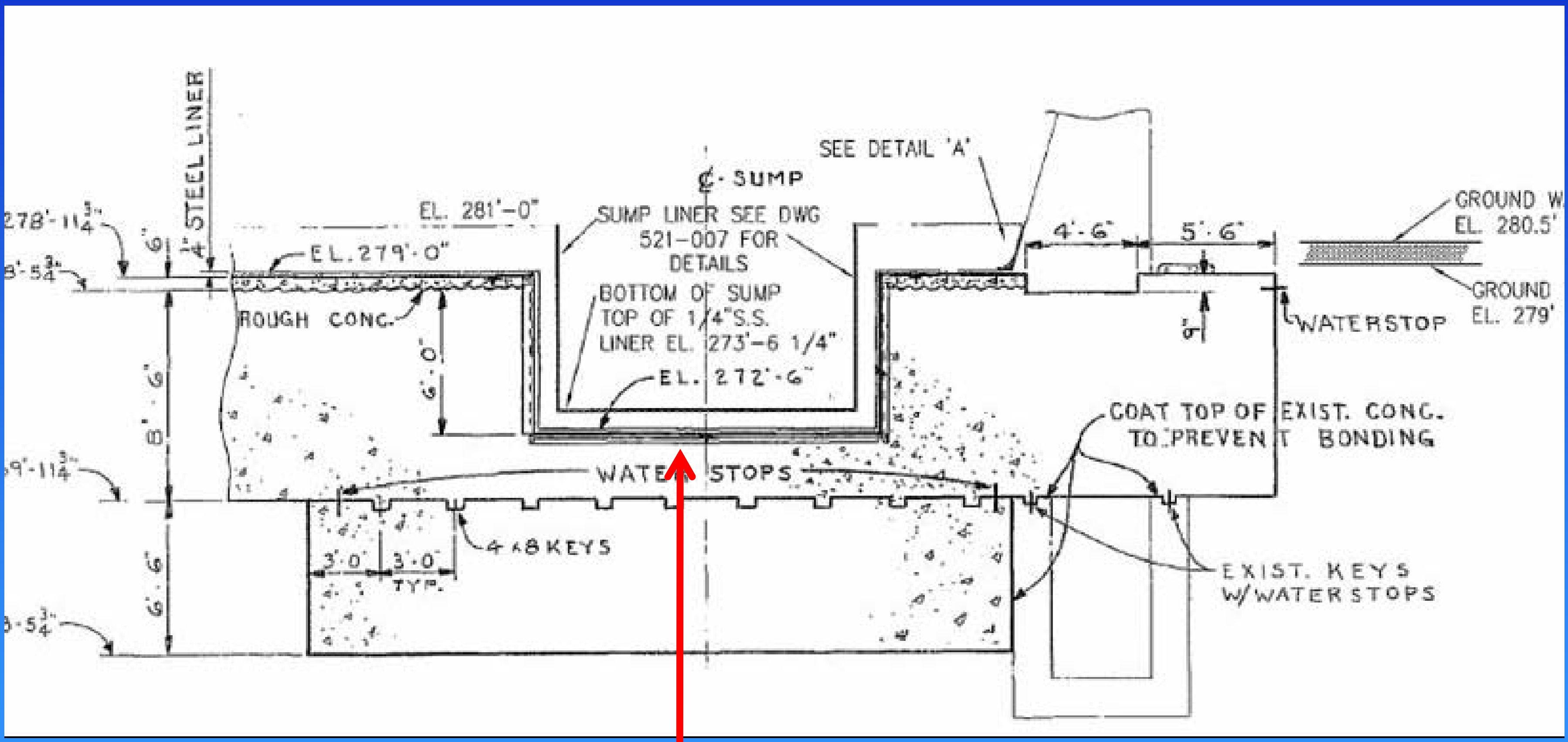
Three Mile Island Containment Corrosion

Three Mile Island Containment



Water!

Corrosion and Corrosion Control in LWRs

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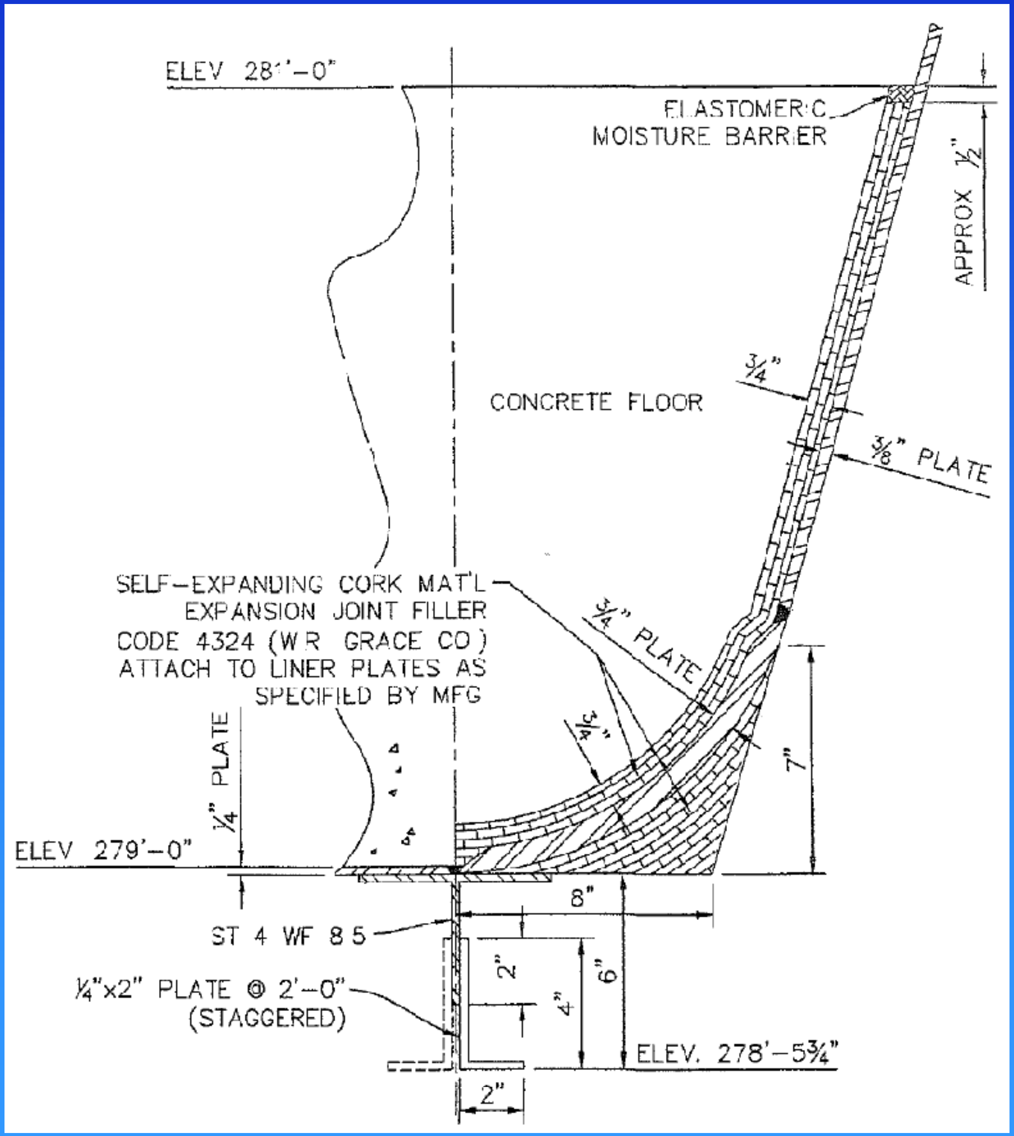
TMI Moisture Barrier Interface



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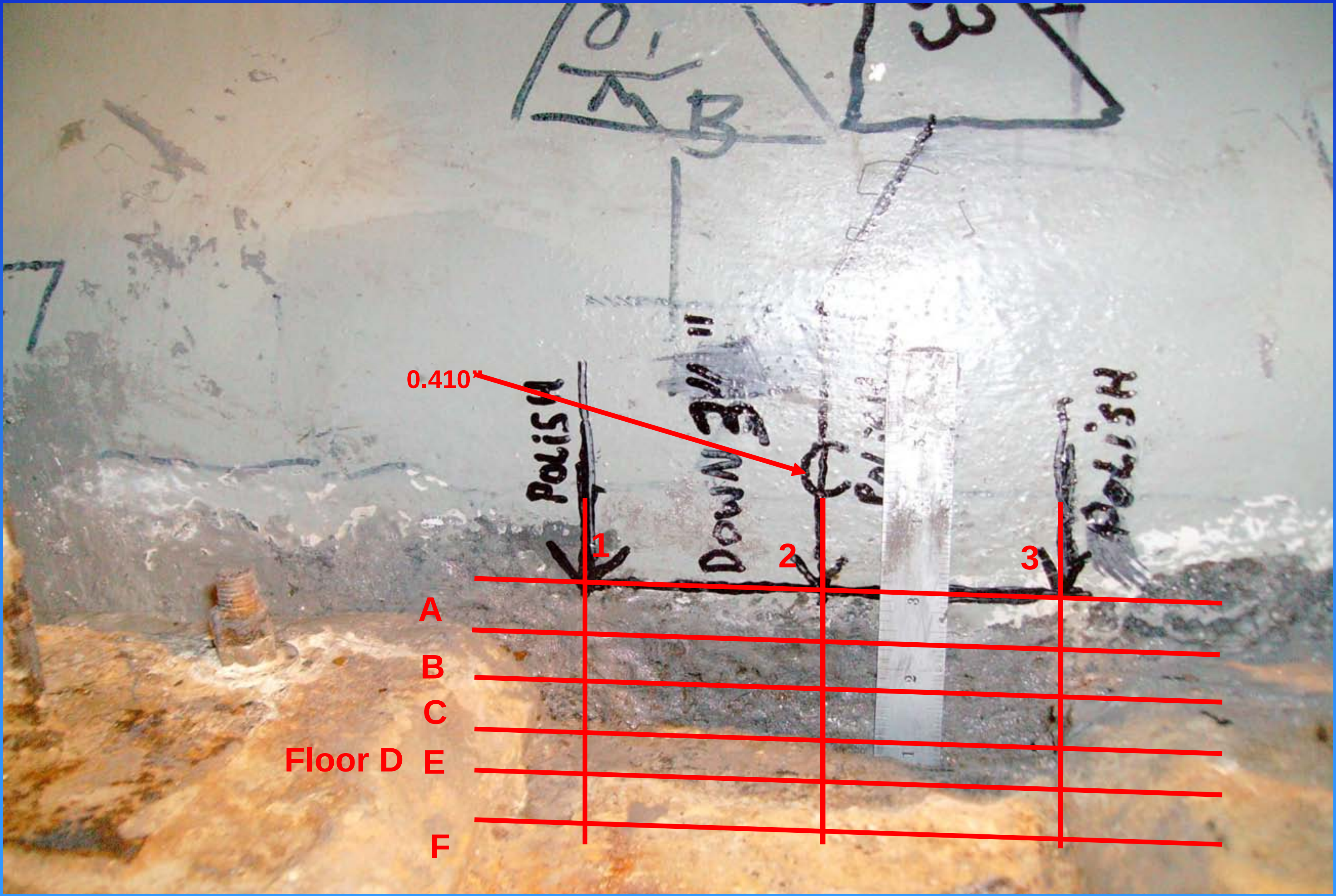
TMI Moisture Barrier Interface Corrosion

TMI Moisture Barrier Interface Corrosion



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TMI Interface Thickness Measurements

Location Description	Depth Designation	Vertical Position		
		1	2	3
5 cm above floor	A	0.95	1.01	1.01
3.4 cm above floor	B	0.88	0.95	0.96
1.7 cm above floor	C	0.84	0.94	0.96
Floor line	D	**0.66**	0.96	0.86
1.3 cm below floor	E	**0.61**	0.80	0.92
2.5 cm below floor	F	1.01	0.84	0.98

Nominal thickness = 0.95 cm

Beaver Valley Unit 1 Containment Liner Corrosion

Beaver Valley Unit 1 Containment Liner Corrosion

Paint blister was identified during 1R19 IWE inspection

Area beneath the blister contained through-wall penetration ~ 10 x 25 mm (3/8" by 1")

D. Weakland and D. Hecht, 092310

Beaver Valley Unit 1
Containment Liner Corrosion

Portion of liner plate removed to investigate the debris behind the liner plate

No "corrosive agents"
"General pitting corrosion"

D. Weakland and D. Hecht, 092310

Beaver Valley Unit 1 Containment Liner Corrosion

Debris was removed from the concrete creating a void ~5 x 15 x 10 cm (~2 x 6 x 4 inches) deep

Debris:
Wood that >37 years in concrete still had 13% moisture content
pH_{wood} = 3.5

Repair Activities:
Welded in a new portion of the liner
Pressure tested the area
Volumetric examination of welds
Restored the paint

D. Weakland and D. Hecht, 092310

Containment Corrosion Summary

- OE shows that containment liner corrosion is often the result of liner plates being in contact with objects and materials that are lodged between or embedded in the containment concrete
  - Organic objects promote accelerated corrosion because they can trap water and also cause a localized low pH region when they decompose
- Visual inspections typically identifies the corrosion only after it has significantly degraded the liner
  - In some cases, corroded areas were found by UT of suspect areas (e.g., areas of obvious bulging, hollow sound)

Containment Corrosion Summary

- Objects that enhanced liner corrosion were lodged between or embedded in the containment concrete include:
  - Foreign material (e.g., wood, workers' gloves, wire brush handles)
  - Design materials (e.g., felt)
- Some licensees have chosen to review design documents to identify locations where organic material was intentionally installed between the liner or penetration sleeve and schedule additional examinations of these areas to monitor for liner corrosion

IN2010-12 - Containment Liner Corrosion

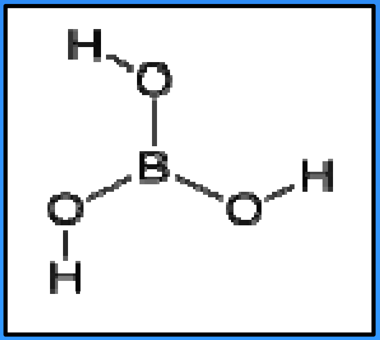
Boric Acid Corrosion

Some NRC BAC Documents

- BL-02-01 - Reactor Pressure Vessel Head Degradation and Reactor Coolant Pressure Boundary Integrity
- GL88005 - Boric Acid Corrosion of Carbon Steel Reactor Pressure Boundary Components in PWR plants
- IN03002 - Recent Experience With Reactor Coolant System Leakage and Boric Acid Corrosion
- IN94063 - Boric Acid Corrosion of Charging Pump Casing Caused by Cladding Cracks
- IN8610S3 - NRC Information Notice 86-108, Supplement 3: Degradation of Reactor Coolant System Pressure Boundary Resulting from Boric Acid Corrosion
- IN86108S2 - Degradation of Reactor Coolant System Pressure Boundary Resulting from Boric Acid Corrosion
- IN86108S1 - Degradation of Reactor Coolant System Pressure Boundary Resulting from Boric Acid Corrosion
- IN86108 - Degradation of Reactor Coolant System Pressure Boundary Resulting from Boric Acid Corrosion

Boric Acid – H_3BO_3

- Weak acid
  - pH 4 at saturation
    - orange juice's pH = 3.3, Coca Cola's pH = 2.5, vinegar's pH = 2.4, lemon juice's pH = 2.2
- Applications:
  - Antiseptic
    - Minor cuts/burns, acne, athlete's foot
    - Eye wash – only acid beneficial to your eyes!
  - Insecticide - cockroaches, termites, fire ants, fleas
  - Flame retardant
  - Fission control in PWRs
- As toxic as ……….. table salt!



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BAC Background

- **BAC rates:**
  - **BAC will be a strong function of the BA concentration, primarily because of the nature and solubility of the corrosion product films**
  - **Influenced by DO, T (reaction kinetics and stability of corrosion products), velocity**
  - **Crevices are important**
  - **Galvanic effects**
    - **SS or Ni alloys vs. carbon steel or low alloy steel**

BAC of Low Alloy Steel
Reactor Coolant Pump Closure Stud

J. Hall, et al., 4th Env. Deg., 1990

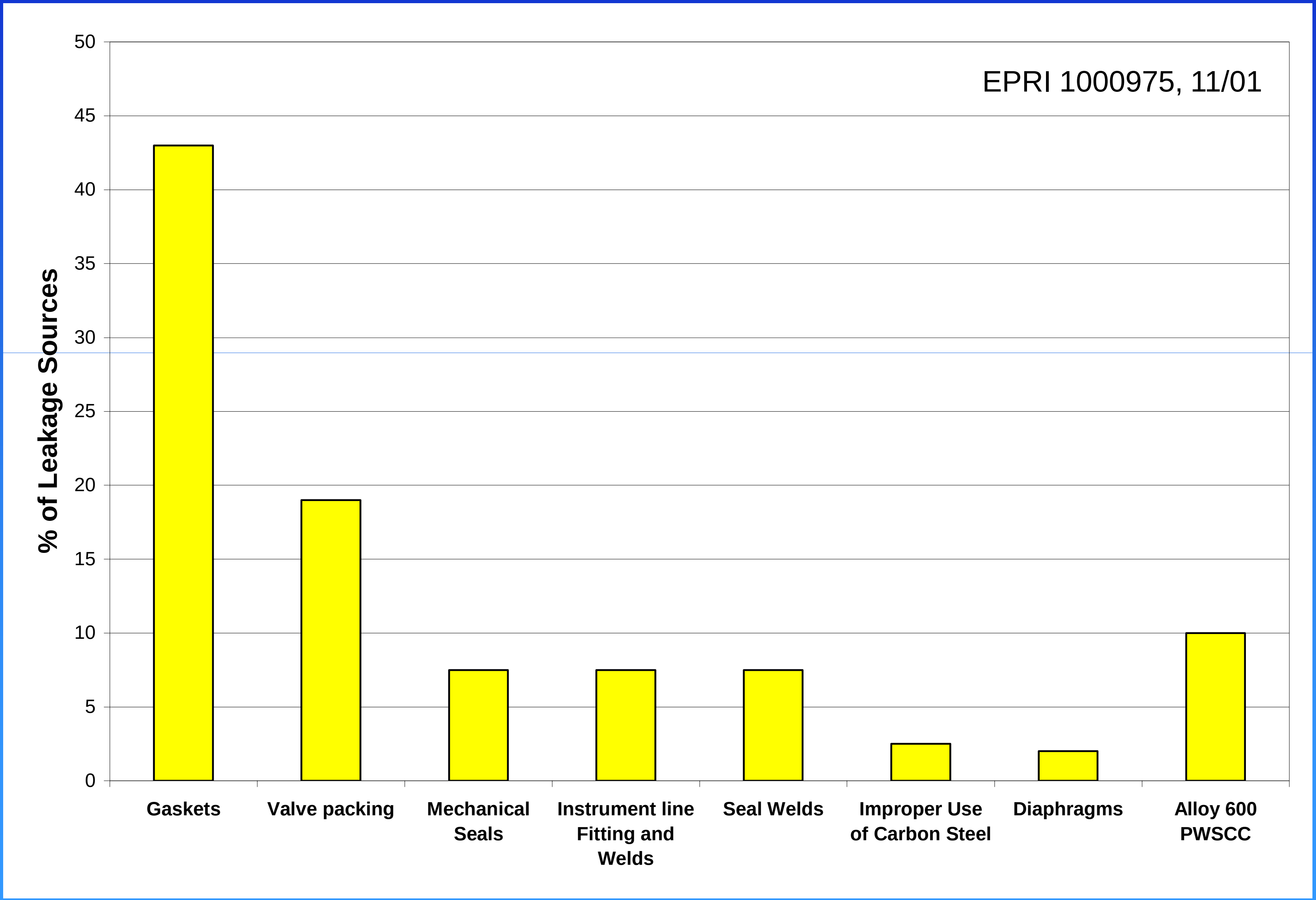
Typical PWR Boron and Boric Acid Concentrations

Location	B, ppm	H_3BO_3, wt%
Reactor Coolant System	0-2000	0-1.14
Refueling Water Storage Tanks	2400-2500	1.37-1.43
ECCS Accumulators	2300-2500	1.37-1.43
Recycle Evaporator	7000	4.00
Boric Acid Storage tanks	7000-7700	4.00-4.39
Boron Injection Tanks		
Early Designs	22,000	12.5
Current Designs	2000	1.14

1 ppm B → 5.7 ppm H_3BO_3

EPRI 1000975, 11/01

Distribution of Reported BA Leakage



Example of Boric Acid Leak
(Not Davis-Besse)

BAC of Low Alloy Steel in PWRs

- LWRs use low alloy steel (LAS) bolts, studs, vessels, etc. in systems that contain borated water
- 1968 – two carbon steel bonnet bolts in a SS valve corroded at Connecticut Yankee after a short exposure to boric acid
- By 1984, 28 additional corrosion failures were attributed to boric acid
- Accelerated general corrosion with rates of up to 43.2 mm/y (1.7 in/y). Rate can be galvanically accelerated.
- Some SCC and H_2 embrittlement of highly stressed bolting

EPRI NP-3784, 12/84

EPRI NP-5985, 8/88

EPRI BAC Guidebook Highlights

- Dissolved oxygen accelerates BAC
- Deaerated (0-80 ppb O_2), 82°C (180°F) boric acid (20,000 ppm B) can corrode 4130 at 0.7 mm/y (0.027 in/y)
- Aerated 104°C (220°F) boric acid (79,000 ppm B) can corrode steel at up to 184 mm/y (7.25 in/y)
- Drip tests with 26,000 ppm B at 99°C (210°F) revealed A302 corrosion rates of 102 mm/y (4 in/y)
- 315°C (600°F) 1000 ppm B downward nozzle leakage test A533 Gr. B corrosion rate was 15 – 56 mm/y (0.6 - 2.2 in/y)
- 315°C (600°F) 2000 ppm B downward nozzle leakage test A302 Gr. B corrosion rate was 22.6 – 60.2 mm/y (0.89 -2.37 in/y)

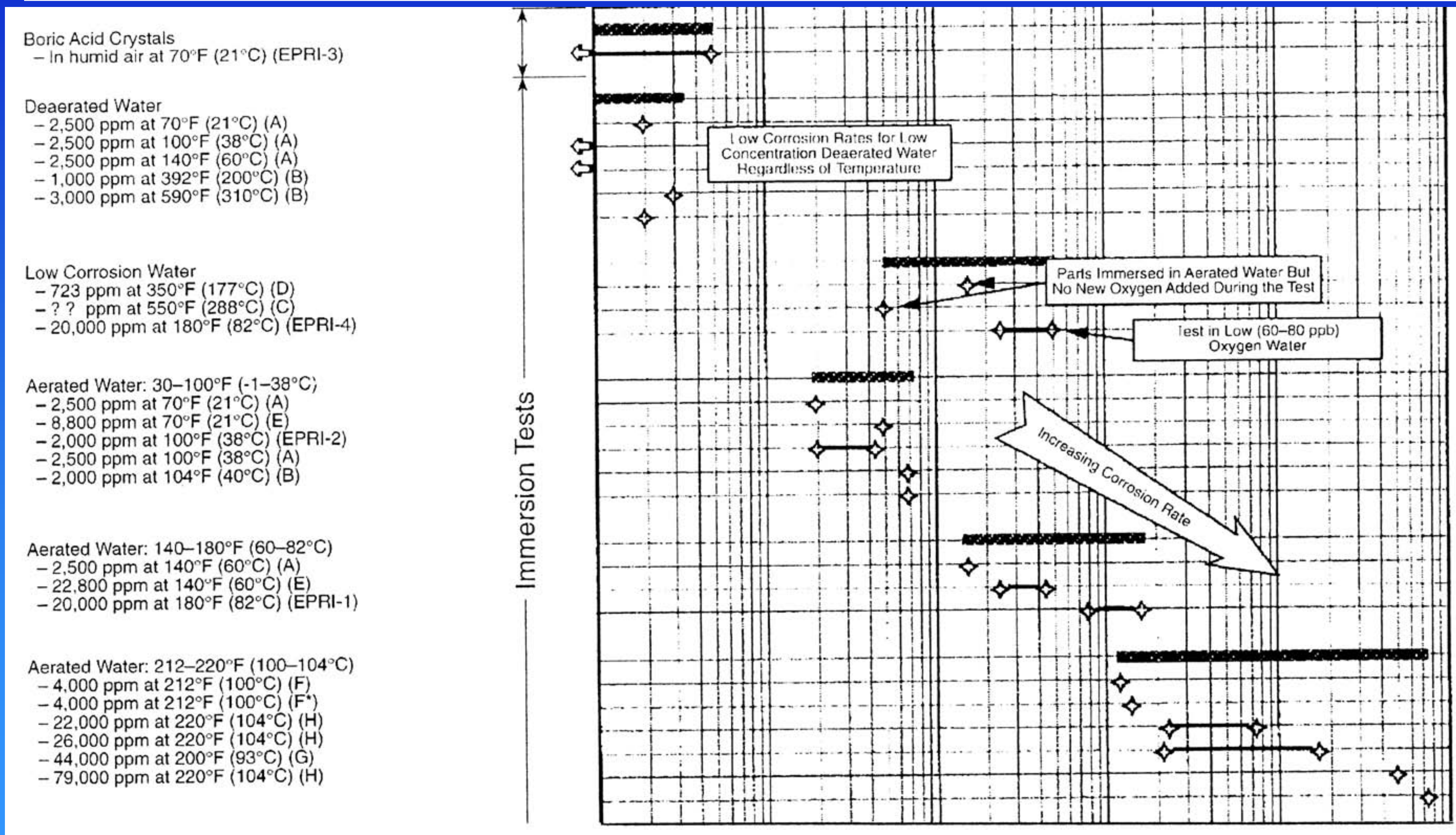
EPRI 1000975, 11/01

Early BAC Mock-up Testing

- Alloy 600 tubes mockups with short axial cracks in LAS collars with a 0.05-0.2 mm (2-8 mil) clearance at 316-343°C (600-650ºF)
- Borated water was supplied to the inside of the tube at 315°C (600°F). Initial leak rates ranged from 0.08 to 0.45 l/min (0.02 to 0.12 gpm). 300-700 h test.
- Results:
  - Very little corrosion on the ID surfaces of the hole in the vessel shell
  - Most corrosion occurred where the leakage left the annulus, rather than opposite the crack
  - Highest localized corrosion rate was 54.6 mm/y (2.15 in/y)
  - Highest corrosion rates resulted from the lowest leak rates suggesting that the surface does not corrode as rapidly if it remains wet

J. Hall, 10/91

BAC Rates



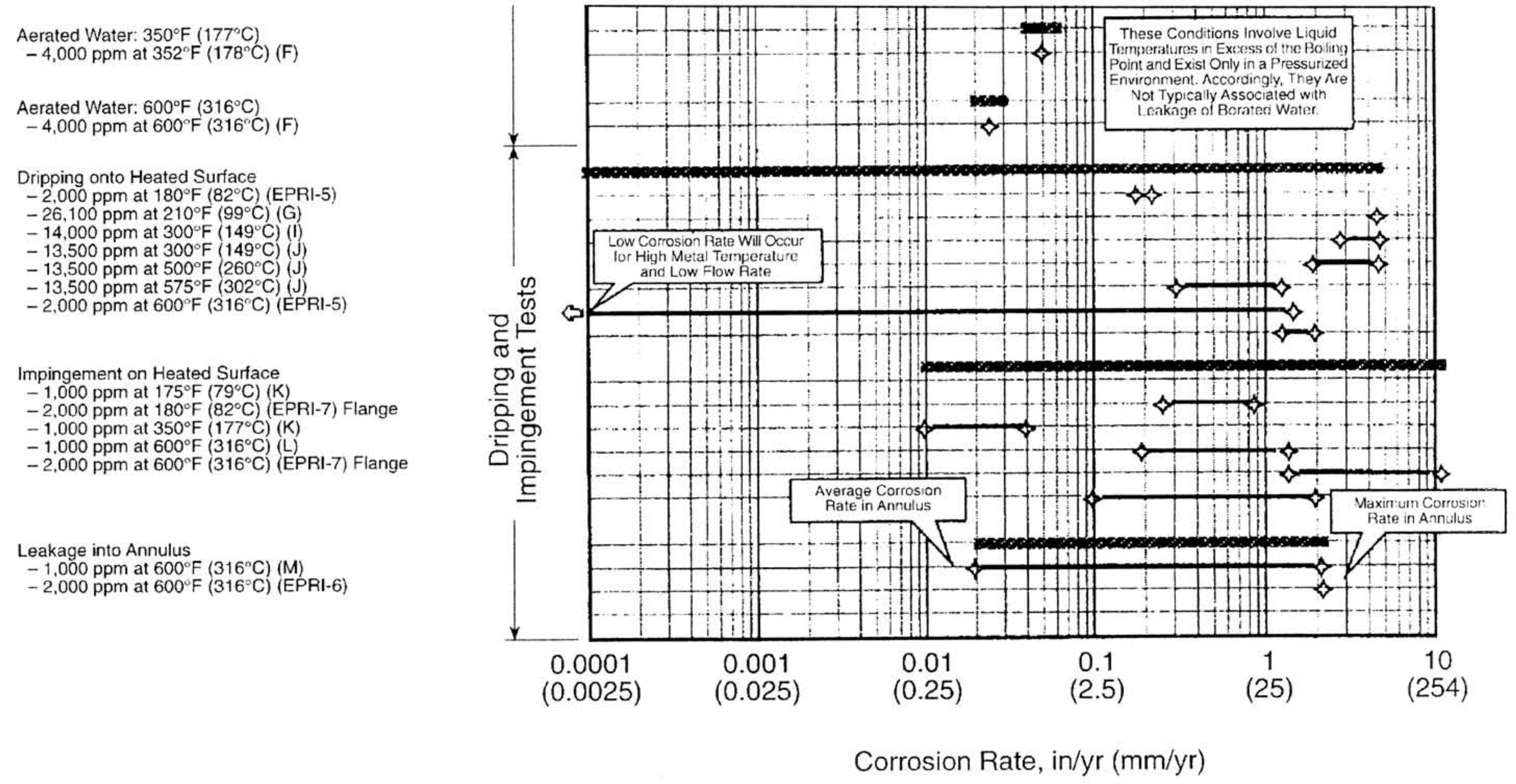
ipy 10^{-4} 10^{-3} 10^{-2} 10^{-1} 1 10

EPRI 1000975, 11/01

Corrosion and Corrosion Control in LWRs

Structural Integrity Associates

BAC Rates

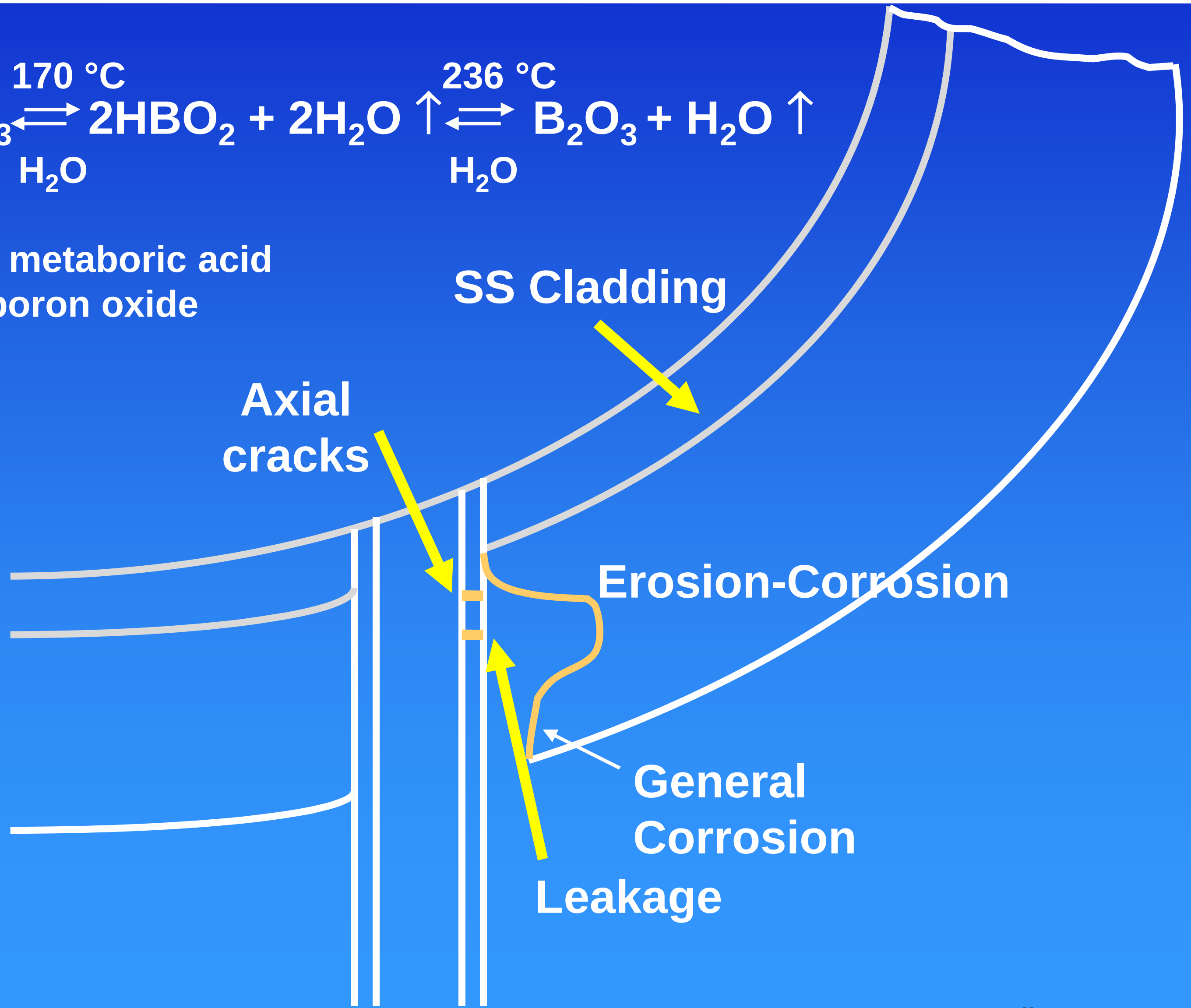


EPRI 1000975, 11/01

Predicted Pattern due to BAC in a Alloy 600 Pressurizer

$$2H_3BO_3 \underset{H_2O}{\overset{170\ °C}{\rightleftarrows}} 2HBO_2 + 2H_2O\uparrow \underset{H_2O}{\overset{236\ °C}{\rightleftarrows}} B_2O_3 + H_2O\uparrow$$

HBO_2 = metaboric acid
B_2O_3= boron oxide



J. Hall, EPRI TR-100852, 7/92

BAC at Davis-Besse in the NY Times

WASHINGTON, March 25, 2002 — Nuclear reactor operators have been ordered to check their reactor vessels after the discovery that acid in cooling water had eaten a hole nearly all the way through the six-inch-thick lid of a reactor at a plant in Ohio. The corrosion left only a stainless-steel liner less than a half-inch thick to hold in cooling water under more than 2,200 pounds of pressure per square inch…….. The discovery of a corrosion problem at the Davis-Besse nuclear power station, near Toledo, Ohio, has puzzled federal regulators.

The Toledo Blade, 3/25/02

Davis-Besse History 1

- Davis-Besse began a refueling outage on 2/16/02 that included inspection of the 69 CRDM nozzles in accordance with NRC Bulletin 2001- 01 August 3, 2001 (Circumferential Cracking of RPVH Penetration Nozzles)
- These inspections identified axial indications in 3 CRDM nozzles (#1, 2 and 3 located near the center of the RPV head), which resulted in pressure boundary leakage
- FirstEnergy decided to repair these 3 nozzles, as well as 2 other nozzles that had indications, but no leakage

Davis-Besse History 2

- Repair process included roll expanding the CRDM nozzle into the RPV LAS head, followed by machining/grinding along the axis of the CRDM nozzle to an elevation above the indications in the nozzle material
- On 3/6/02, the machining process on nozzle #3 was prematurely halted because the machine, which had been cutting away the nozzle material below the surface of the head inner surface, jumped when it hit the space next to the nozzle above the liner. The tech running the machine knew something was wrong and stopped the work.
- During the removal process, nozzle #3 fell over away from the top of the RPV head until its flange contacted the flange of the adjacent CRDM nozzle
- **Uh oh!**

Davis-Besse History 3

- CRDM nozzle was removed from the RPV head along with the BA deposits to identify the cause of the problem
- UT measurements of the RPV head in the vicinity of CRDM nozzles #1, 2, and 3 were performed
- Upon completing the BA removal on 3/7/02, visual examination of the area revealed a large cavity in the RPV head on the downhill side of nozzle #3
- Follow-up UT indicated corrosion of the low alloy steel RPV head adjacent to the nozzle
- 32 kg (70 lbs) of missing low alloy steel head!

Davis-Besse History 4

- Minimum remaining thickness of the RPV head in was 10 mm (~3/8 in), i.e., the thickness of the RPV stainless steel cladding
- Nozzles were probably leaking since 1994 at rates as high as 45 l/h (0.2 gpm)
- NRC noted that there were several “missed opportunities” for the operators to identify the problem
  - Several indications that serous corrosion (e.g., corrosion product clogged air cooler and radiation monitor filter)
  - BA was pried off head with a crow bar in 2000!
- BA deposits on the head were first discovered in 1990! Request for larger inspection windows (mouse holes) to monitor deposits was ignored

Davis-Besse Missed Opportunities to Identify Corrosion #1

- Containment air cooler clogging
  - Increase in boric acid collected on cooling coils in 1999
  - Change in the color of boric acid deposits in 1999
  - DB staff assumed changes in volume of boric acid deposits due to flange leakage
  - DB staff assumed changes in boric acid color due to corrosion of air cooler

NRC 4/02

Davis-Besse Missed Opportunities to Identify Corrosion #2

- Containment radiation monitor filter clogging
  - Detect radioactivity in containment air from reactor coolant leakage
  - Beginning in May 1999, frequency of filter changes increased from monthly to every other day
  - Filters clogged with corrosion products from reactor coolant leakage

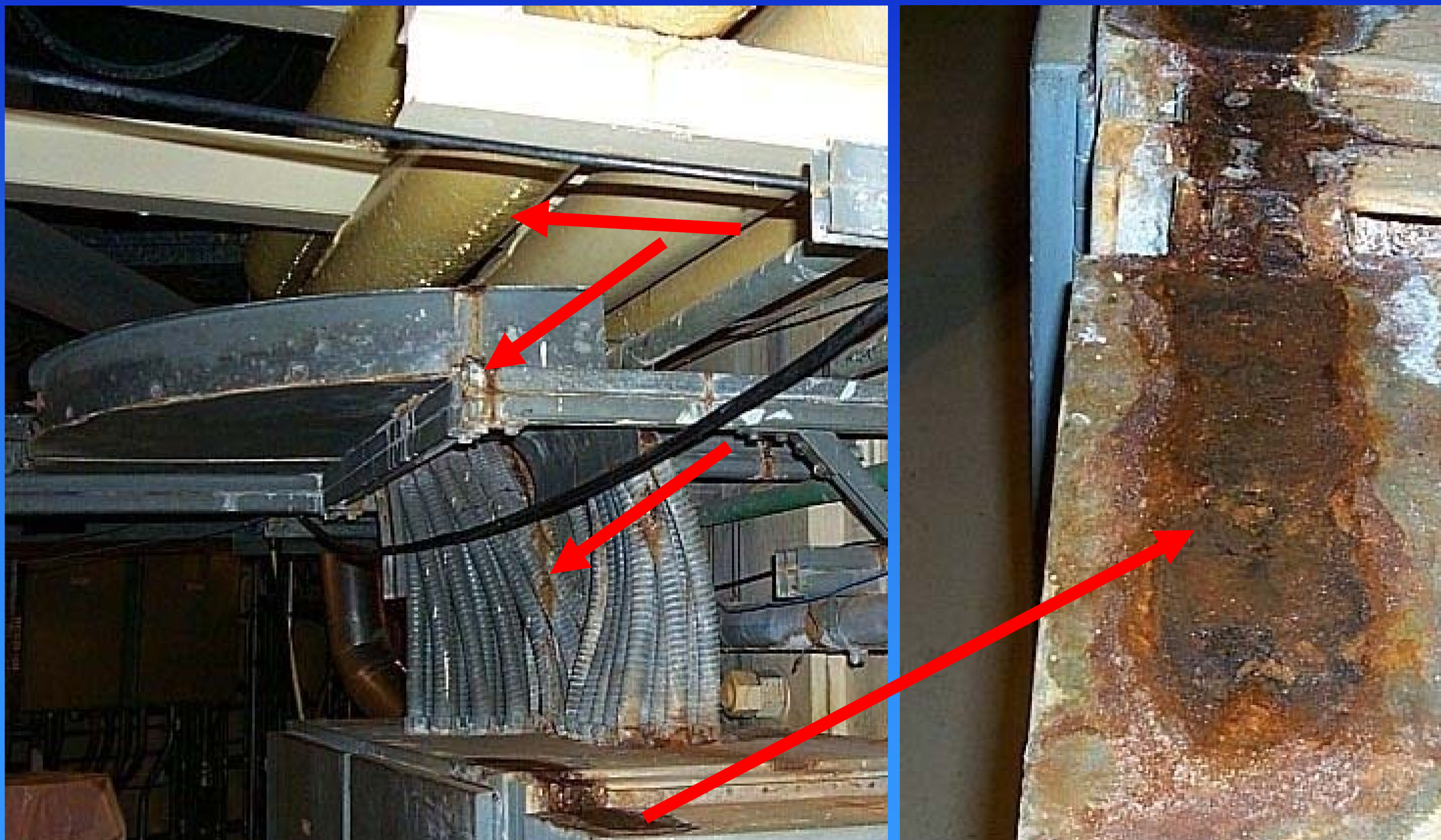
NRC 4/02

Davis-Besse Missed Opportunities to Identify Corrosion #3

- Boric acid buildup and corrosion on reactor head
  - Ongoing nozzle flange leakage continued to be a source of boric acid deposits
  - 1990 modification to improve reactor vessel head access was not installed
  - Reactor vessel head boric acid deposits were not completely removed
  - Indications of reactor vessel head corrosion were not recognized or evaluated

NRC 4/02

Lots of Corrosion Clues



"Jury: Worker Covered Up Damage at Ohio Nuke Plant"

Nuclear facility workers indicted

2 former FirstEnergy employees, contractor accused of covering up details of damage at Davis-Besse

By Dave Scott
Beacon Journal business writer

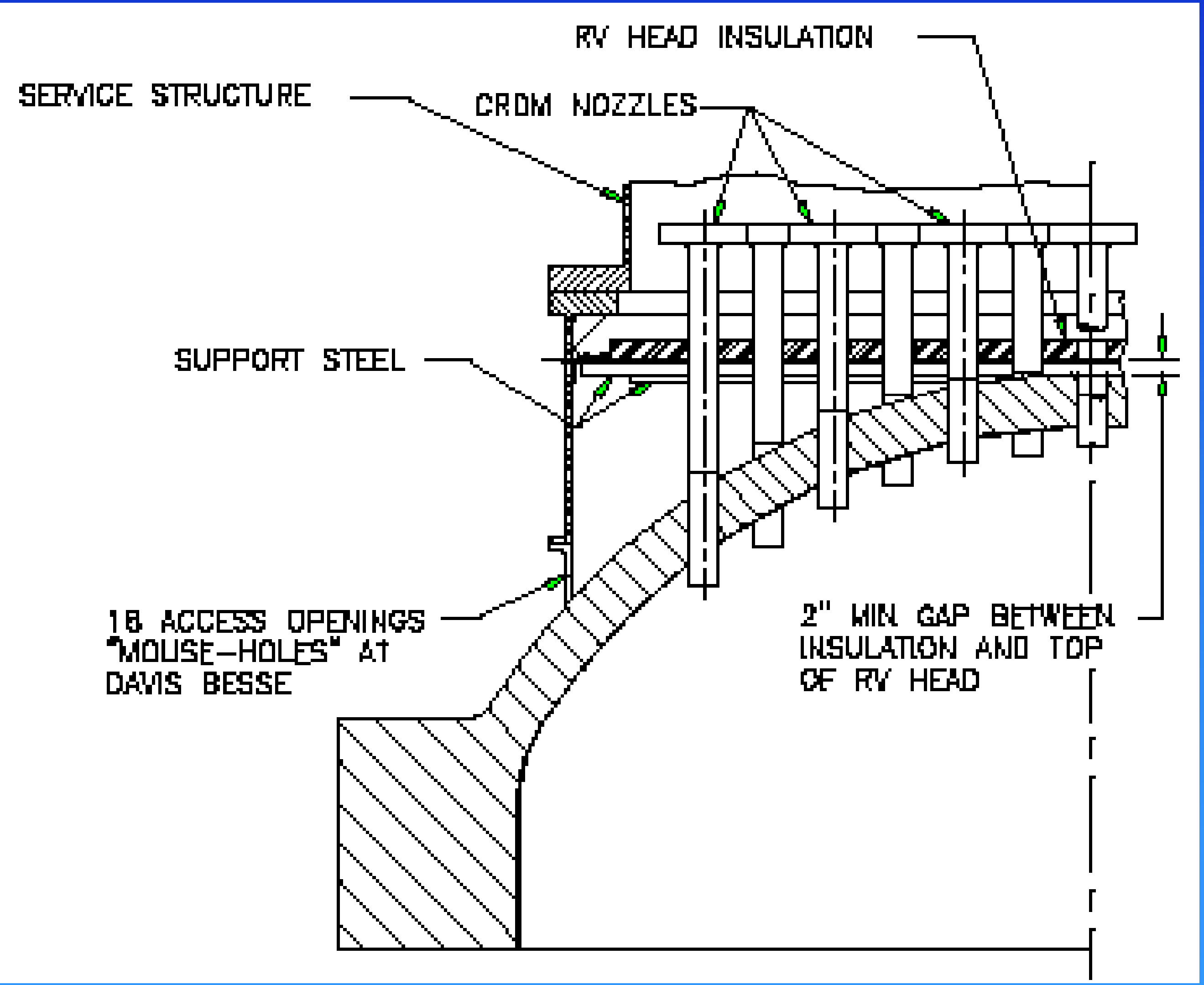
Two former FirstEnergy employees and a contractor allegedly used "tricks, schemes and devices" to cover up details about damage at the Davis-Besse nuclear power plant, according to a five-count federal indictment issued Thursday.

TOLEDO, Ohio — Jurors on August 26, 2008 convicted a former nuclear plant engineer of hiding information from government regulators about the worst corrosion ever found at a U.S. reactor.

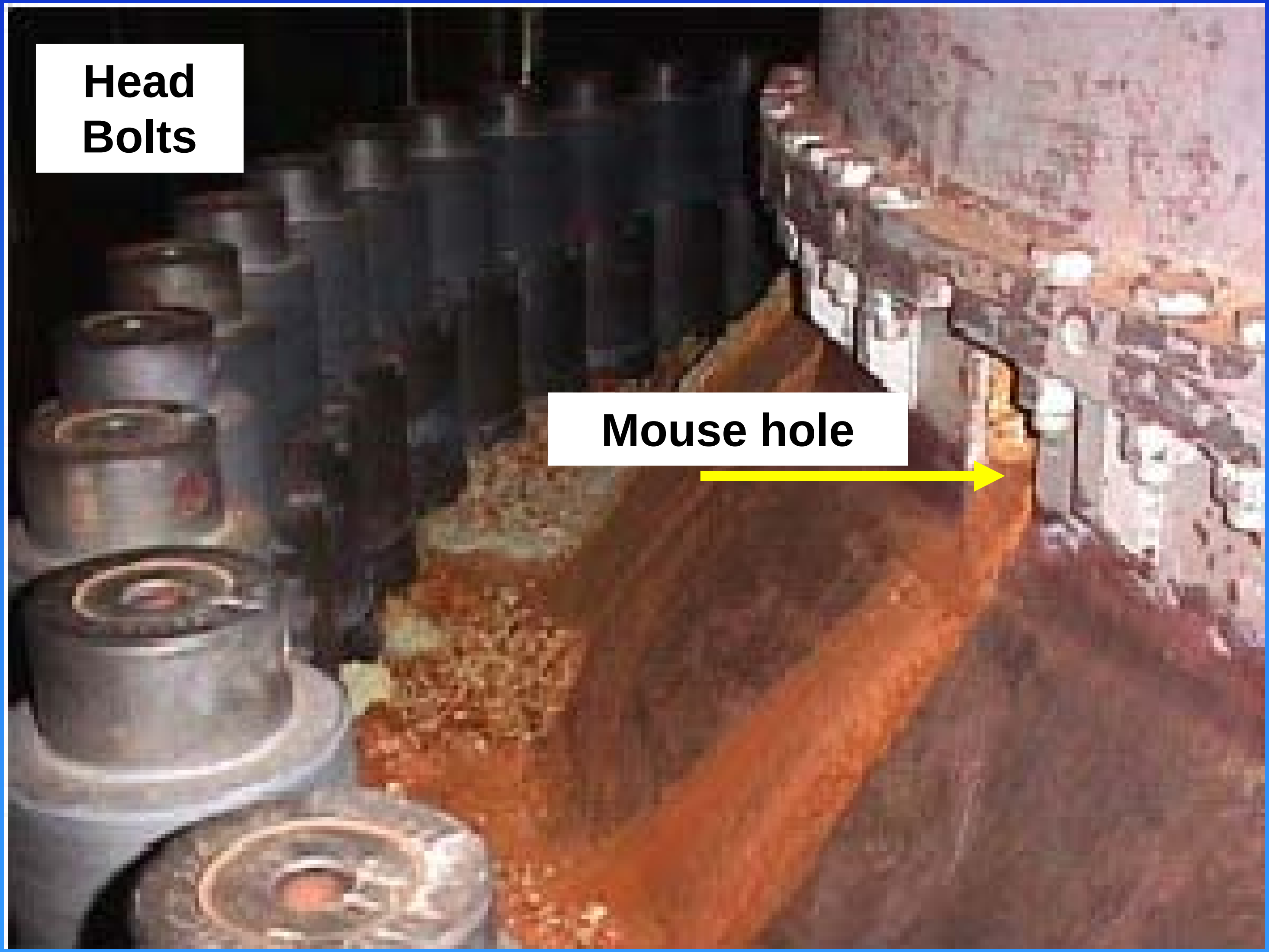
Prosecutors said Andrew Siemaszko and two other workers lied in 2001 so the Davis-Besse plant along Lake Erie could delay a shutdown for a safety inspection.

Siemaszko faced up to 5 years in prison and $250,000 per felony conviction. He was convicted on 3 of 5 counts, including concealing material information from the government. Sentenced on 2/3/09 to 3 years probation and $4,500 fine. FENOC paid $33.5M to settle civil and criminal cases.

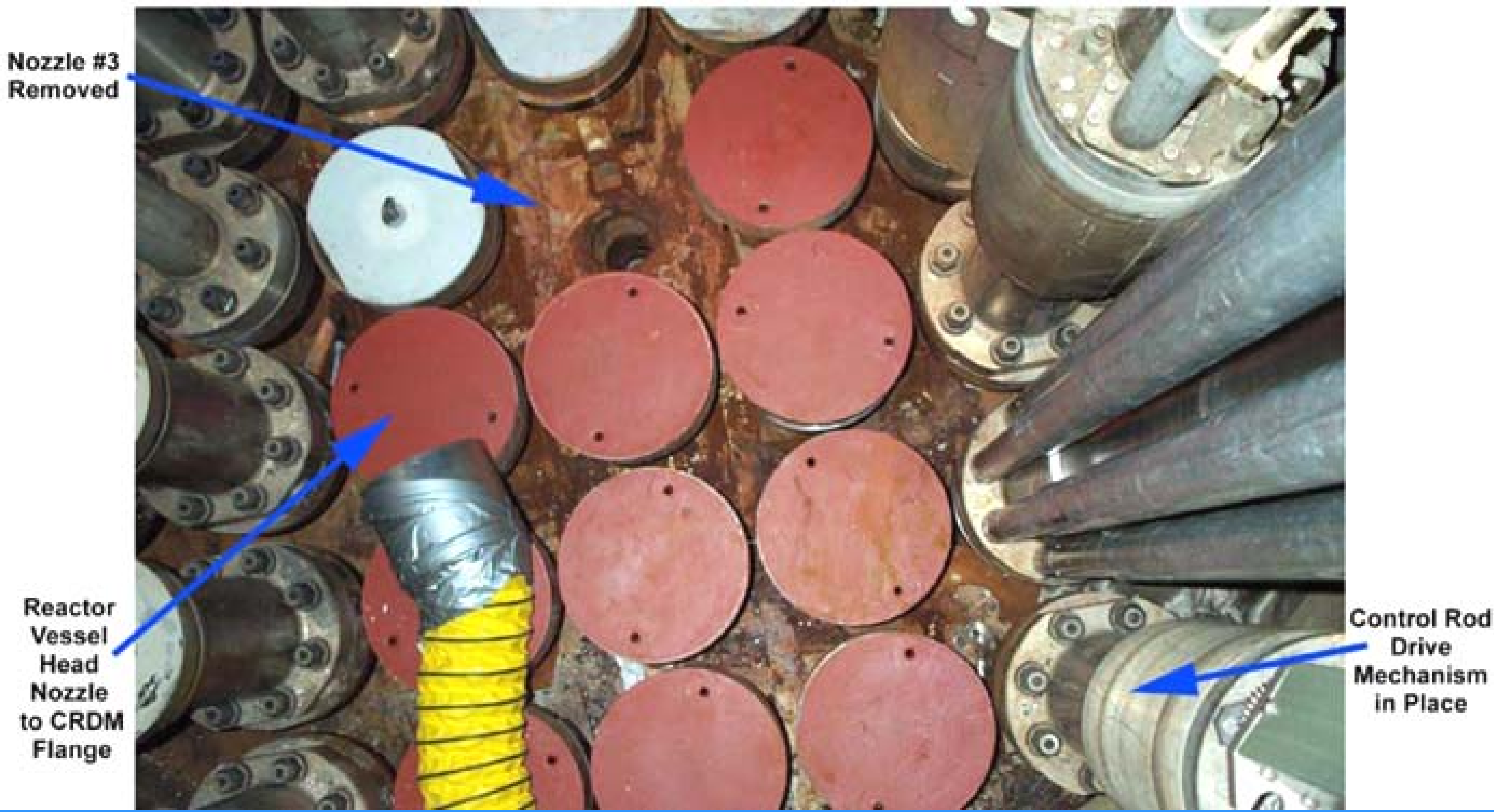
Davis-Besse Top Head Section View



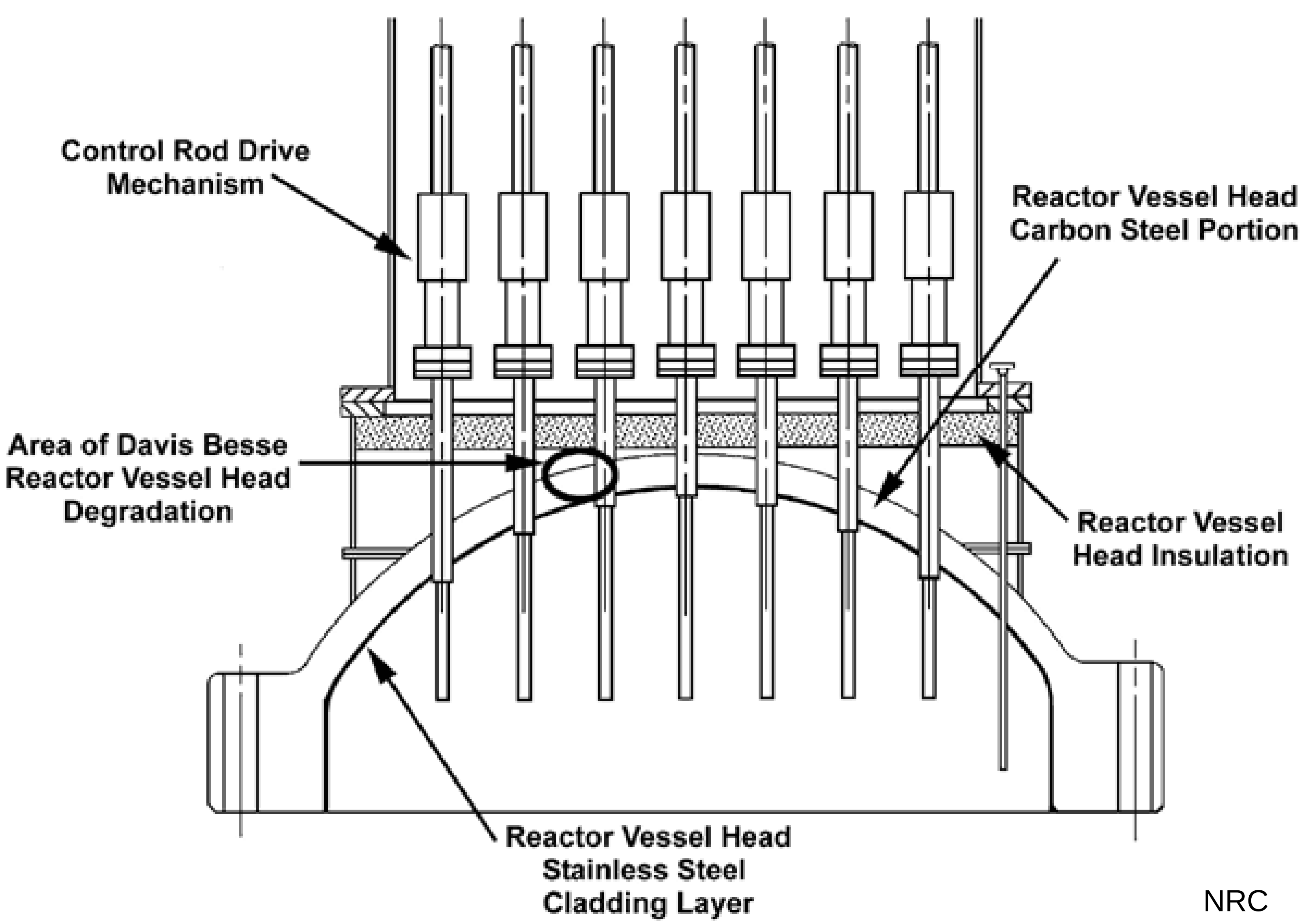
Boric Acid and Iron Oxide on Vessel Closure Flange



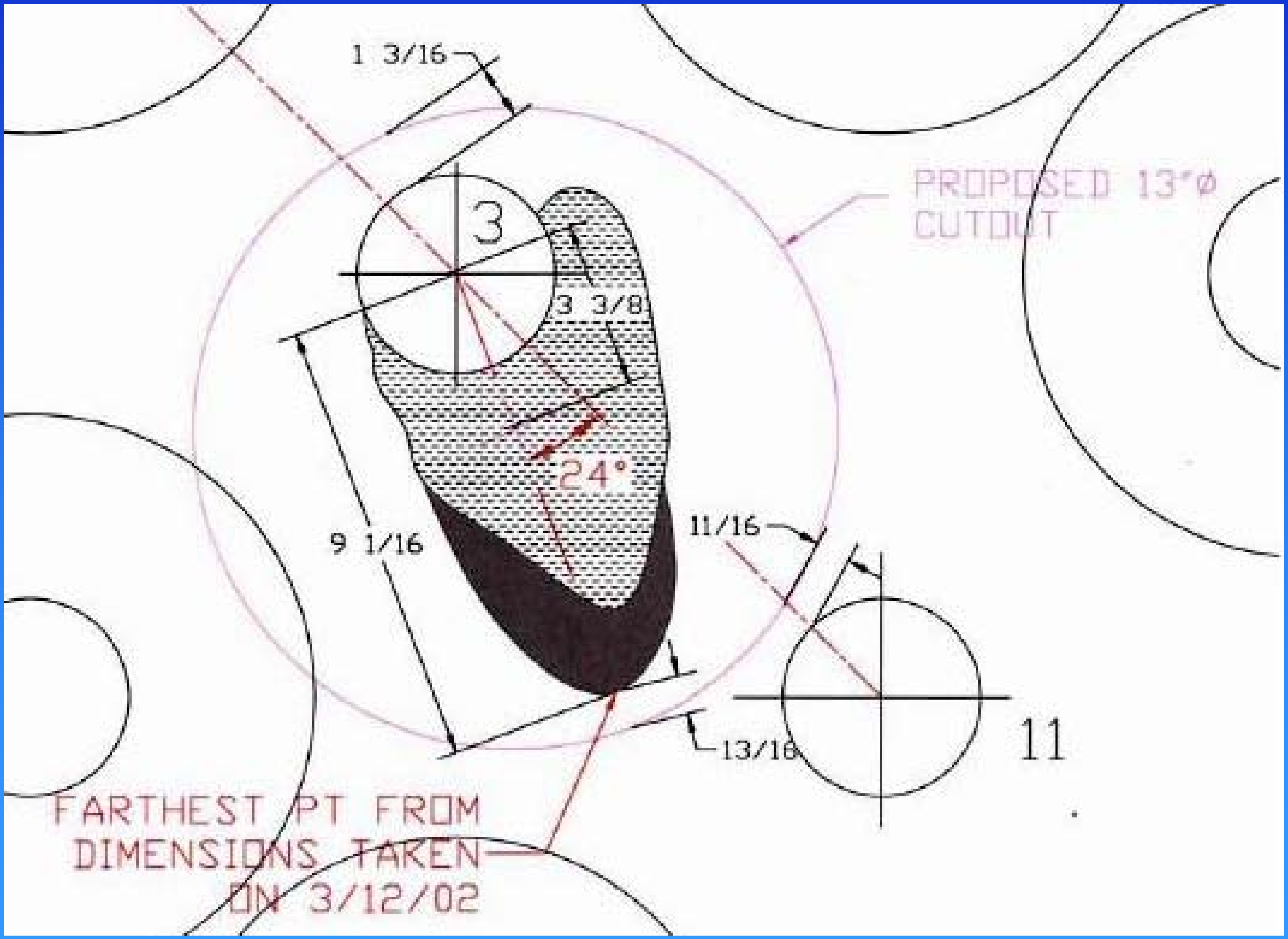
Davis-Besse RPV Head Removed Nozzle #3



Davis-Besse Degradation Location



Sketch of Large Cavity Downhill of Nozzle 3 towards Nozzle 11



Sketch of Davis-Besse BAC

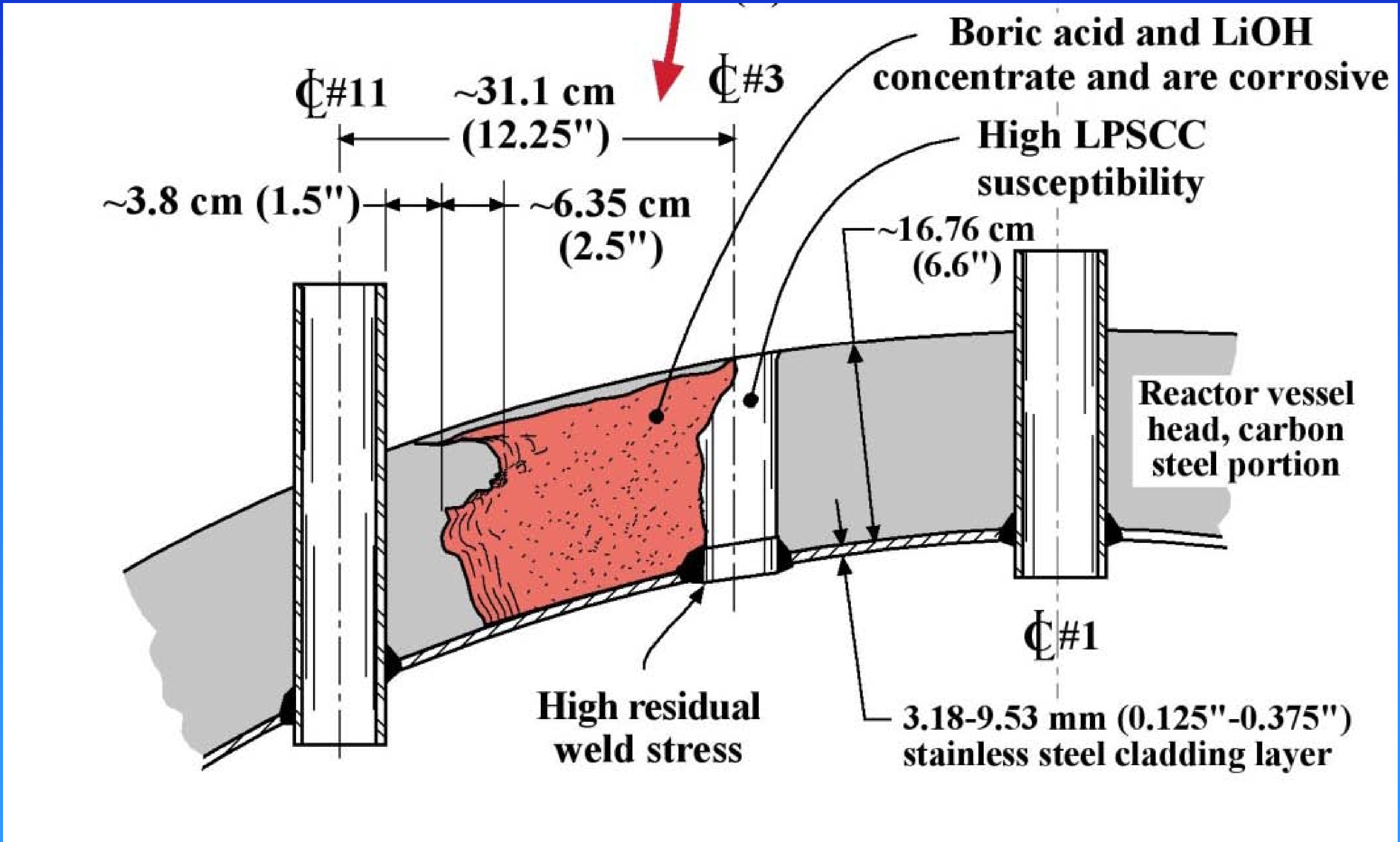


Photo of Large Cavity Downhill of Nozzle 3 towards Nozzle 11

Large Cavity Downhill of Nozzle 3

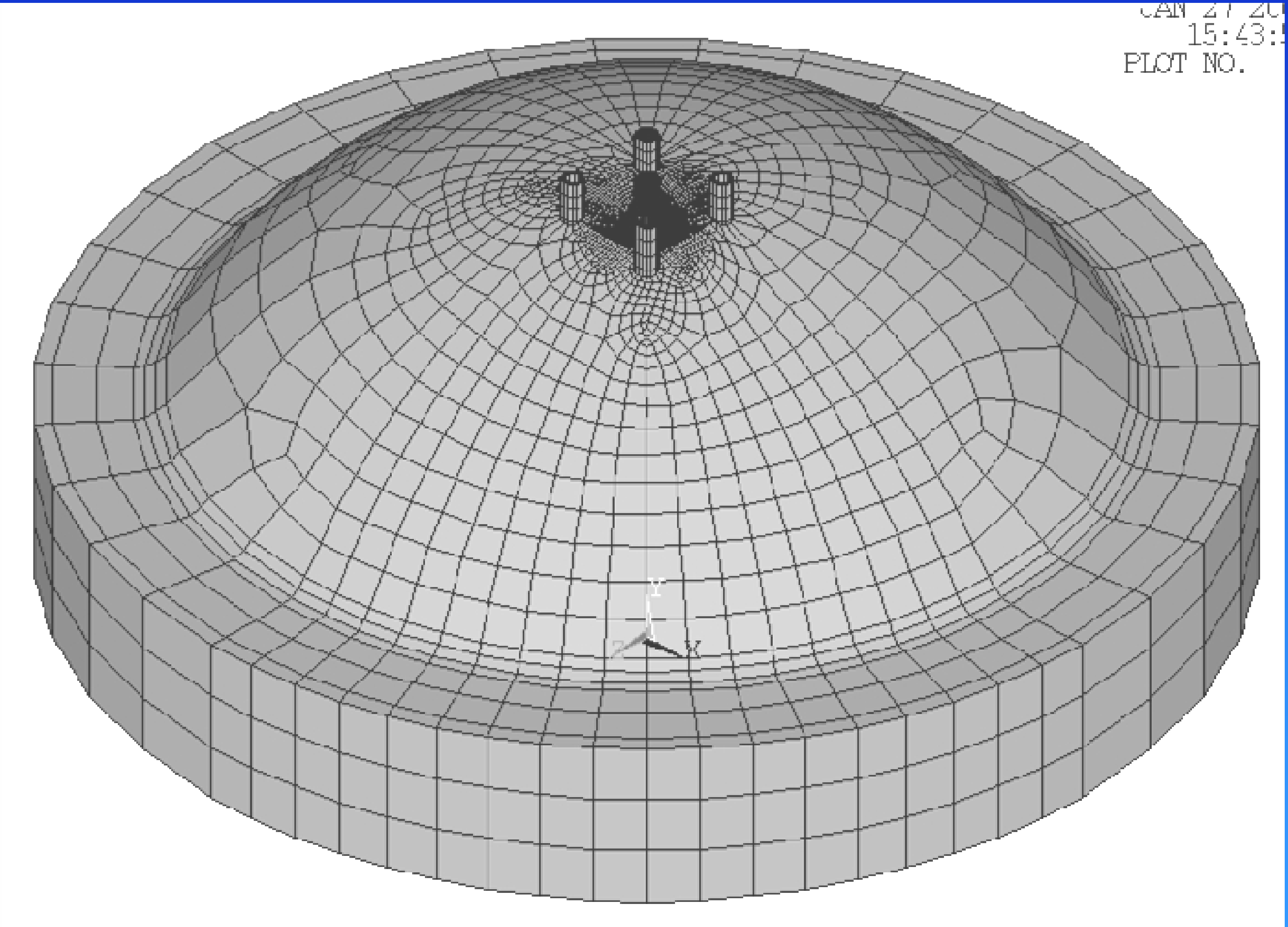
Undercut Area Toward Nozzle 11

Undercut Area Toward Nozzle 3

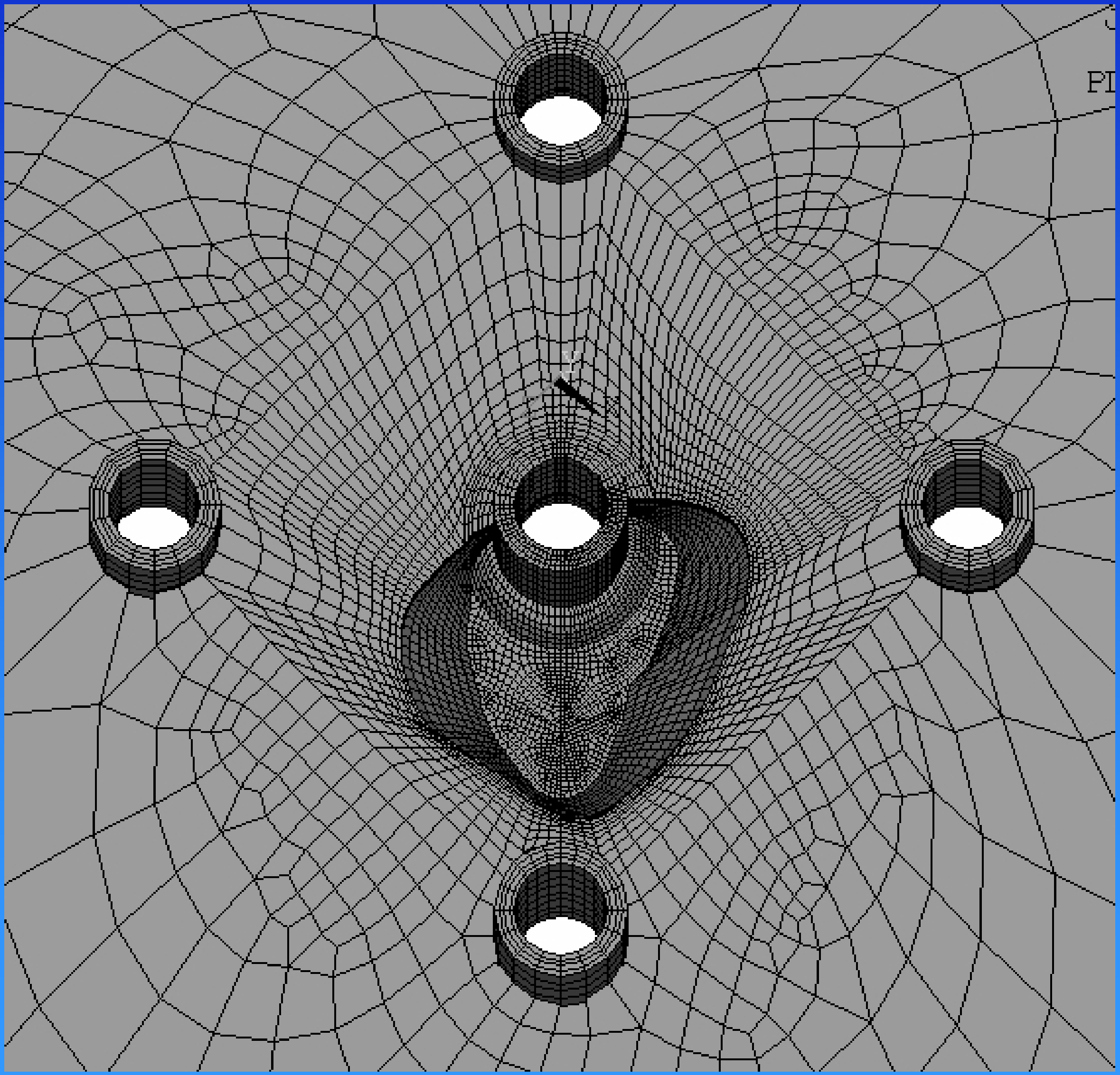
L. Mathews, NSRC, 10/02

Nozzle 3 in Discarded Davis-Besse Head

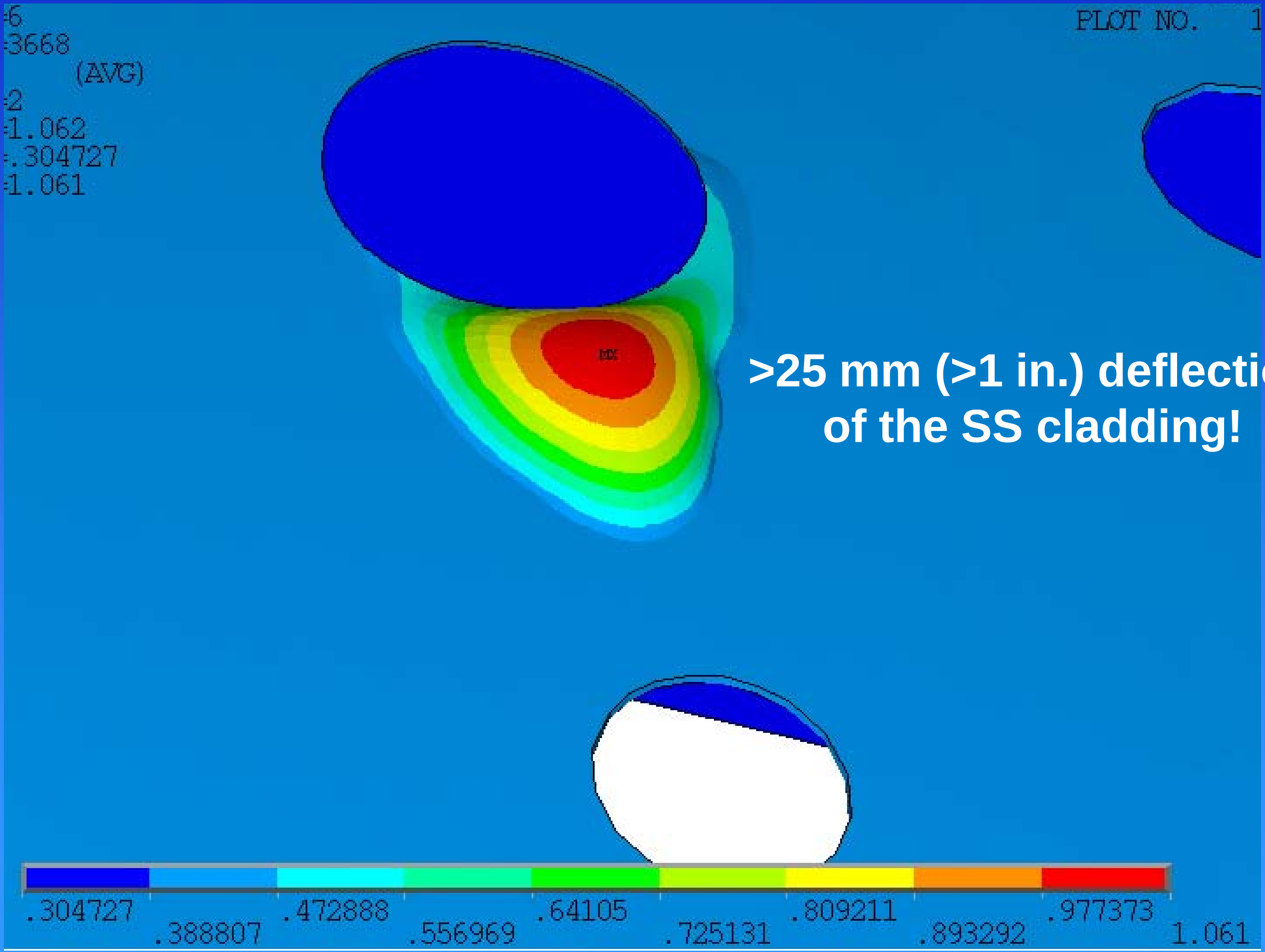
Modeling of Davis-Besse Cavity



Modeling of Davis-Besse Cavity

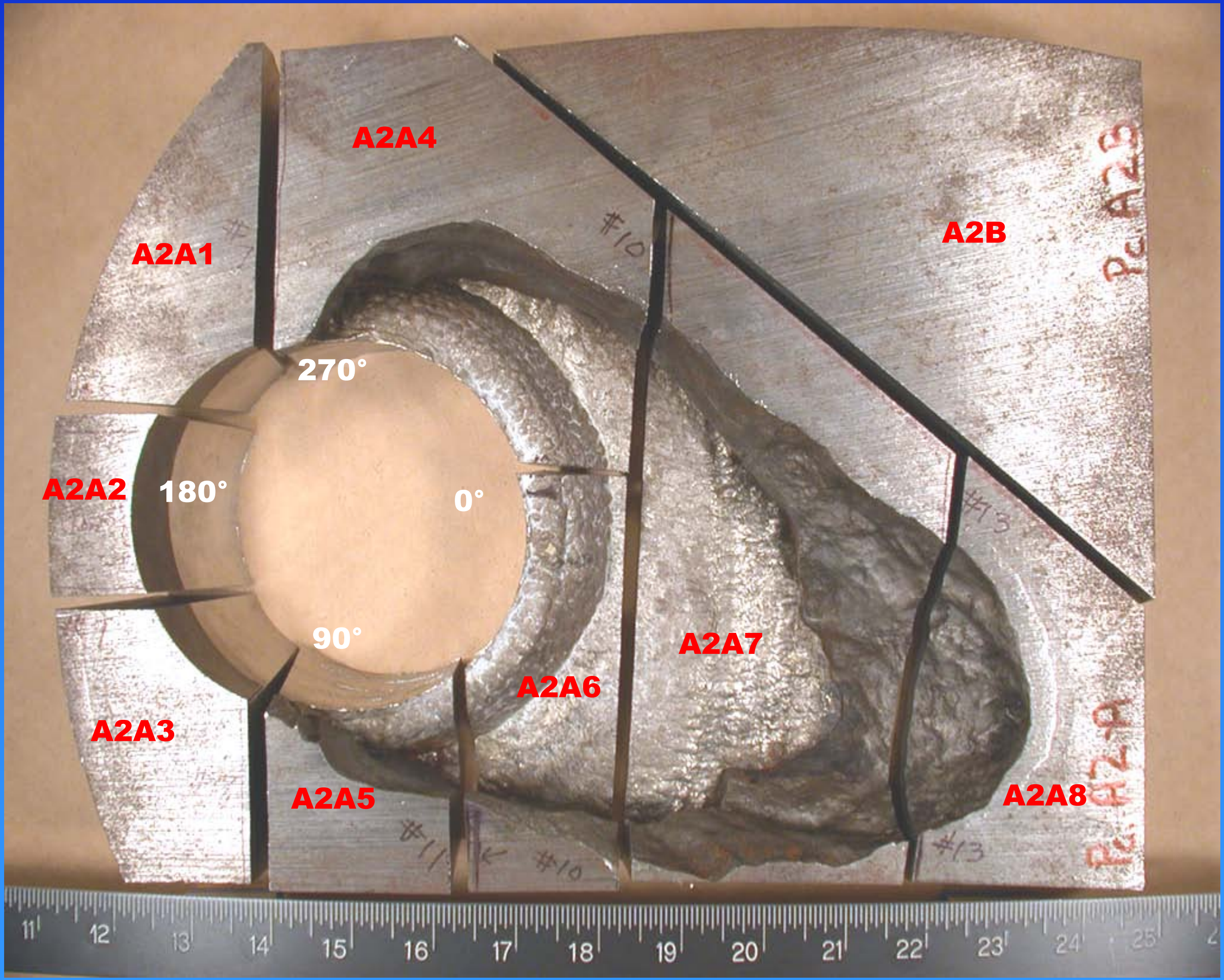


Modeling of Davis-Besse Cavity



>25 mm (>1 in.) deflection of the SS cladding!

Sectioning of Davis-Besse Cavity



W. Cullen, ACRS Mtg., 4/22/03

Structural Integrity Associates

Photographs of Davis-Besse Cavity Walls

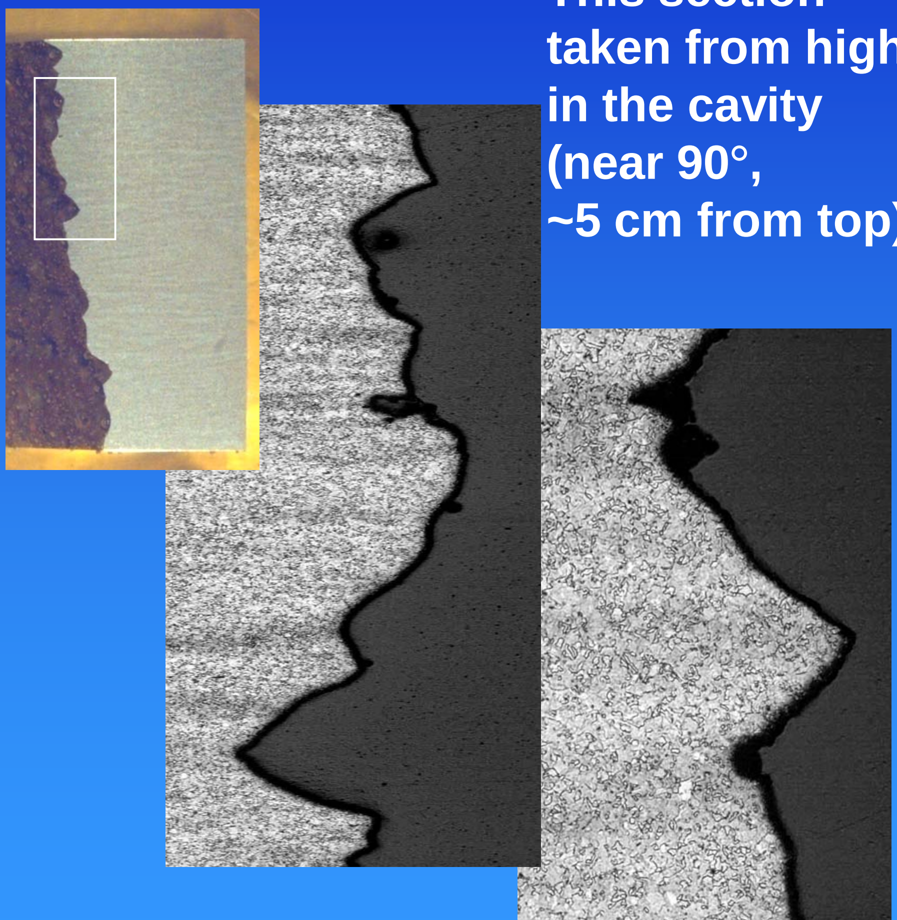
Looking up near nose of the cavity

Near 90°

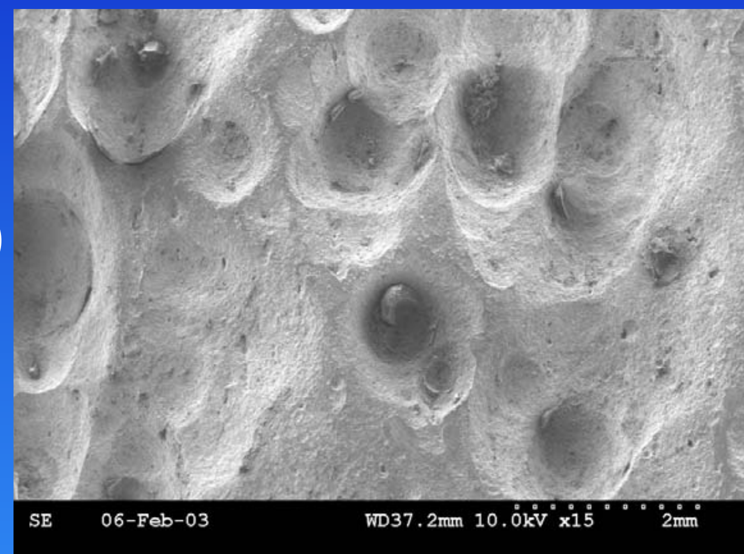
Near 270°

W. Cullen, ACRS Mtg., 4/22/03

Characterization of the Walls of the Davis-Besse Cavity



This section taken from high in the cavity (near 90°, ~5 cm from top)



Metallography (stack of three at left at increasing magnification), and SEM show that cavity walls are characterized in places by ~1 mm diameter pits "associated with banded microstructure"

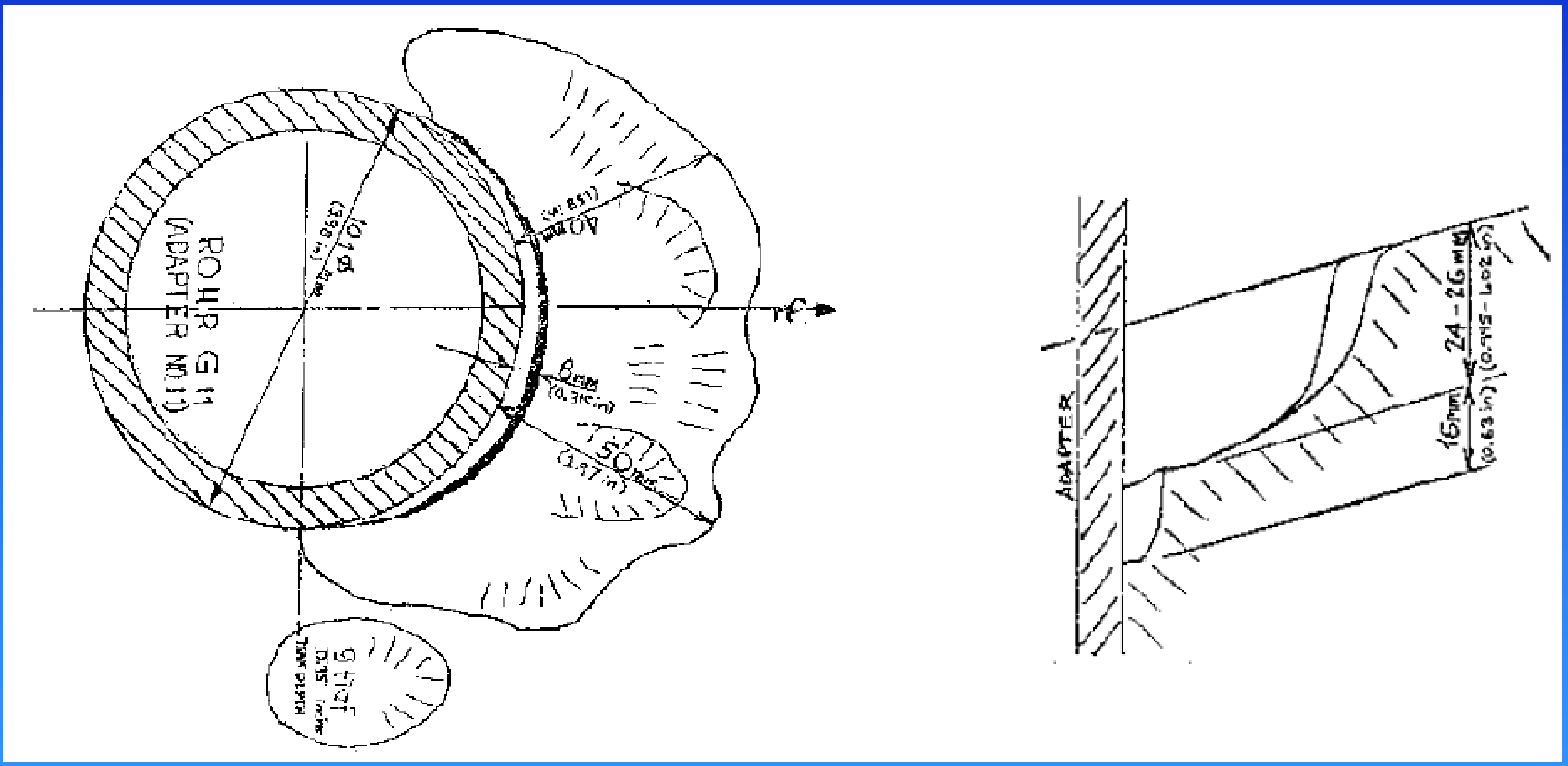
W. Cullen, ACRS Mtg., 4/22/03

Summary Boric Acid Corrosion in Europe (2002)

- France
  - Two plants with BA deposits on upper heads after leaks from a bolted flange and a canopy seal
    - Maximum attack depth was several mm, no repairs were necessary after removal of the BA deposits
    - Stainless steel seal faces were damaged by erosion-corrosion (steam cutting) that necessitated local repair
- Switzerland
  - Crescent shaped zone of attack 50 mm wide and 40 mm deep due to canopy seal leak
    - Head cleaned, PT, stress analysis performed and returned to service without repair with periodic inspection
- Germany
  - One upper head flange seal leak at 70°C (158ºF), but no serious significant BAC
    - Inspection and assessment is mandatory after leakage
    - Continuous monitoring for steam leaks

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

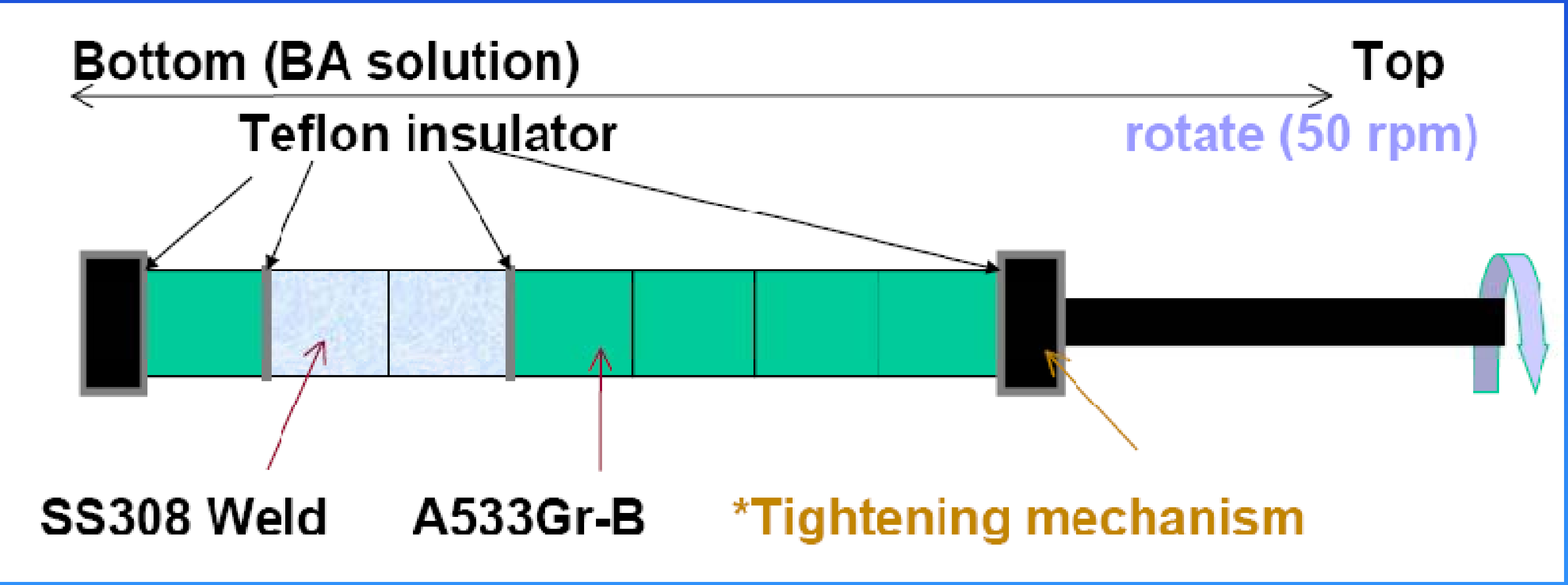
Beznau Unit 1, Nozzle 11: Corrosion Area Location, Size and Profile



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

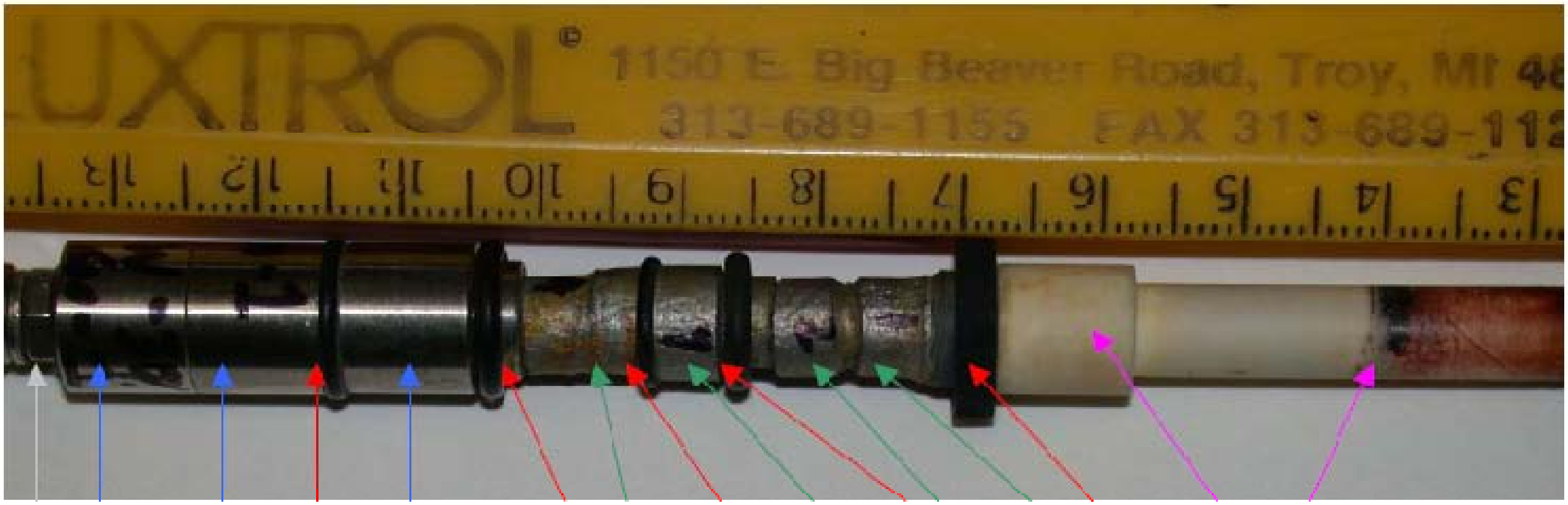
Structural Integrity Associates

ANL BAC Test Specimen



J. Park, et al., ANL, 1/05

BAC Results for A533Gr-B, Alloy 600, Type 308 SS at 97.5ºC



A B C D E F G H I J K L M N O

A: Screw tightening mechanism with flat O-ring a the bottom

B: A600 (30%CW), C: A600-1, E: SS308 clad weld

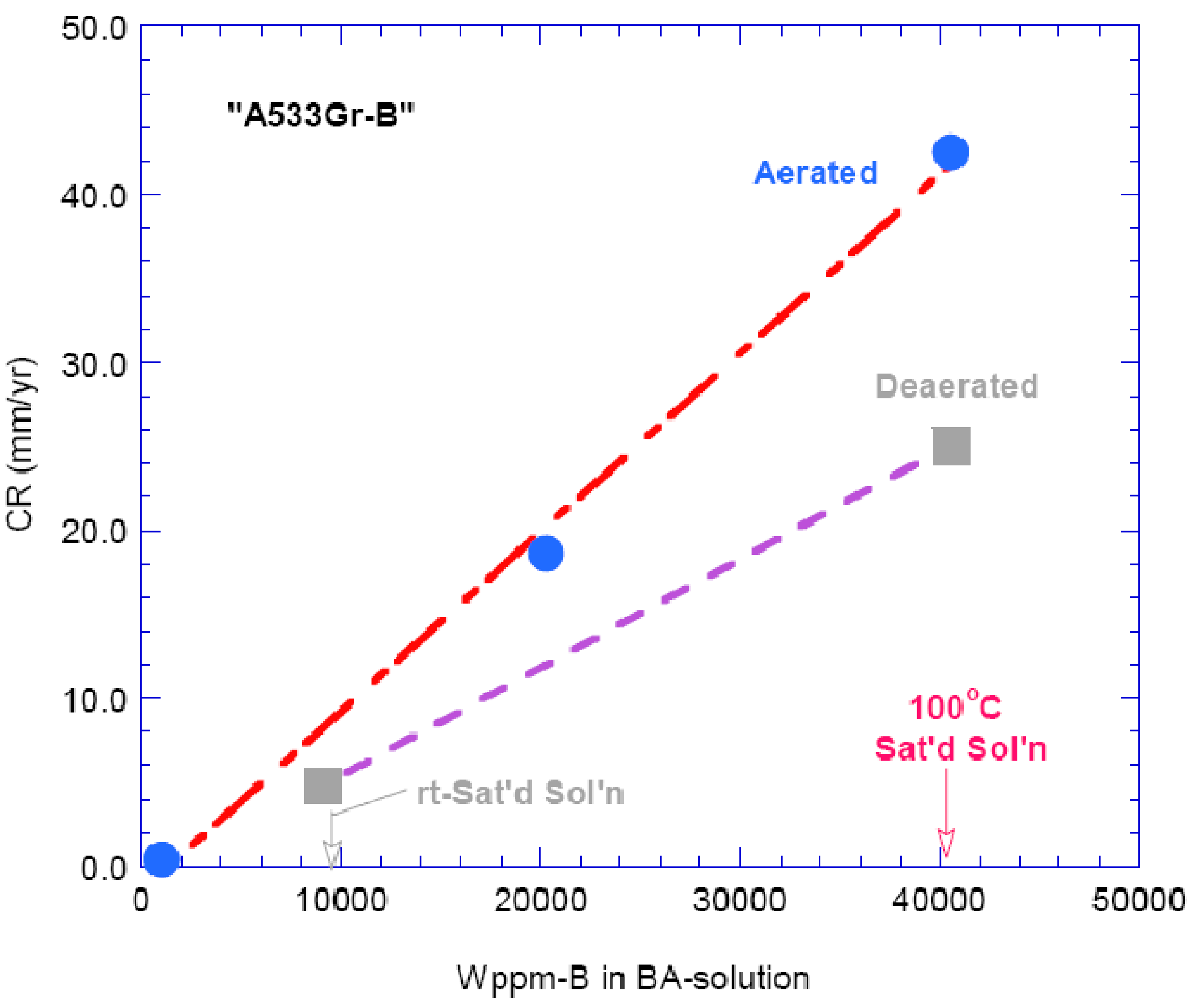
D,F,H,J, & M: O-rings,

G, I, K, & L: A533Gr-B #1,2,4, &7.

N & O: Alumina (N, in the solution & O, interface solution/vapor)

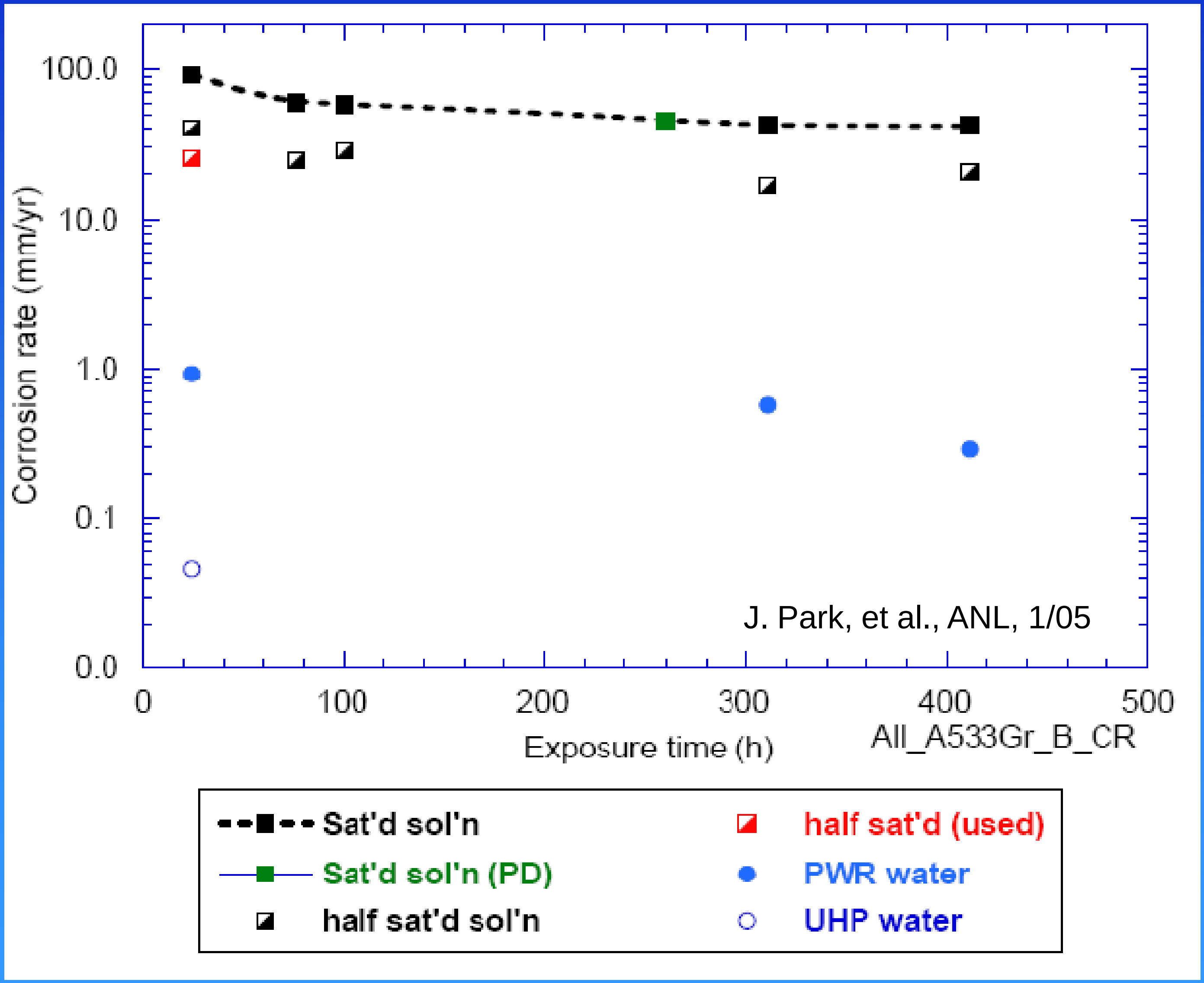
J. Park, et al., ANL, 1/05

Corrosion rate for A533-Gr. B in Aerated and Deaerated BA solutions near 100ºC

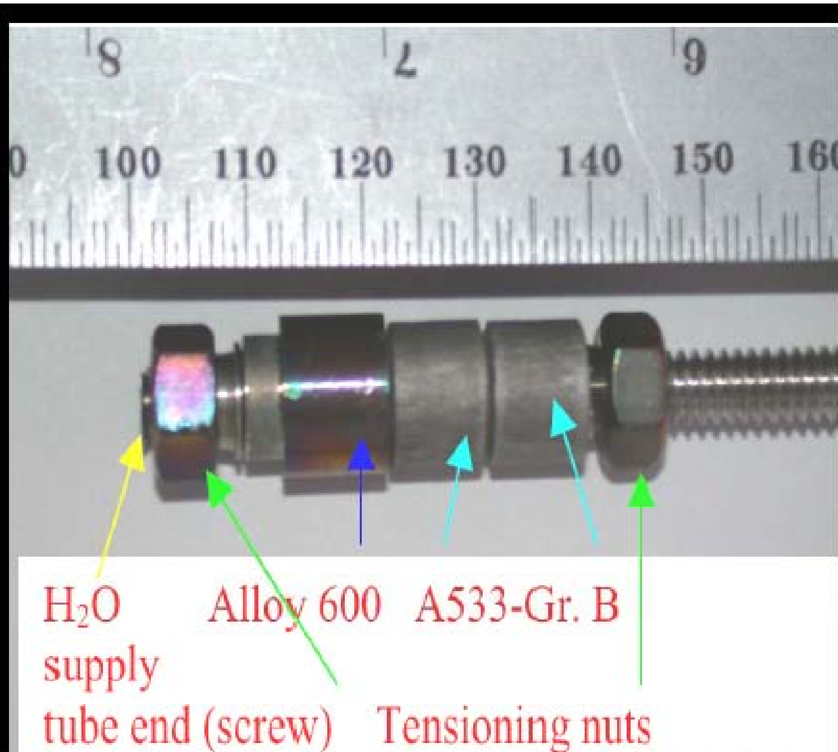


J. Park, et al., ANL, 1/05

Corrosion Rates for A533Gr-B Steel in BA Solutions at 97.5°C



Higher Temperature BAC Tests

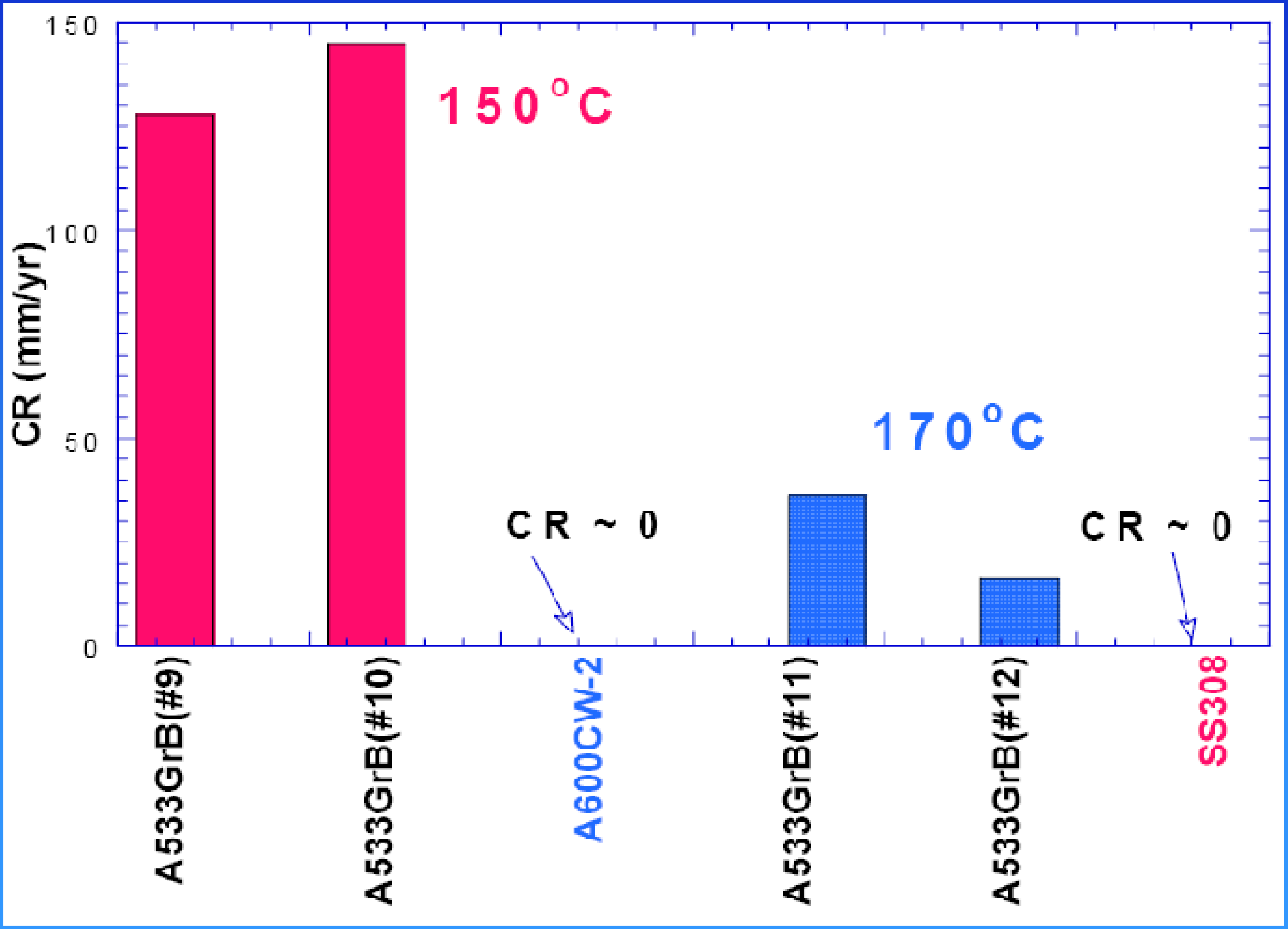


T = 150 °C
water additions for test times between 45 h.

T = 170 °C
water additions for test times between 40 h.

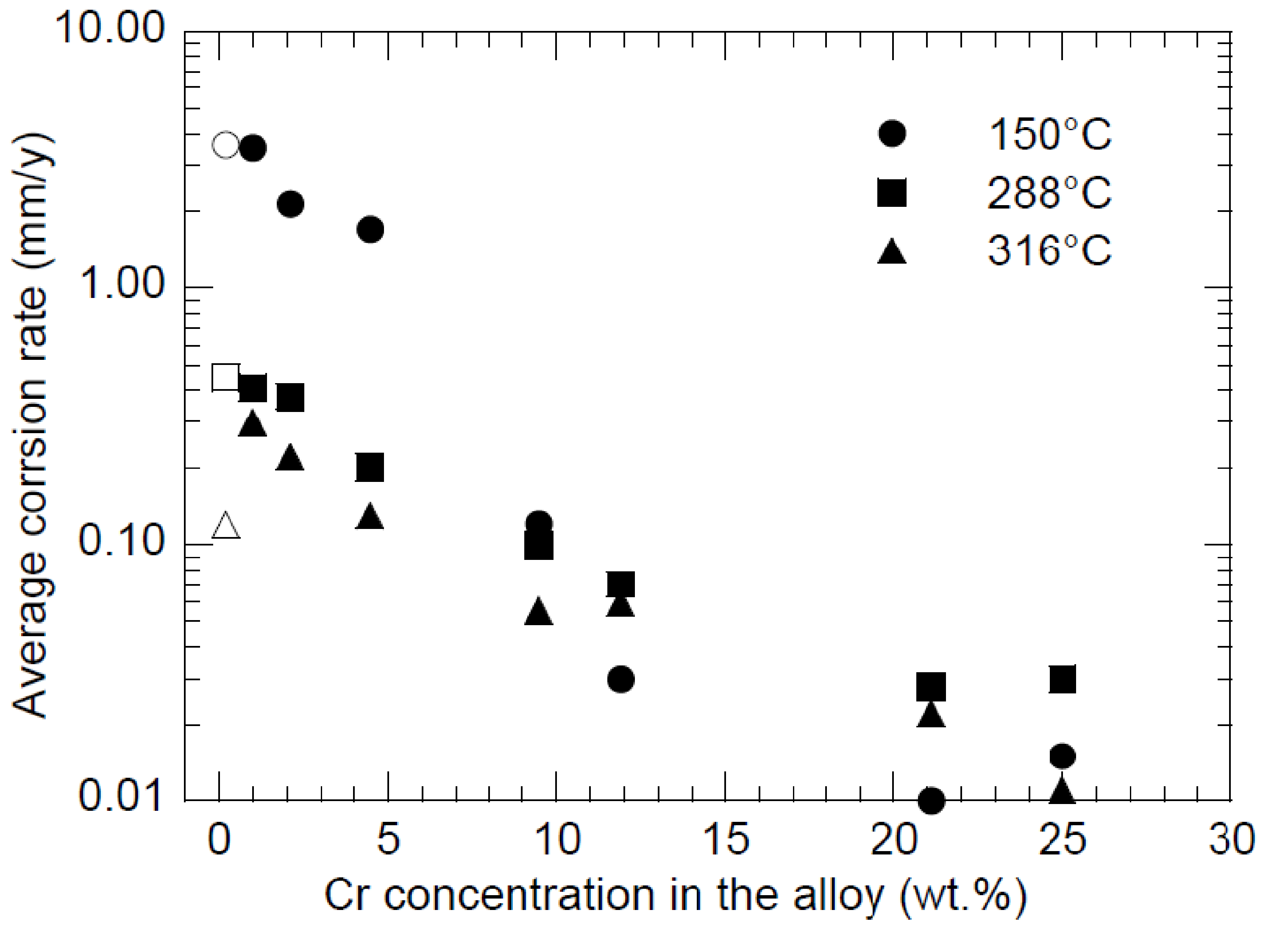
J. Park, et al., ANL, 1/05

BAC 150 and 170°C Test Results



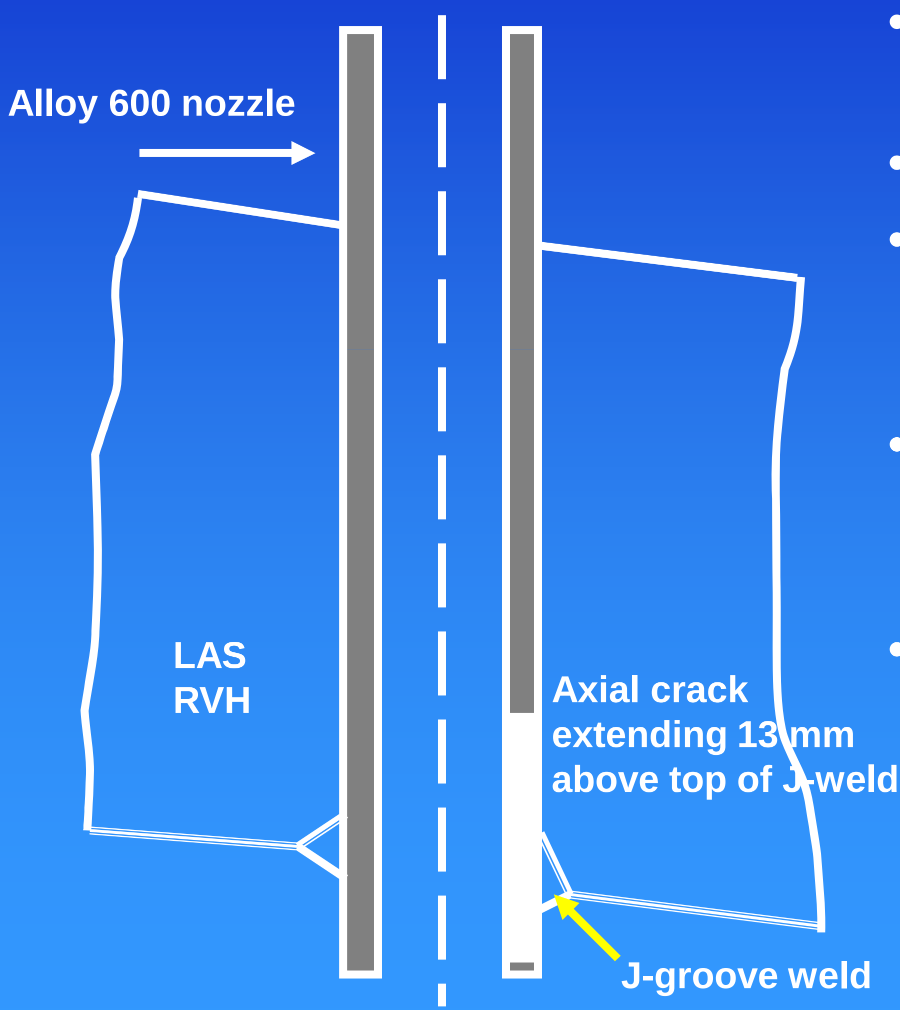
J. Park, et al., ANL, 1/05

Effect of Cr on BAC



NUREG/CR-6875, 7/05

Phase 1 of Postulated Mechanism of RVH Boric Acid Corrosion

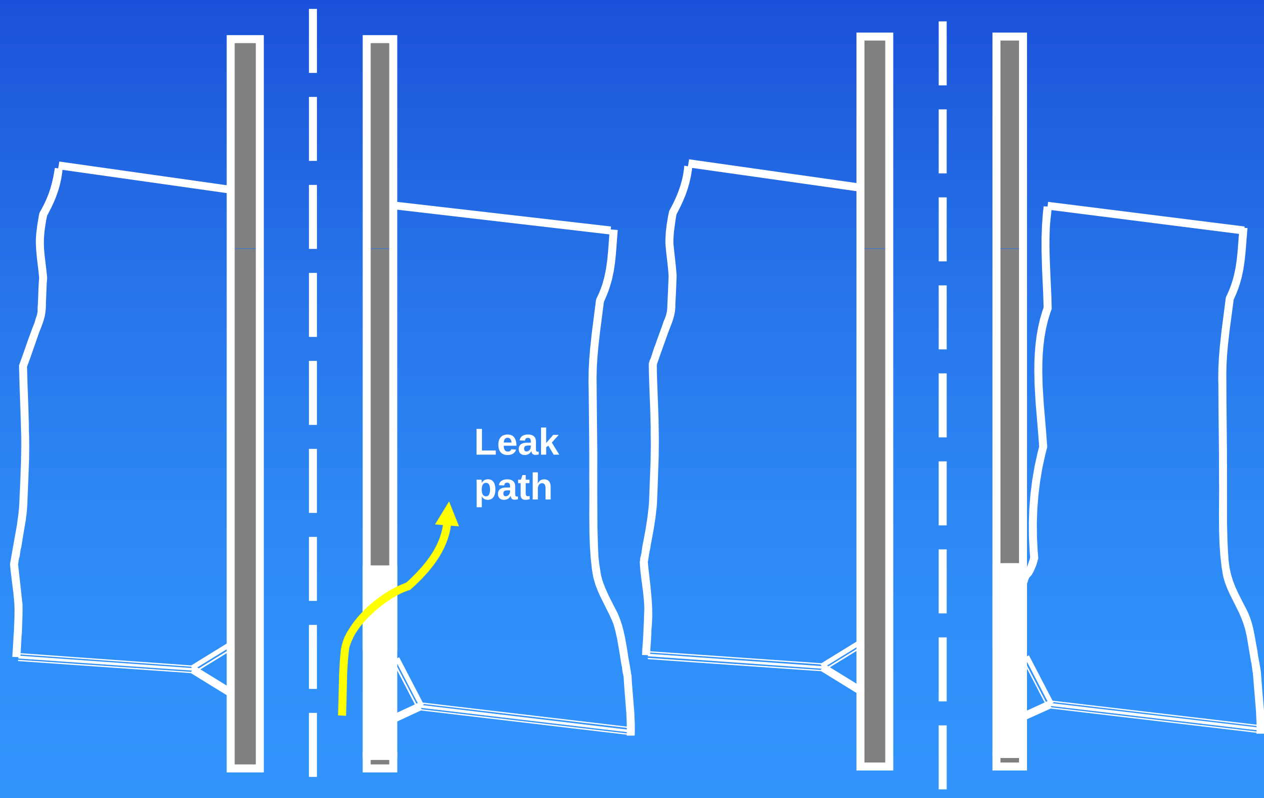


Phase 1 - Stagnant/Low Flow

- PWSCC penetrates A600 nozzle/J-weld
- Primary water enters annulus
- Depending on interference fit and possible deposit clogging, small leak (<1.1 l/h) may occur
- Slow corrosion of LAS with possible galvanic enhancement by Alloy 600
- Crack continues to grow and primary water flow rate increases

EPRI RFP57758-1, 3/03

Phase 2 of Postulated Mechanism of RVH Boric Acid Corrosion

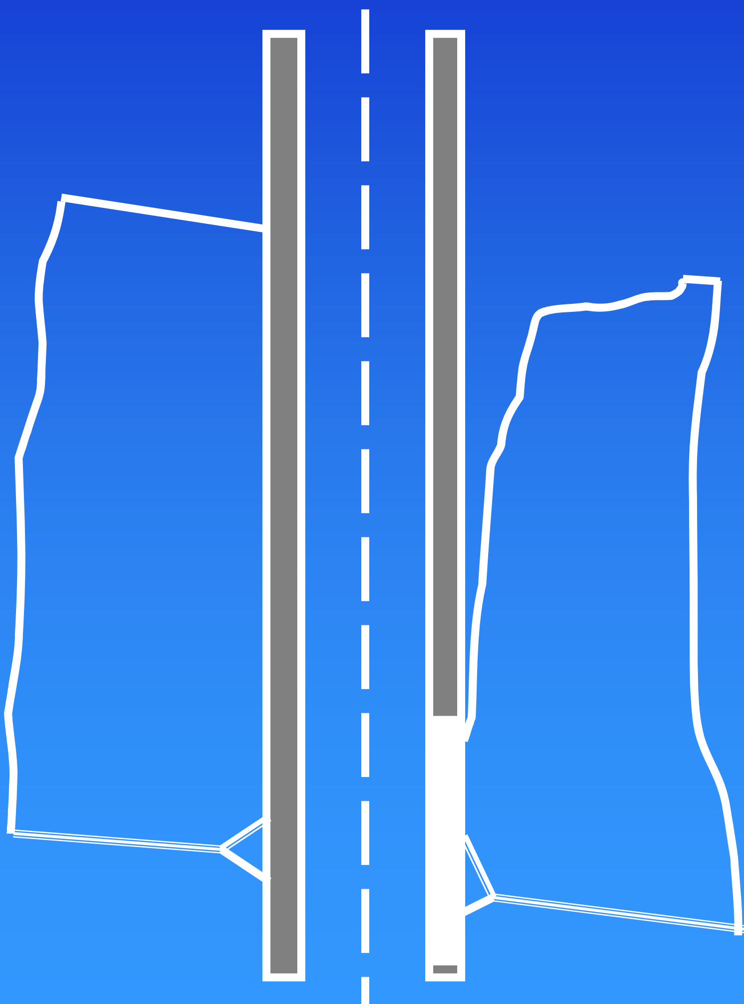


Phase 2 - Bottom Up
Flowing/Impingement

- Laminar single and two-phase flow in gap
- Water flashes to steam and leaves boric acid deposits behind
- 2.3 to 23 l/h leakage flow
- As gap widens, impingement contributes to cavity increase

EPRI RFP57758-1, 3/03

Phase 3 of Postulated Mechanism of RVH Boric Acid Corrosion

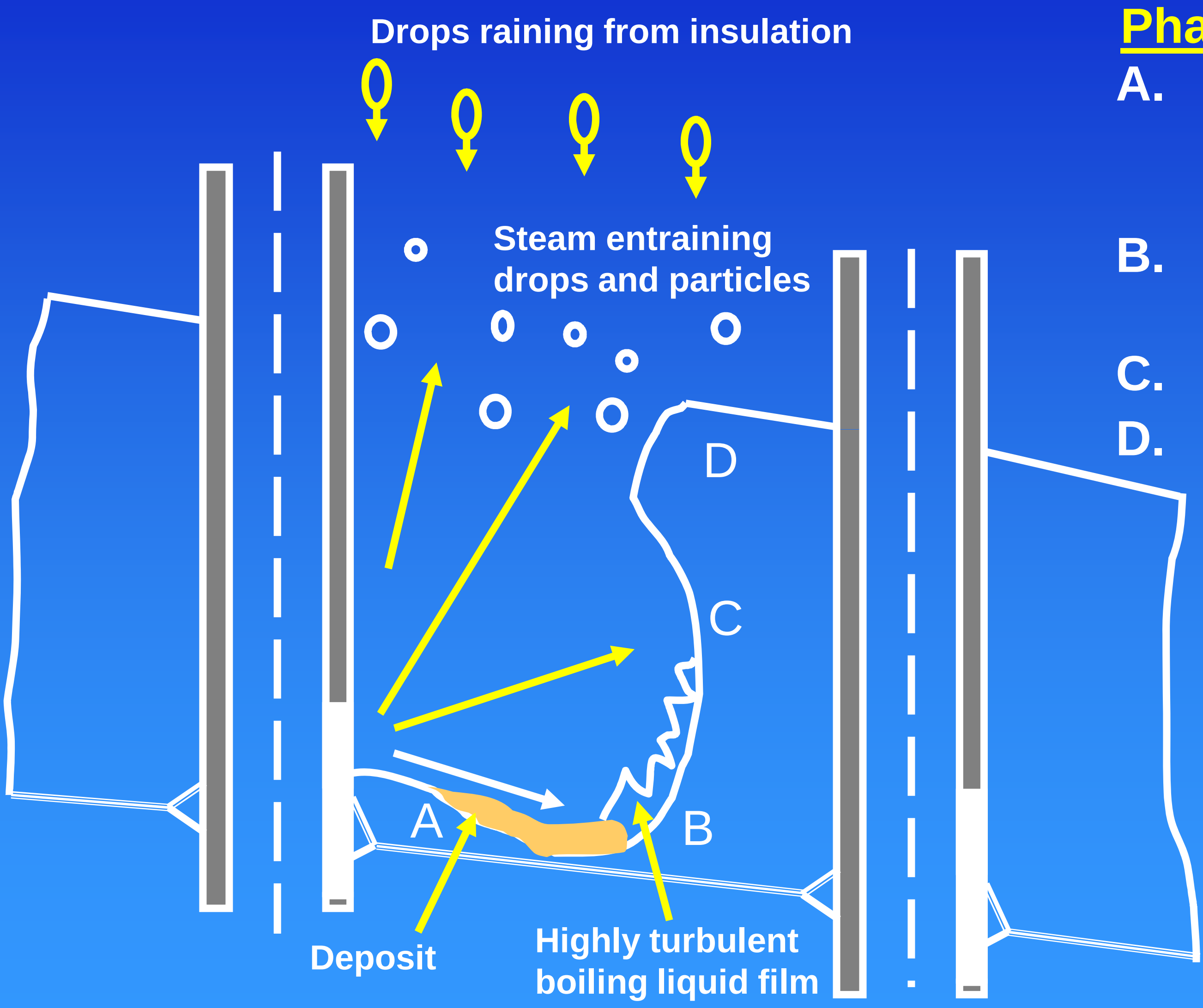


Phase 3 – Top-Down Concentrated BAC

- Large leak rate leads to local cooling of the RPV head
- Allows development of pools of concentrated and aerated boric acid and, perhaps, molten boric acid on top of head
- Results in a top-down corrosion path
- Some “FAC” and/or E/C may still occur at original leak

EPRI RFP57758-1, 3/03

Phase 4 of Postulated Mechanism of RVH Boric Acid Corrosion



Phase 4 - Full-Scale BAC

A. Galvanic corrosion and differential aeration
B. Galvanic corrosion and “FAC”
C. “FAC” and E/C
D. Differential aeration

EPRI RFP57758-1, 3/03

Criteria that Contribute to High BAC Rates

- Leak rate must be sufficient to impart a measure of evaporative cooling to the surface of the CS or LAS
- Very high leak rates also open up the possibility of a further damage mechanism due to erosion-corrosion
- Leak rate must be sufficient to maintain the boric acid crystals in a wet condition since the corrosion rates with dry boric acid on the CS or LAS surface are very low
- Corrosion rate will increase when O_2 is in the leakage region
  - Note that although aeration may be achieved in open geometries, it might be difficult under slurries in restricted geometries

EPRI 1016486, 5/08

BAC Great Debate

- Debate continues for the mechanism of BAC in very tight crevices (e.g., CRDM tube/RPV - Davis Besse in 2002)
- Mechanistic concern is that it is hard to clearly rationalize the maintenance of sufficient oxygen at the end of such a tight crevice due to both corrosion on the crevice sides and the purging effect of the escaping steam
- Work is continuing on BAC!

Still Some Specific BAC Unknowns

- How does the BAC process progress?
  - Bottom-up?
  - From a subsurface cavity?
  - Top down?
- Can a pool of water exist on the RVH?
- What is the dominate corrosion process?
  - General corrosion?
  - E/C?
- What is the corrosion rate as a function of leak rate?
- Is there a “critical” leak rate?
- What is the corrosion rate of RPV LAS?
  - w/wo heat flux in boiling boric acid
  - w/wo heat flux and jets of primary water
  - crevice corrosion rates

2010 - Déjà Vu All Over Again

Power Reactor	Event Number: 45764
Facility: DAVIS BESSE Region: 3 State: OH Unit: [1] [ ] [ ] RX Type: [1] B&W-R-LP NRC Notified By: LARRY MYERS HQ OPS Officer: VINCE KLCO	Notification Date: 03/13/2010 Notification Time: 04:45 [ET] Event Date: 03/12/2010 Event Time: 21:43 [EST] Last Update Date: 03/13/2010
Emergency Class: NON EMERGENCY	Person (Organization):
10 CFR Section: 50.72(b)(3)(ii)(A) - DEGRADED CONDITION	MONTE PHILLIPS (R3DO)

On March 12, 2010, during the Davis-Besse refueling outage, the documented results of planned UT examinations performed on the CRDM nozzles penetrating the RVCH identified that two of the nozzles inspected to date did not meet the applicable acceptance criteria. Each of these two nozzles have similar indications that appear to penetrate into the nozzle walls from a lack of fusion point at the outer diameter of the nozzle and the J-Groove weld.

Davis-Besse in the Plain Dealer

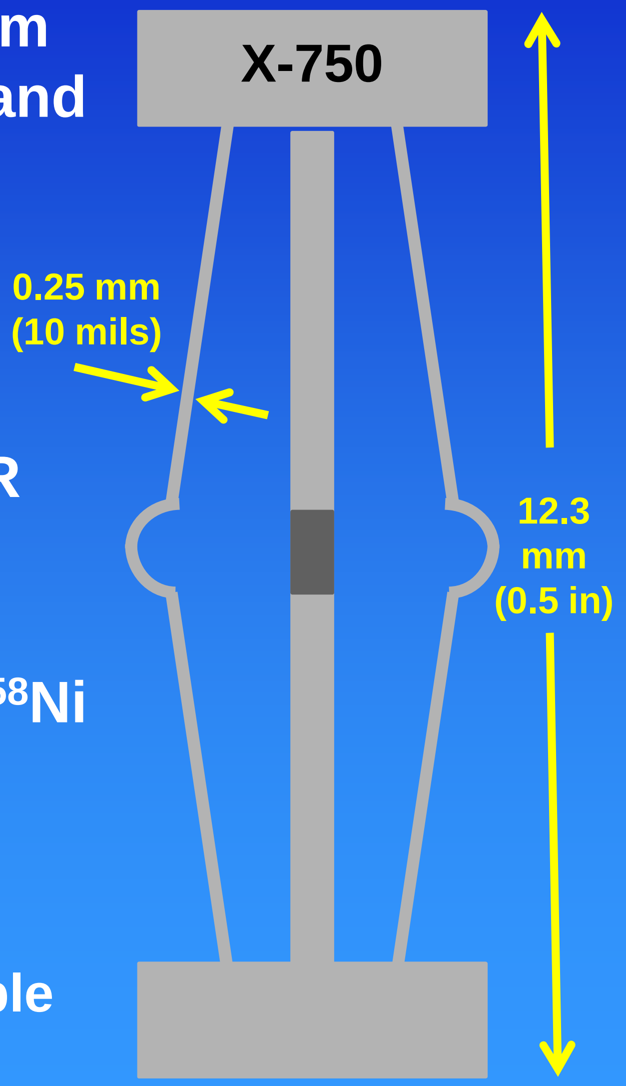
OAK HARBOR, Ohio , March 15, 2010-- Inspectors working at FirstEnergy Corp.'s Davis-Besse power plant near Toledo have uncovered the same kind of cracking in critical reactor lid parts that were the cause of massive corrosion found at the plant eight years ago. In a routine report filed early today with the Nuclear Regulatory Commission, the company said inspectors using sophisticated ultrasonic instruments had found indications of cracking in 12 of the 69 metal tubes that carry control rods through the reactor lid.

The Toledo Blade, 3/25/02

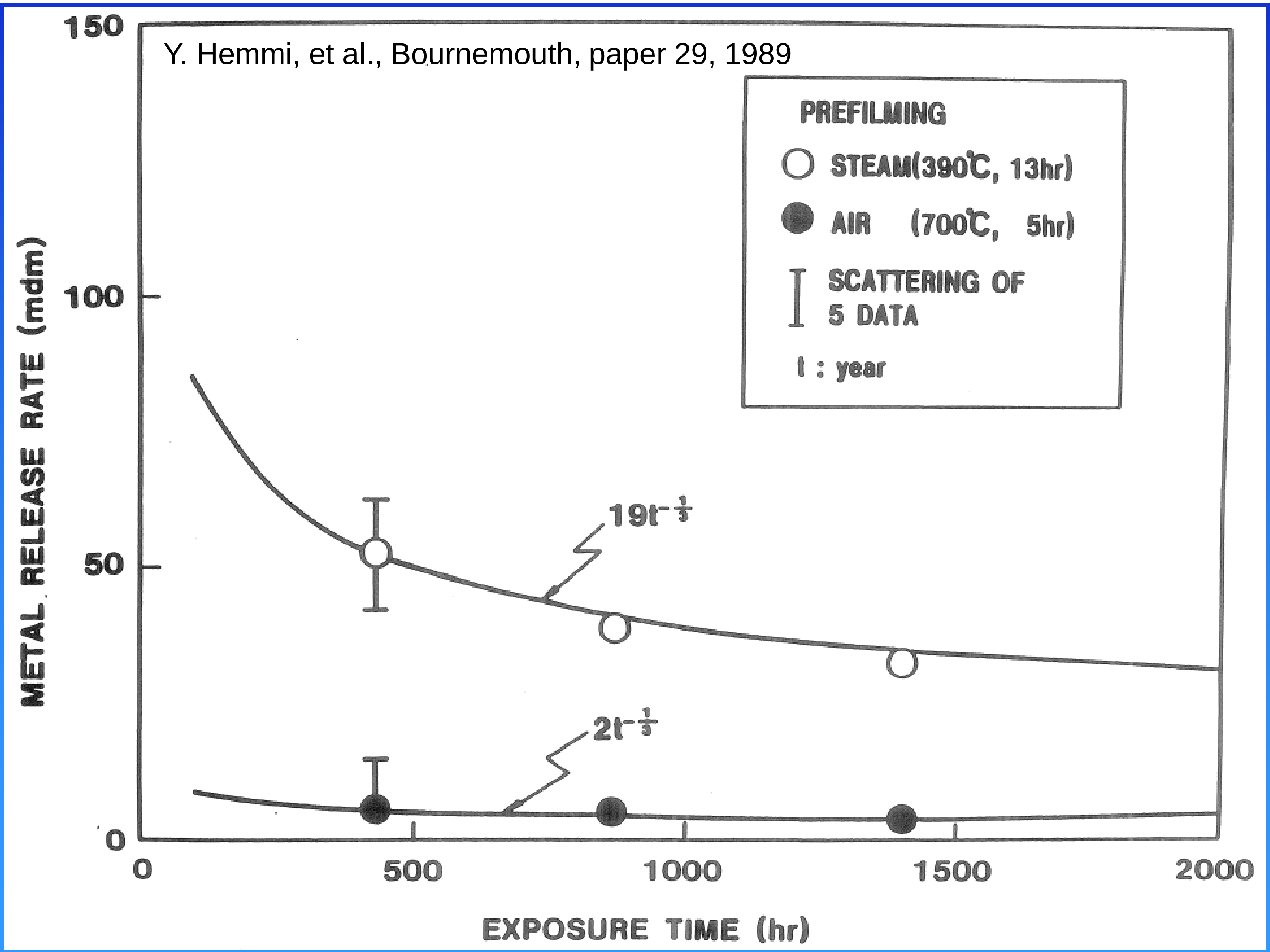
Alloy X-750 Corrosion in BWRs

General Corrosion of Alloy X-750 in BWRs

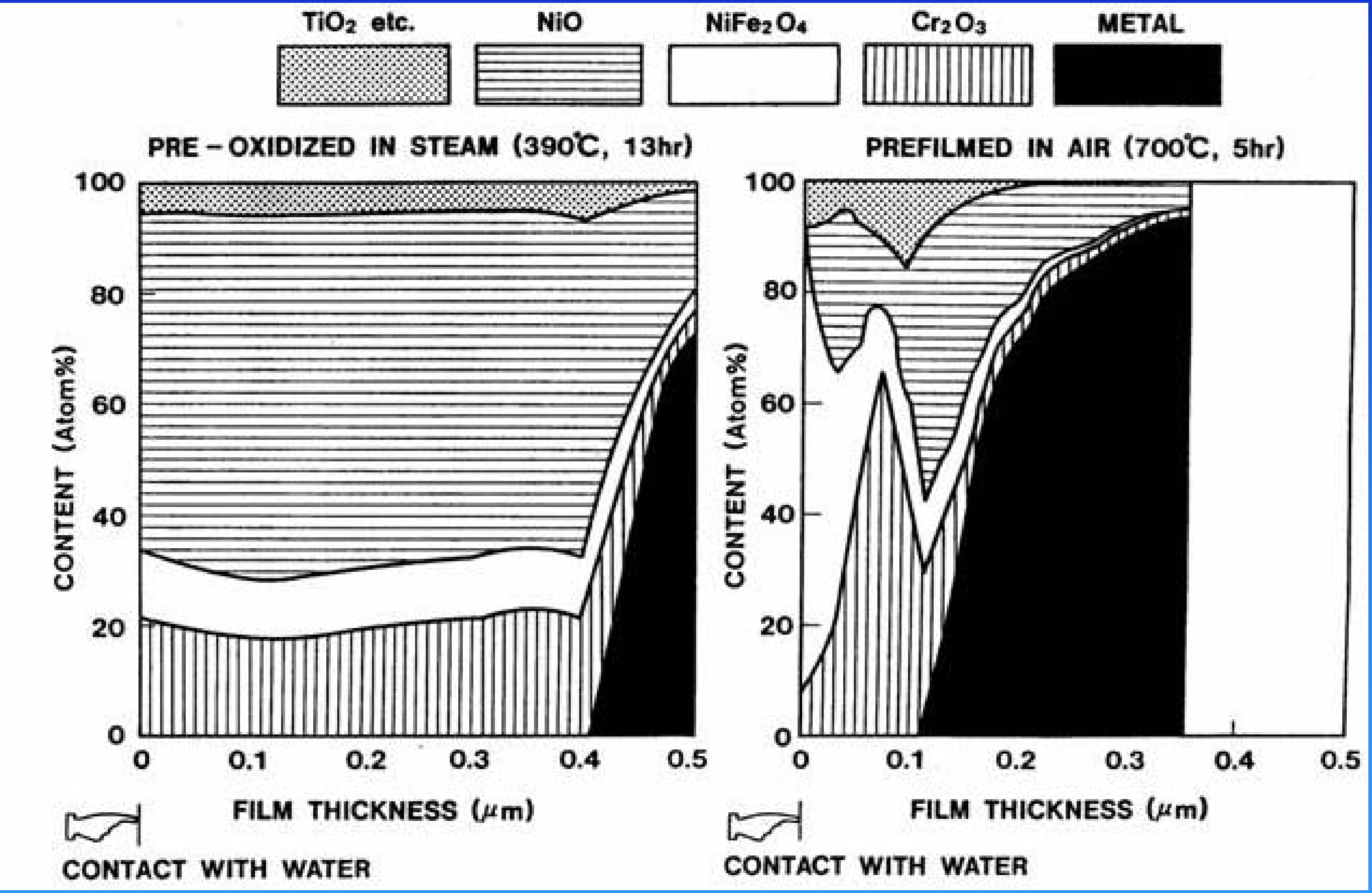
- A quality "improvement" in ABB's vacuum aging treatment leads to high corrosion and "flaking" of Alloy X-750 fuel springs
- Japanese investigators also notice high corrosion rates on fuel springs
- Alloy X-750 has high general corrosion rates in the highly oxidizing O_2/H_2O_2 BWR core environment
- Inhibition of ^{58}Co and ^{60}Co directly generated from the corrosion release of ^{58}Ni and ^{59}Co, respectively, from Alloy X-750 would be an effective method to reduce radiation exposure
  - ABB: Ni alloy corrosion may be responsible for 75% of radiation buildup in BWRs!



Metal Release Rate from Alloy X-750



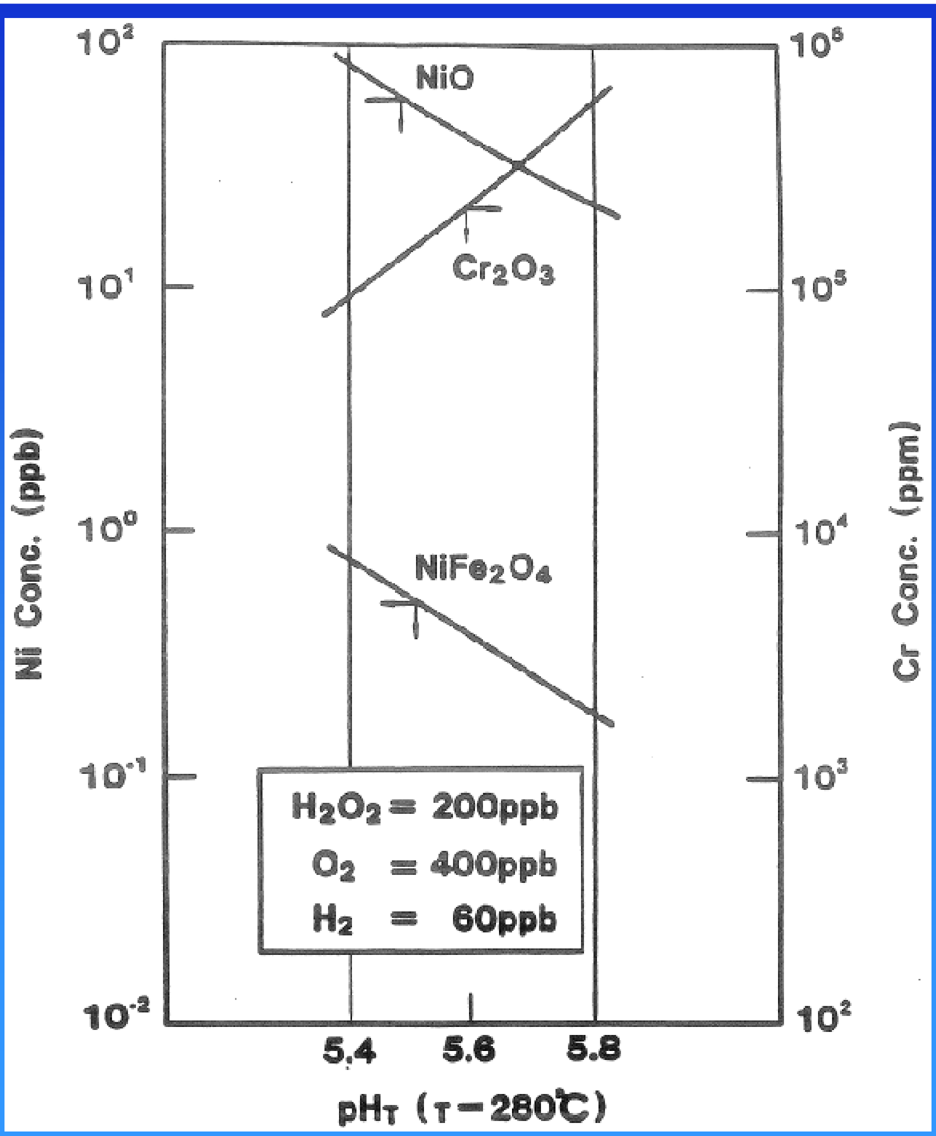
Distribution of Corrosion Oxides formed on Alloy X-750 in Steam and Air



Y. Hemmi, et al., Bournemouth, paper 29, 1989

Structural Integrity Associates

Solubility of Ni and Cr in High Temperature Water



Y. Hemmi, et al., Bournemouth, paper 29, 1989

Mitigation of Alloy X-750 General Corrosion in BWRs

- ~700°C (~1300°F) air pre-oxidation of Alloy X-750 can reduce general corrosion
- There are thermodynamic and chemical bases for the improvement in general corrosion resistance of pre-oxidized Alloy X-750
- Alloy X-750 aging at 704°C (1300°F)/20h can be combined with pre-oxidation treatments to minimize Alloy X-750 general corrosion

Corrosion of Zr Alloys

Zr Alloys in LWRs

- Uranium dioxide (UO_2) fuel pellets are encased in Zr alloy cladding (fuel rods)
- Zr is used because of its very low thermal neutron absorption cross section
- Zr alloys were developed for nuclear applications and were not initially used for other industries basically due to its higher cost
  - Zircaloy 2 – BWRs: 1.2–1.7 Sn, 0.07-0.2 Fe, 0.05-0.15 Cr, 0.03-0.08 Ni
  - Zircaloy 4 – PWRs and CANDU: 1.2–1.7 Sn, 0.18-0.24 Fe, 0.07-0.13 Cr (No Ni)
  - ZIRLO™ – PWRs: 1.0 Sn, 0.1 Fe, 1.0 Nb

    ZIRLO = **zir**conium **l**ow **o**xidation

Characteristics of LWR Fuel Assemblies

	Fuel Rod				Assembly		Coolant	
LWR Type	OD, mm	Thick-ness, mm	Length, m	Alloy	Geometry	# of rods	T, °C	P, MPa
PWR	9.5 -10.5	0.6 - 0.7	3.7- 4.3	Zr-4 Zr-1%Nb (M5®)	Square	240-300	290-335	15.5
BWR	12-13	0.8	3.5-4	Zr-2	Square with channels	55-65	275-285	7
CANDU	13.8	0.41	0.5	Zr-4	Cylinder in pressure tube	37	Heavy water 265-310	10
WWER 1000	9.1	0.7	3.5	Zr-1%Nb (E110)	Hexagonal	331	290-320	15.7
RBMK	13.6	0.825	2 * 3.5		Cylinder in pressure tube	2 * 18	270 – 284	6.7

M5 is Areva's Zr alloy

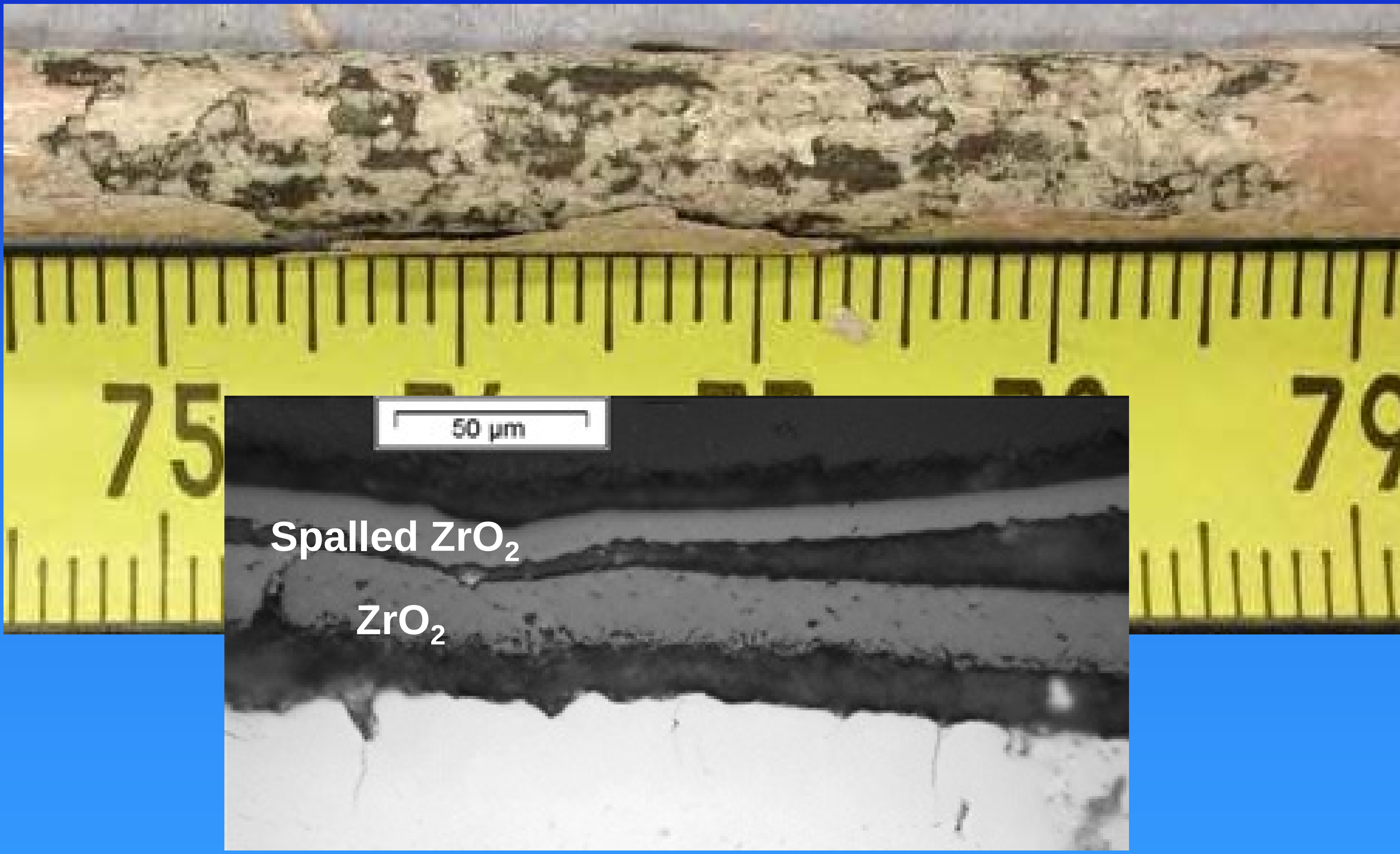
C. Lemaignan, Vol 13C, ASM, 2006

Structural Integrity Associates

Corrosion of Zr Alloy Fuel Cladding

- Zr alloys form a passive lustrous black oxide film on the surface at 200-400°C (392-752°F)
- Oxide stability is a strong function of its thickness
  - Above a “threshold” thickness, the oxide film may not be protective and spall off the surface
- Second phase particles (SPPs)
  - Zr-2: $Zr(Fe, Cr)_2$ and $Zr_2(Fe, Ni)$
  - Zr-4: $Zr(Fe, Cr)_2$
- $Zr + 2H_2O \rightarrow ZrO_2 + 2H_2$ (Fukushima!) or $ZrO_2 + 4H$
- Some of atomic H is absorbed into the Zr and form brittle hydrides (γ-ZrH, δ-$ZrH_{1.6}$, ε-ZrH_2)

Oxidation Spalled Zr-Nb Alloy at 850ºC



M. Steinbrück, et al., ERMSAR-2008

Factors Affect the Corrosion of Zr Alloys In LWRs

- **Ability of Zircaloy and other Zr alloys to withstand corrosion and in-reactor degradation is determined by:**
  - **Temperature**
  - **Water chemistry**
  - **Microstructure (especially the second phase particles [SPP]). The key precipitate parameters affecting corrosion are:**
    - **Size**
    - **Morphology**
    - **Composition and distribution**
- **Corrosion and hydrogen pickup rates vary not only with alloy composition, but also with the thermo-mechanical treatment (and resulting microstructure)**

Effect of Precipitate Size on Zr Relative Corrosion Rate

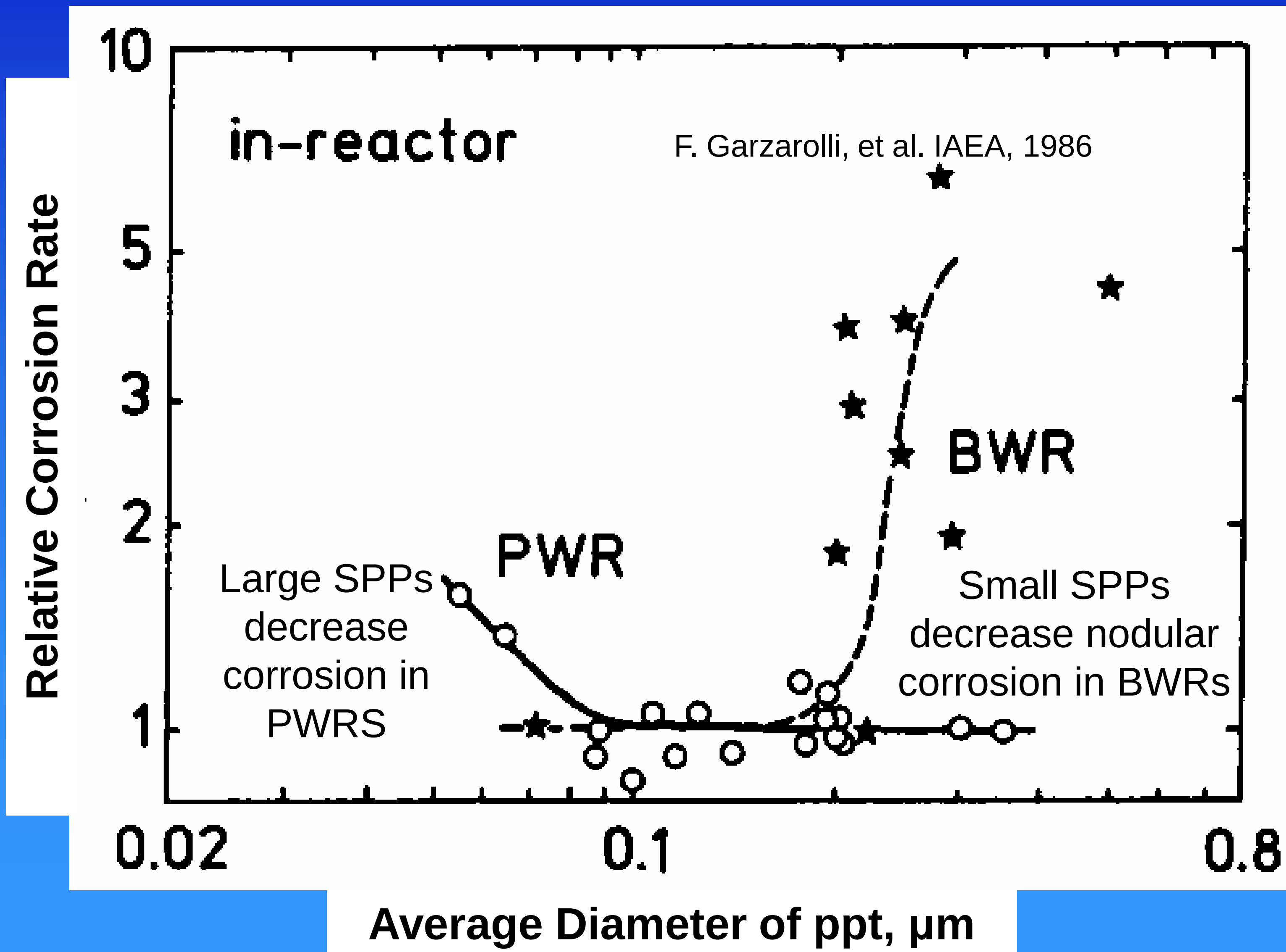
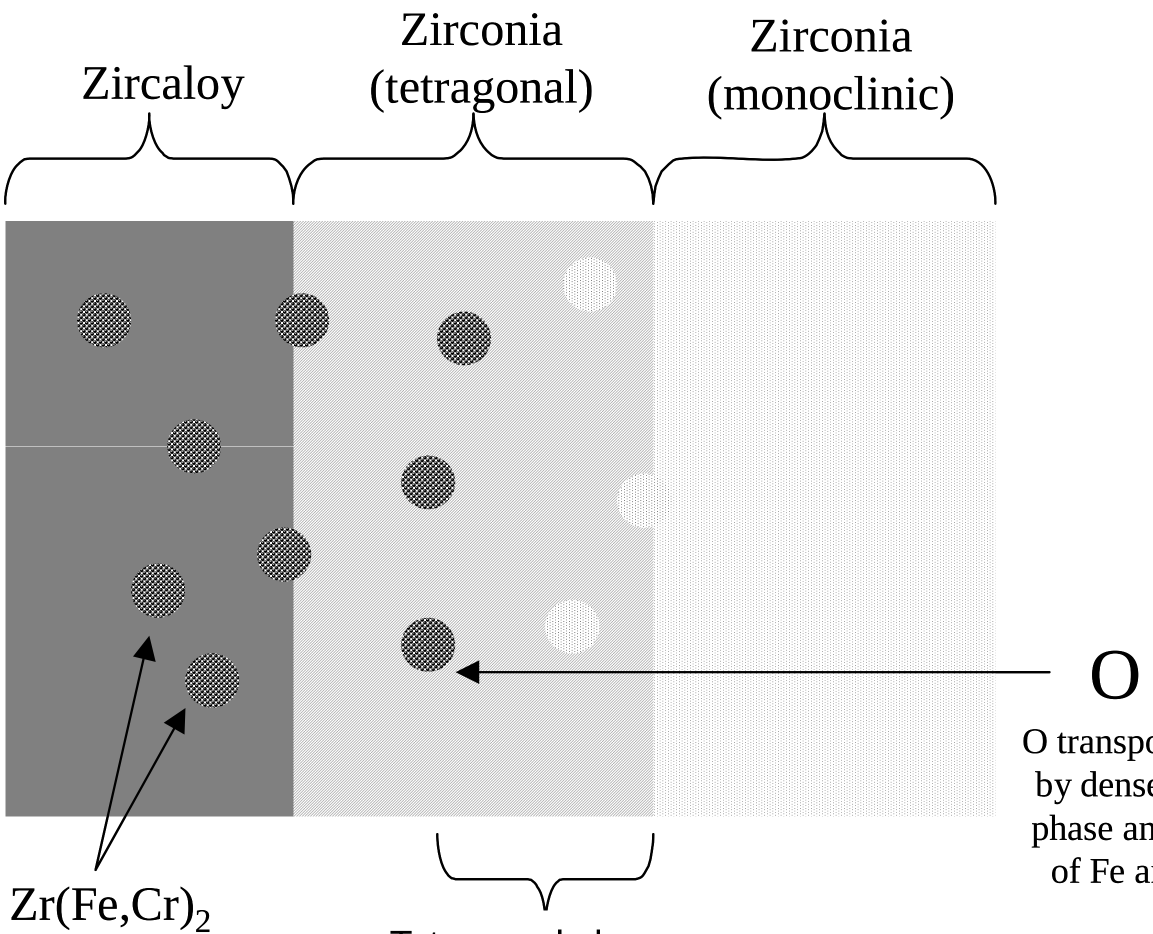
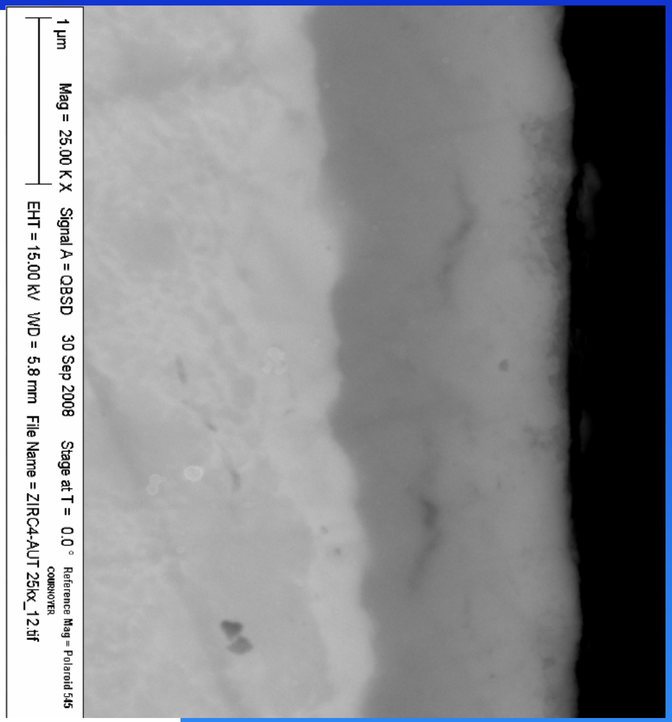


Illustration of the Role of Precipitates in Corrosion of Zircaloy-4



O transport is slowed by dense tetragonal phase and oxidation of Fe and Cr ions

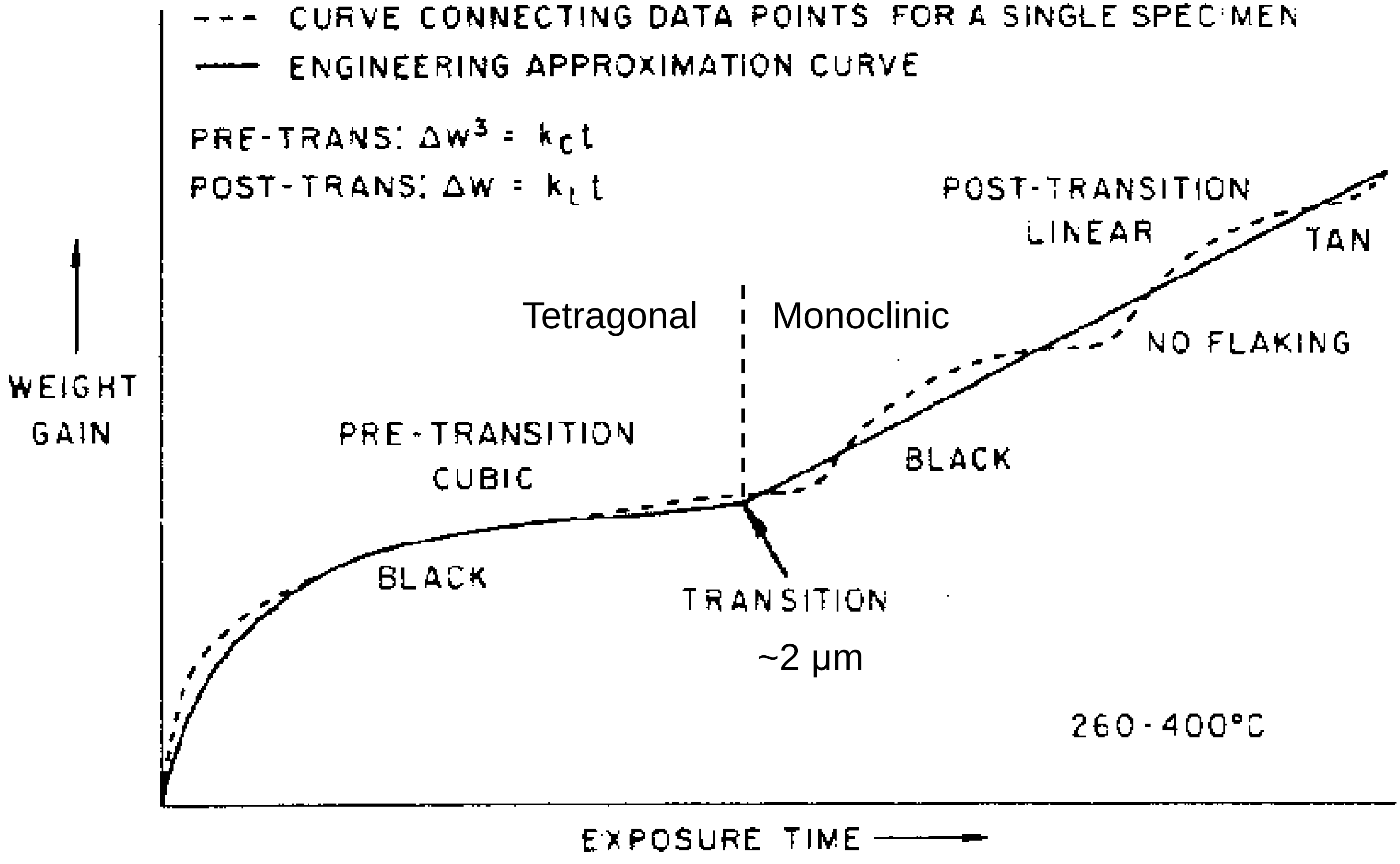
Tetragonal phase is stabilized by the oxidation of SPPs



14 hr exposure to steam at 400°C (752°F)

Structural Integrity Associates

General Corrosion Kinetics of Zircaloy

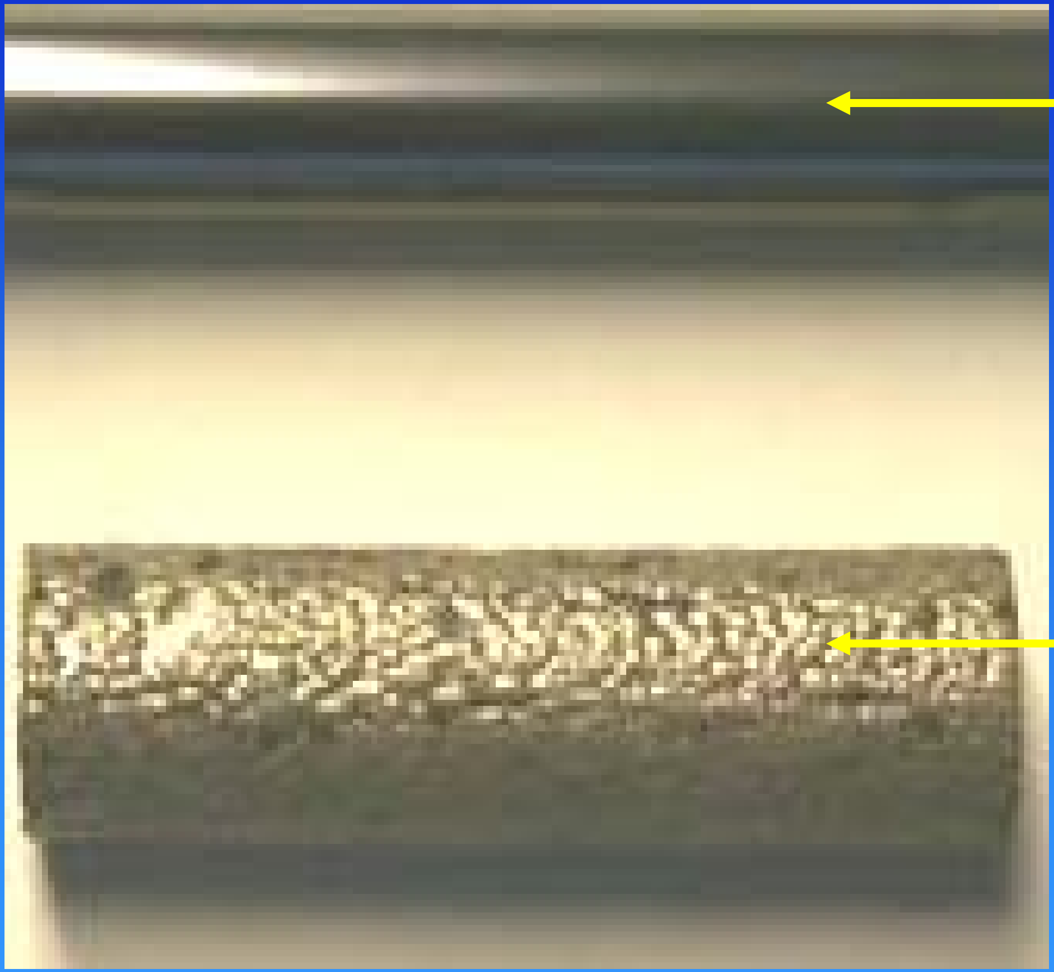


E. Hillner, ASTM 633, 1977

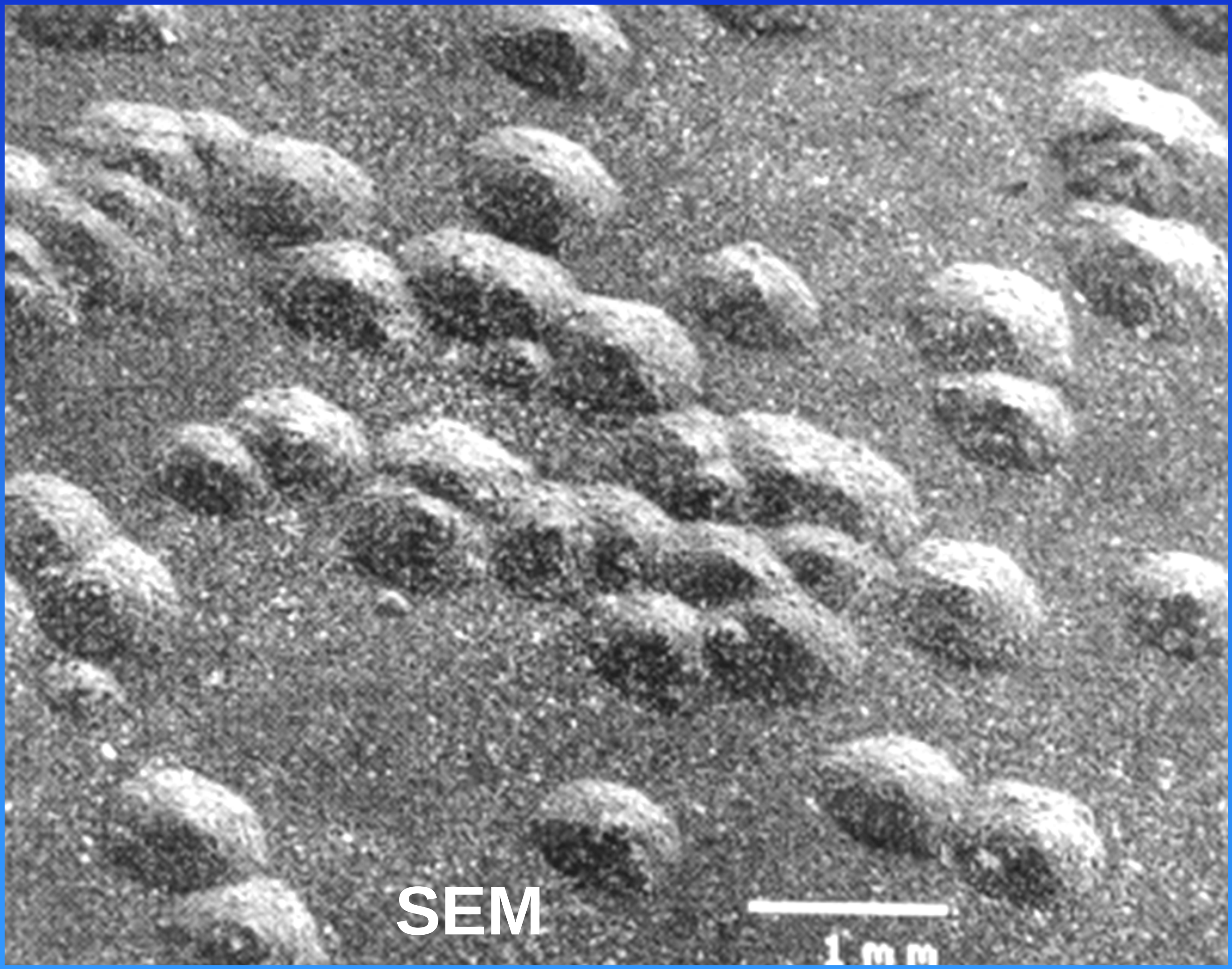
General and Nodal Corrosion of Zircaloy

- Occurs in Zr-2 in BWRs due to large SPPs: $Zr(Fe, Cr)_2$ $Zr_2(Fe, Ni)$

- Need homogeneous distribution of small SPPs to prevent nodular corrosion

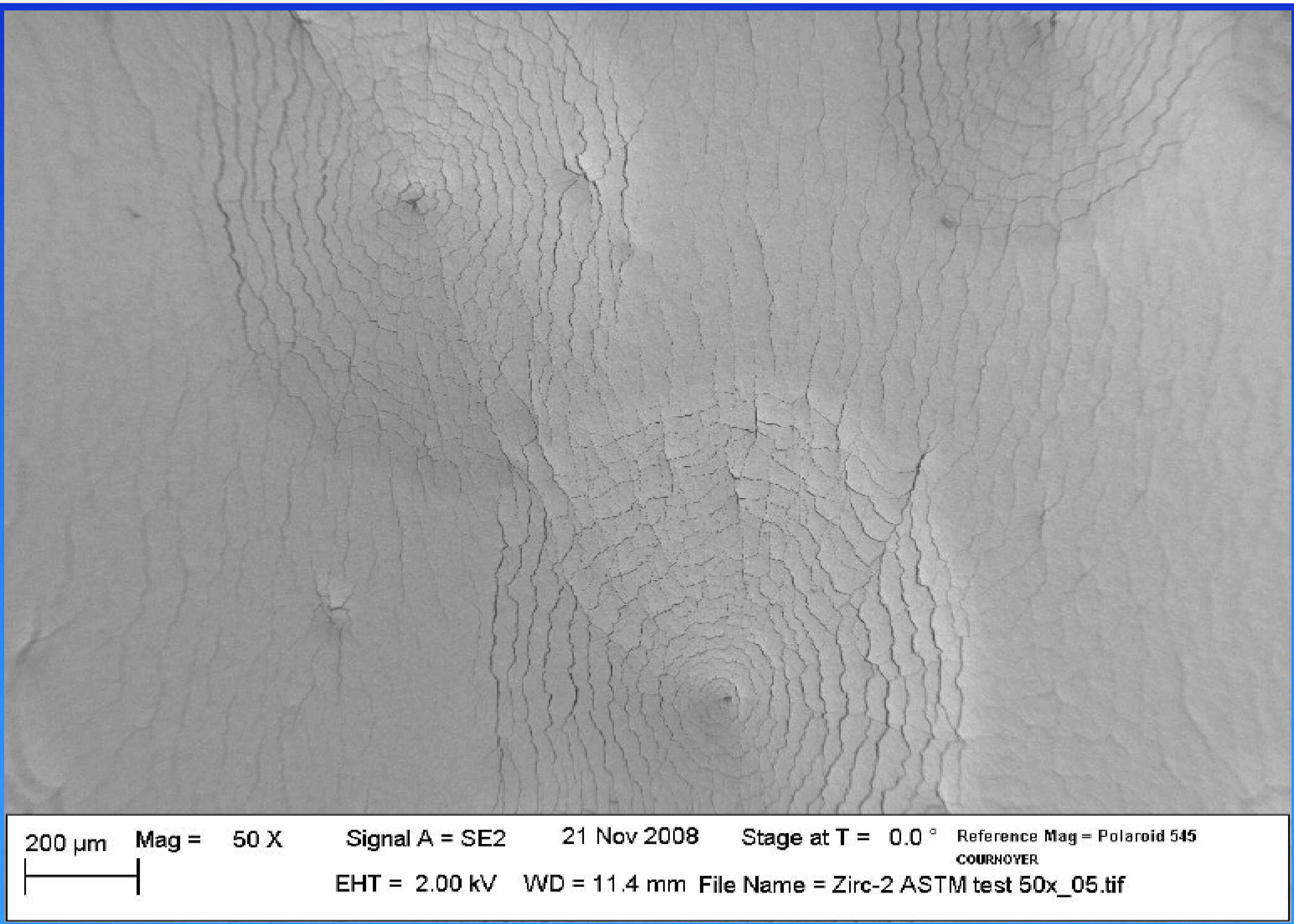


Nodular Corrosion of Zircaloy 2



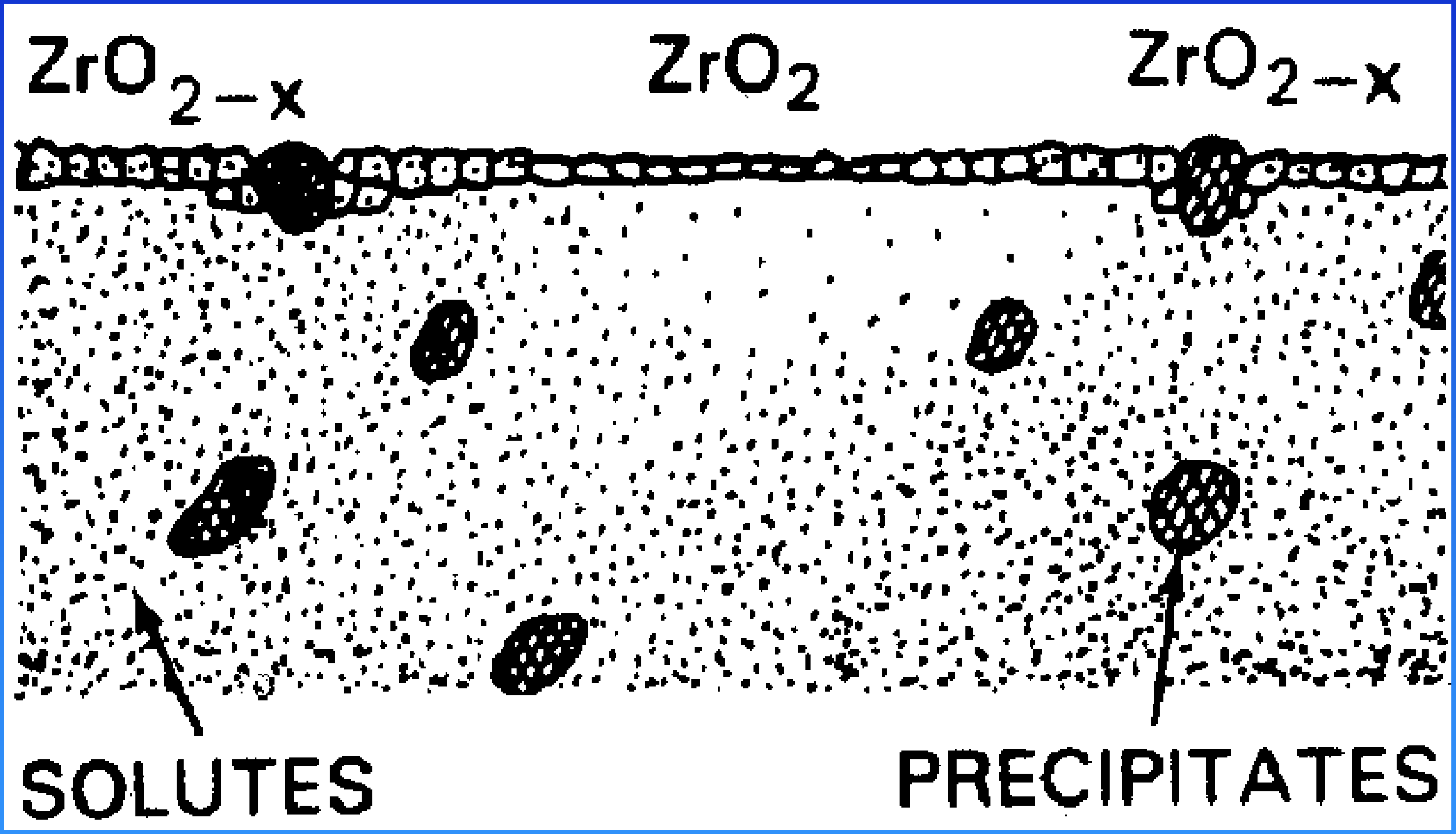
C. Lemaignan, Vol 13C, ASM, 2006

Nodular Corrosion of Zircaloy 2



R. Rebak, paper 09497,Corrosion 2009

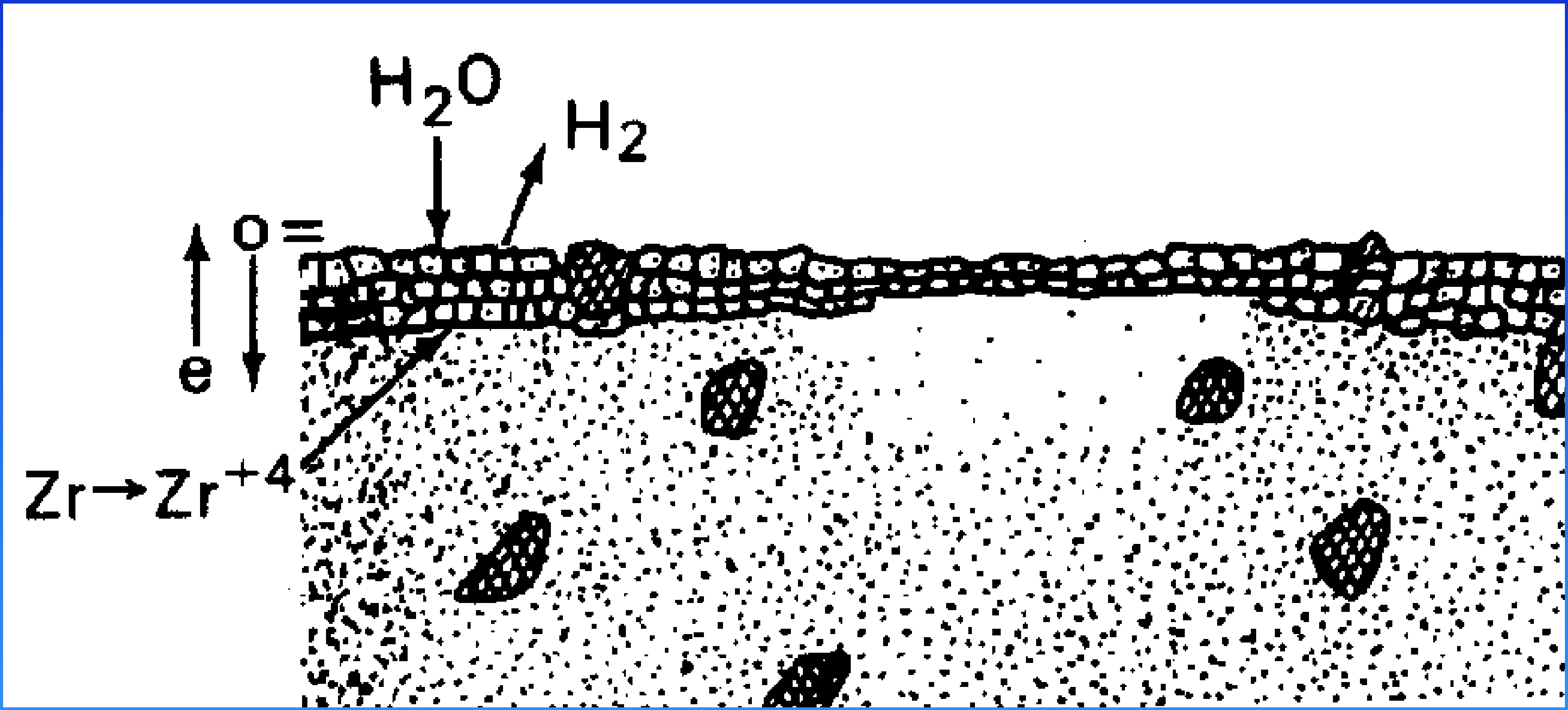
Model of Nodular Corrosion – Step 1



Step 1: Formation of initial uniform oxide of ZrO_2 or ZrO_{2-x}

R. Adamson and B. Cheng, ASTM 939, 1987

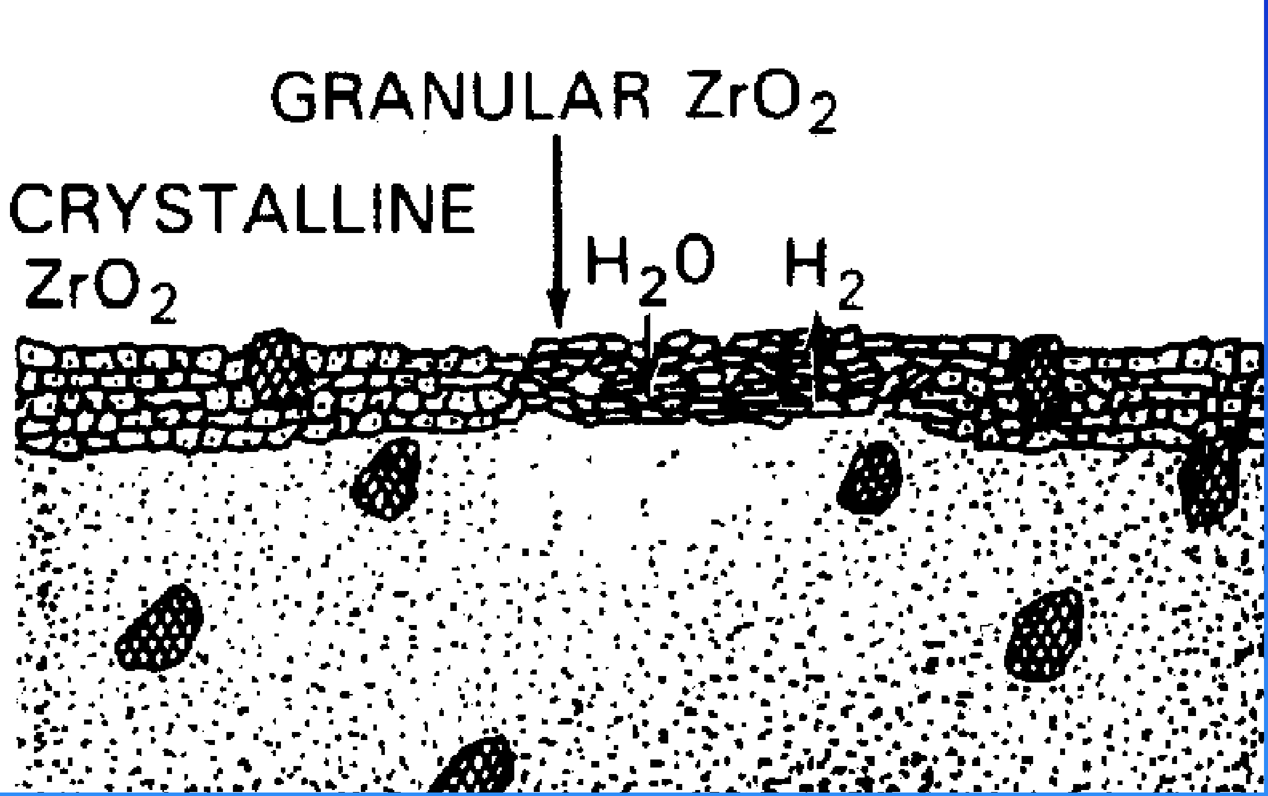
Model of Nodular Corrosion – Step 2



Step 2: Thickening and growth of initial oxide

R. Adamson and B. Cheng, ASTM 939, 1987

Model of Nodular Corrosion – Step 3

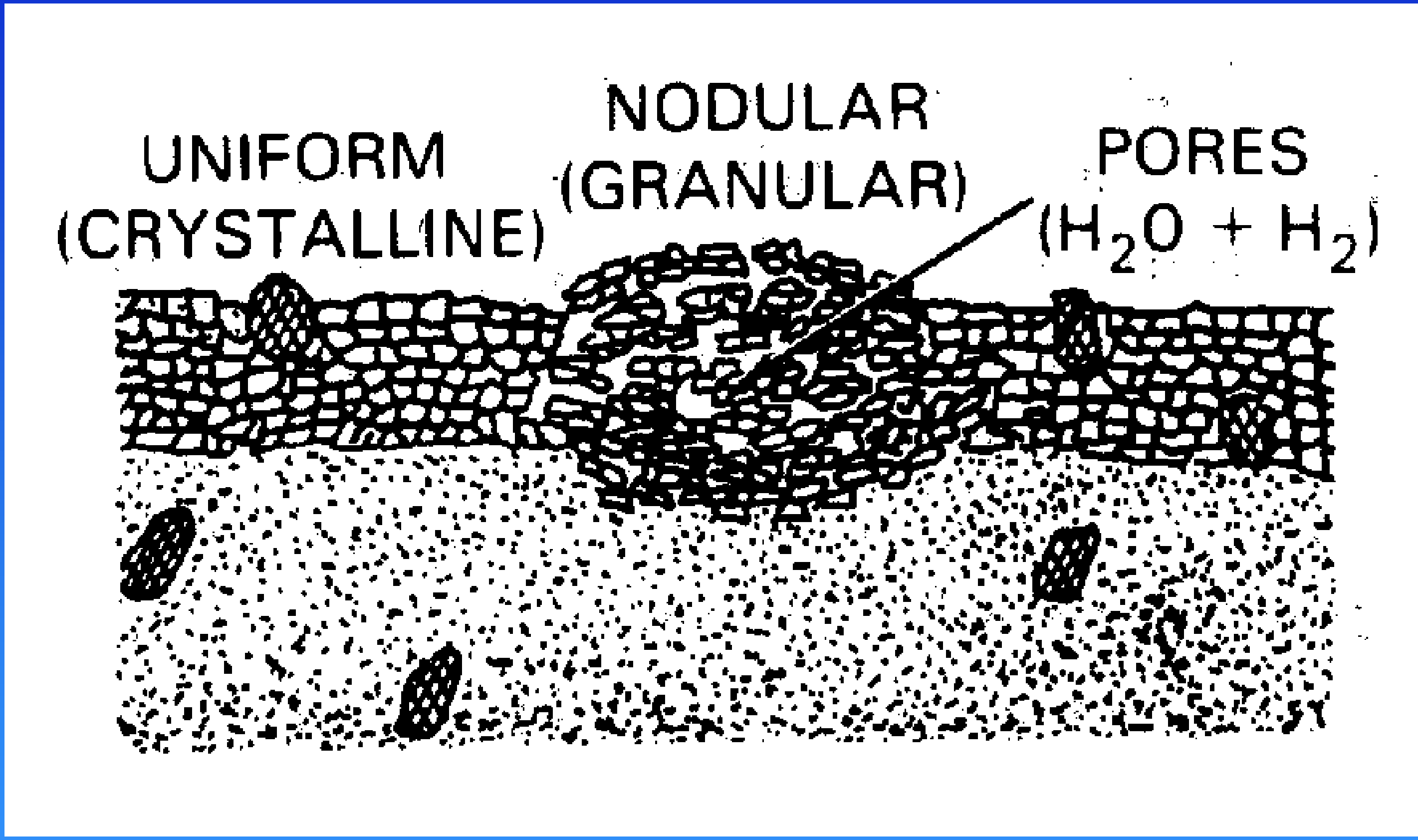


Ron Adamson
U of Wisconsin
Quarterback

Step 3: Rupture of near stoichiometric ZrO_2 leading to direct access of water to the metal/oxide interface

R. Adamson and B. Cheng, ASTM 939, 1987

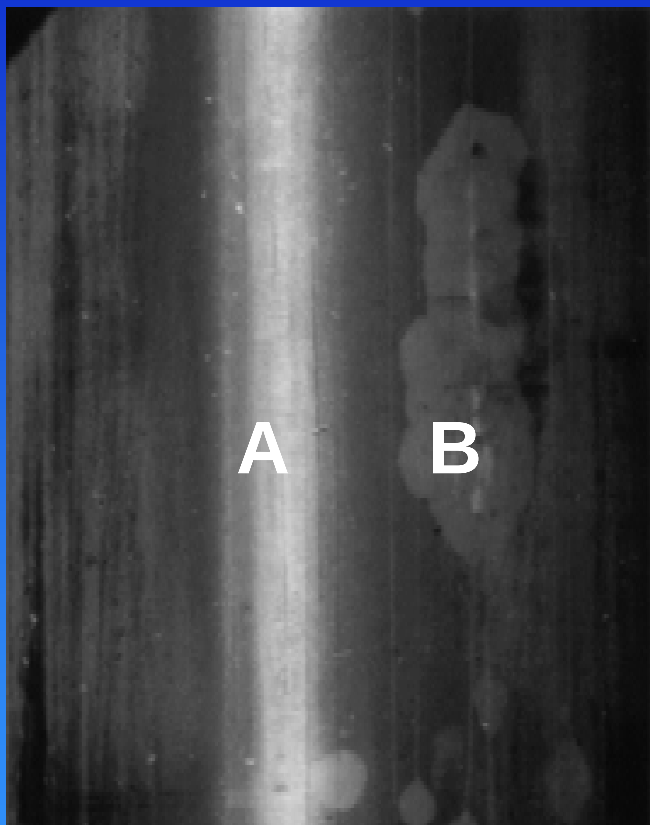
Model of Nodular Corrosion – Step 4



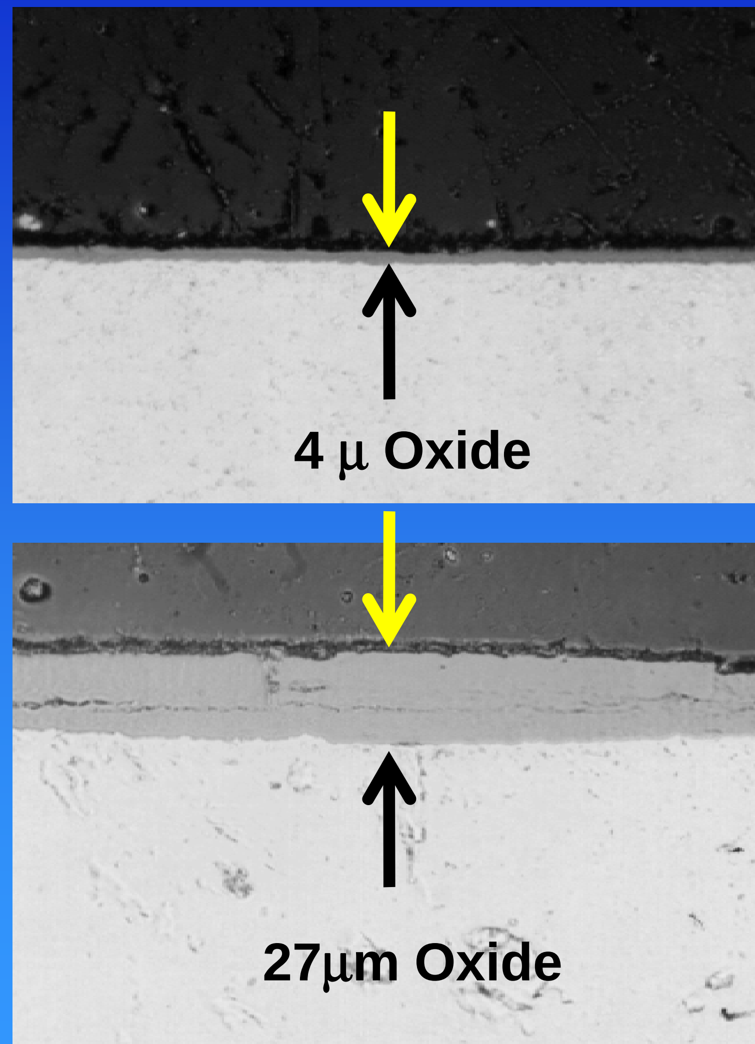
Step 4: Repetitive formation and rupture of ZrO_2 leading to highly porous, granular ZrO_2 that retains corrosion produced H_2 and prevents repassivation of the metal surface

R. Adamson and B. Cheng, ASTM 939, 1987

Zircaloy Shadow Corrosion in BWRs



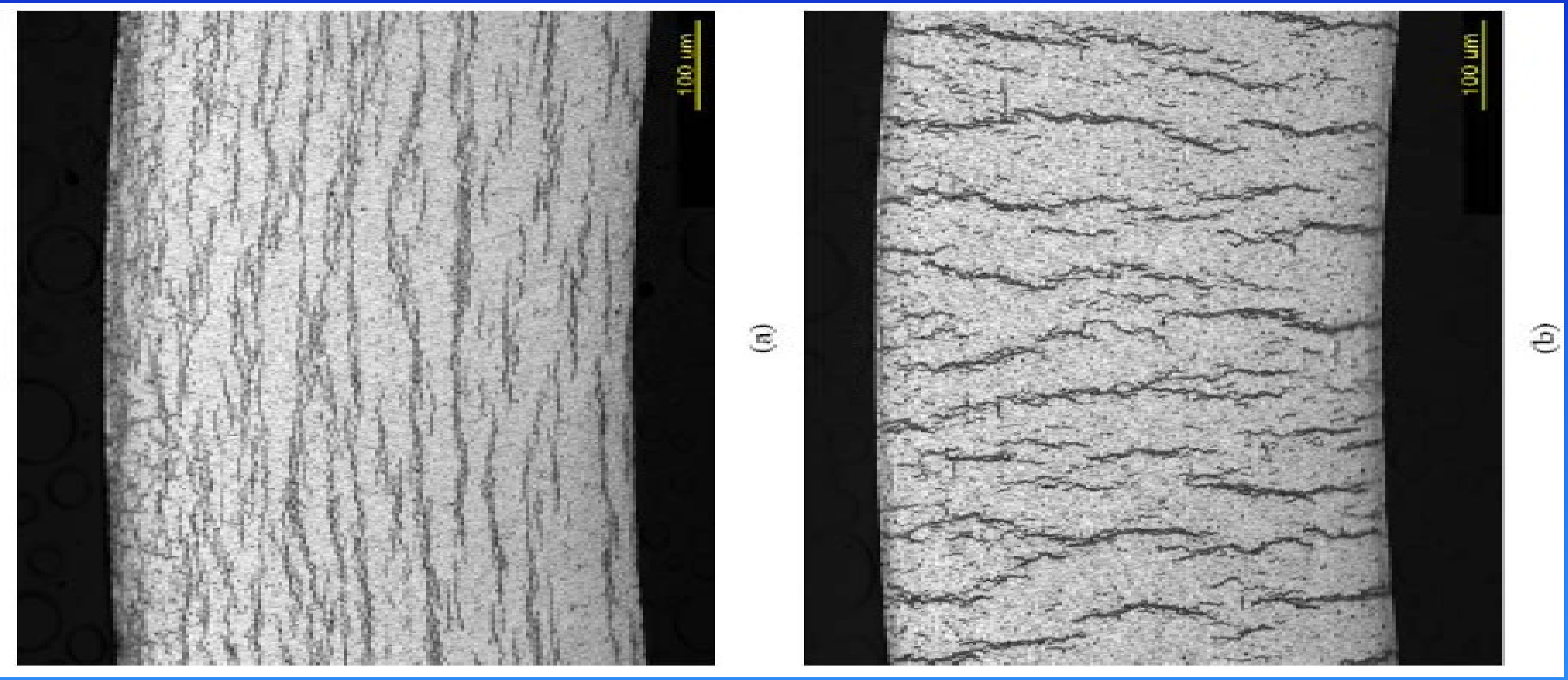
Enhanced corrosion shape resembles the adjacent metallic component



(A) Away from a X-750 spacer ring

(B) Below X-750 spacer ring

Hydriding of Zircaloy



Circumferential **Radial**

Which hydriding orientation is worse?

R. Rebak, paper 09497,Corrosion 2009

General Corrosion Summary

- Least “dangerous” form of corrosion
  - Rates can typically can be calculated and considered in design
- BAC is the primary general corrosion concern in PWRs
- Containment general corrosion is also a major LWR concern