U.S.NRC

United States Nuclear Regulatory Commission

Protecting People and the Environment

PWSCC/LPSCC in PWRs

(+ Steam Generator Corrosion)

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.

PWSCC/LPSCC Learning Objectives

- Taste of Primary Water SCC history
- Examine proposed mechanisms for the PWSCC
- Effect of various parameters on PWSCC
  - Materials/Stress/Water chemistry
- Crack growth rate studies
- Techniques for PWSCC mitigation
- SCC of stainless steels in PWRs
  - LPSCC
  - Canopy seals
- Steam generator degradation mechanisms and mitigation

Some NRC PWSCC Documents

- IN200627 - Circumferential Cracking in the Stainless Steel Pressurizer Heater Sleeves of Pressurized Water Reactors
- IN01005 - Through-Wall Circumferential Cracking of Reactor Pressure Vessel Head Control Rod Drive Mechanism Penetration Nozzles at Oconee Nuclear Station, Unit 3
- IN00017S2 - Crack in Weld Area of Reactor Coolant System Hot Leg Piping at V. C. Summer
- IN00017S1 - Crack in Weld Area of Reactor Coolant System Hot Leg Piping at V. C. Summer
- IN00017 - Crack in Weld Area of Reactor Coolant System Hot Leg Piping at V. C. Summer
- IN90010 - Primary Water Stress Corrosion Cracking (PWSCC) of Inconel 600
- IN84018 - Stress Corrosion Cracking in PWR Systems
- IN82014 - TMI-1 Steam Generator/Reactor Coolant System Chemistry/Corrosion Problem

Some NRC PWSCC Documents

- IN03011S1 - Leakage Found on Bottom-Mounted Instrumentation Nozzles
- IN03011 - Leakage Found on Bottom-Mounted Instrumentation Nozzles
- IN02013 - Possible Indicators of Ongoing Reactor Pressure Vessel Head Degradation
- IN02011 - Recent Experience with Degradation of Reactor Pressure Vessel Head
- BL-03-02 - Leakage From Reactor Pressure Vessel Lower Head Penetrations And Reactor Coolant Pressure Boundary Integrity
- BL-01-01 - Circumferential Cracking of Reactor Pressure Vessel Head Penetration Nozzles
- GL97001 - Degradation of Control Rod Drive Mechanism Nozzle and Other Vessel Closure Head Penetrations

PWSCC History

The 1959 Coriou Alloy 600 Test

Henri Coriou

- July 1959
- H. Coriou, L. Grall, Y. LeGall and S. Vettier
- "Stress Corrosion Cracking of Inconel in High Temperature Water" presented at the 3rd Metallurgy Symposium on Corrosion
  - SCC of A600 bent beams at 0.5% strain in 360ºC (662ºF) "degassed" (3 ppb DO) water in 9 months!
  - SCC should not have "manifested" itself in Alloy 600
- Corrosion community goes more crazy
  - Researchers cannot duplicate results even with borrowed Coriou laboratory water
  - Blame results on lead contamination, evildoers, etc.

History of Ni Alloy SCC in PWRs - 1

- 1959 – H. Coriou, et al. identify first Alloy 600 SCC in the lab
- 1971 – Cracks in Obrigheim U-bend region of SG
- 1972 – Cracks in Obrigheim SG roll transition
- 1975 – SG tube denting at Turkey Point
- 1976 – EdF recommends 700°C/16h thermal treatment
- 1976 – PWSCC in Turkey Point/Surrey SG tubes at support plate and U-bends due to SG tube denting
- 1976 – Leak in row 1 U-bend at Takahama without denting
- 1977 – Axial PWSCC at roll transition in partially rolled tube at Doel 2
- 1980 – EdF recommends Alloy 690 SG tubing
- 1981 – First Circumferential PWSCC observed at expansion transition of explosively expanded SG tubes in Fessenheim
- 1982 – Guide tube pins crack in France
- 1982 – PWSCC leak in pressurizer heater sleeves at ANO-2

P. Berge, EPRI TR-103345 12/93, EPRI TR-103696 7/94, NRC IN 2002-02

History of Ni Alloy SCC in PWRs - 2

- 1984 – Moderate PWSCC at tube support plate dents at North Anna 1
- 1984 – PWSCC in SG cold leg transitions at Ringhals 2
- 1984 – Decision to universally adopt Alloy 690 in France
- 1985 – Shot peening SG tubes
- 1986 – Leak from pressurizer instrument nozzle at San Onofre 3
- 1987 – Leak from heater sleeves Arkansas Nuclear One
- 1988 – Leaks in roll expanded SG drain nozzles at Shearon Harris
- 1989 – PWSCC in 20 heater sleeves at Calvert Cliffs 2
- 1989 – TT Alloy 600 SG tube plug SCC, failure, ejection and subsequent U-bend rupture at North Anna 1
- 1989 – Leaks in rolled pressurizer instrument nozzles at Nogent 1 and Cattenom 2
- 1990 – First PWSCC in explosive expanded HT MA SG tubing at Maine Yankee
- 1991 – THP CRDM axial PWSCC – Bugey 3 after 84,000h
- 1991 – PWSCC in 2 of 8 hot leg piping instrument lines at PV 2

P. Berge, EPRI TR-103345 12/93, EPRI TR-103696 7/94, NRC IN 2002-02

History of Ni Alloy SCC in PWRs - 3

- 1992 – ATR pressurizer elbow circumferential cracking
- 1992 – CRDM nozzle PWSCC in a “cold” (552 °F) head EdF plant
- 1992 – Circumferential PWSCC at j-groove weld at Bugey 3 (First A690 replacement head. No PWSCC through 2007)
- 1993 – Circumferential PWSCC in pressurizer relief valve nozzle safe end at Palisades
- 2000 – Axial PWSCC in weld metal Oconee-1 CRDM
- 2000 – Hot leg nozzle Alloy 182/82 weld PWSCC at V. C. Summer
- 2001 – PWSCC in Ringhals 3 and 4 safe ends
- 2001 – Axial and circumferential CRDM PWSCC at ANO-1
- 2001 – Circumferential PWSCC in THP base metal at Oconee-1
- 2001 – NRC Bulletin 2001-01 - CRDM circumferential cracking
- 2002 – Davis-Besse PWSCC induced BAC
- 2003 – 1st SCC (OD) of TT A600 – axial – hot/cold legs – Seabrook
- 2003 – 1st bottom head penetration boric acid at STP
- 2004 – 80% of French PWRs with TT A690 RPVHs (now all)

P. Berge, EPRI TR-103345 12/93, EPRI TR-103696 7/94, NRC IN 2002-02

PWSCC in Alloy 600 by Component

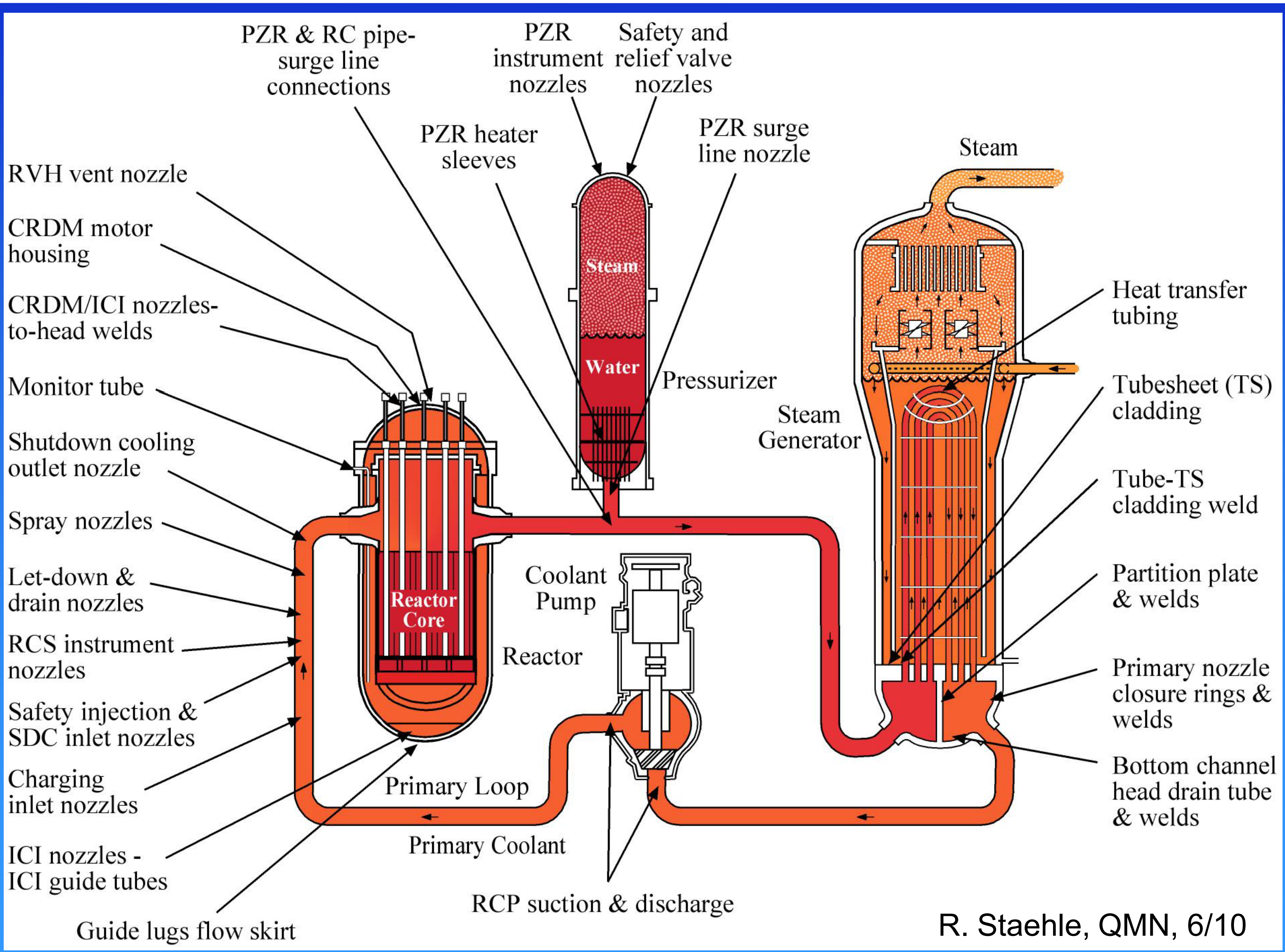
- Steam generator tubes: Obrigheim (1971), Surrey (1976)
- Pressurizer heater sleeves: ANO-2 (1982, 1987), Calvert Cliffs-2 (1989), Palo Verde-2 (2003)
- Pressurizer instrument nozzles: EdF plants (1989), San Onofre-3 (1992), St. Lucie-2 (1993), Oconee-1 (2000), Crystal River-3 (2003)
- CRDM nozzles: Bugey-3 (1991), DC Cook-2 (1994), Oconee-1 (2000), North Anna-2 (2001), ANO-1 (2001), Surry-1(2001), Davis Besse (2002), Millstone-2 (2002)
- RPV hot leg nozzle pipe butt weld: VC Summer (2000)
- RPV BMI penetration: STP-1 (2003)
- Pressurizer nozzle weld: Wolf Creek (2006)
- SG drain nozzle weld: Yonggwang-3, 4 (2007)

US VHP Cracking Incidents 2000-2005

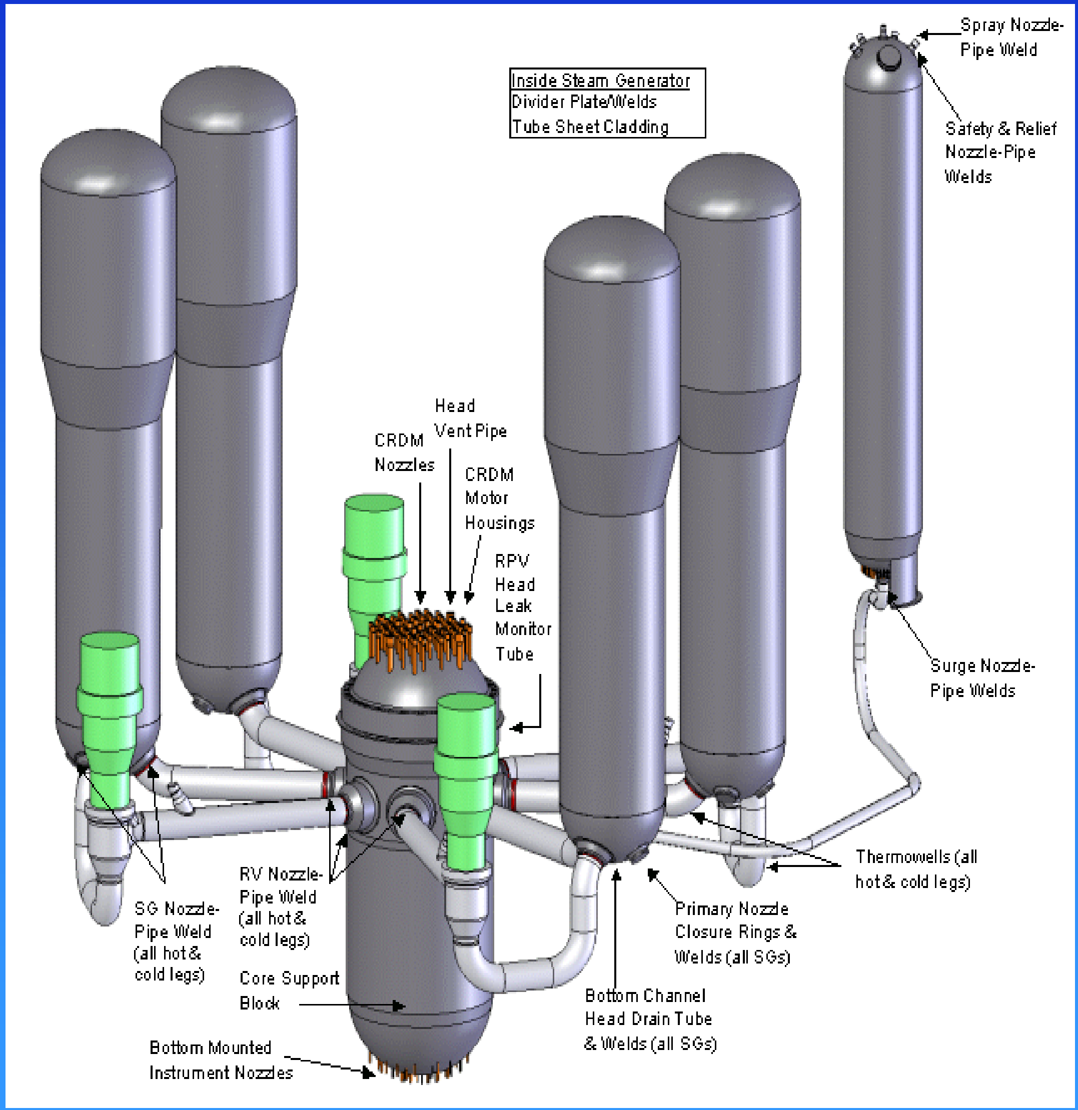
Plant	Nature of Cracking, Head Replacement Plans
Oconee 1	Leaks/cracks in 3 VHPs + 5 instrument nozzles (Head replaced 2003)
Oconee 2	19 VHPs repaired, 1 circ. crack above the J-weld (Head replaced 03/04)
Oconee 3	14 VHPs repaired, 4 with circ. cracks above J-weld (Head replaced 2003)
ANO-1	8 VHPs repaired (Head replaced 2005)
Surry 1	6 VHPs repaired (Head replaced 2003)
N. Anna 2	14 VHPs repaired, 6 with circ cracks (Head replaced 2002)
D-Besse	5 VHPs with cracks, 2 nozzles with wastage (Head replaced 2003)
TMI-1	6 VHPs and 8 instrument nozzles plugged (Head replaced 2003)
Cry. River 1	1 VHP with circ. crack (Head replaced 2003)
Ginna	Head replaced in 2003
Millstone 2	3 CEDMs repaired (Head replaced 2005)
STP-1	2 bottom head instrumentation nozzles repaired

NUREG-1823, 4/05

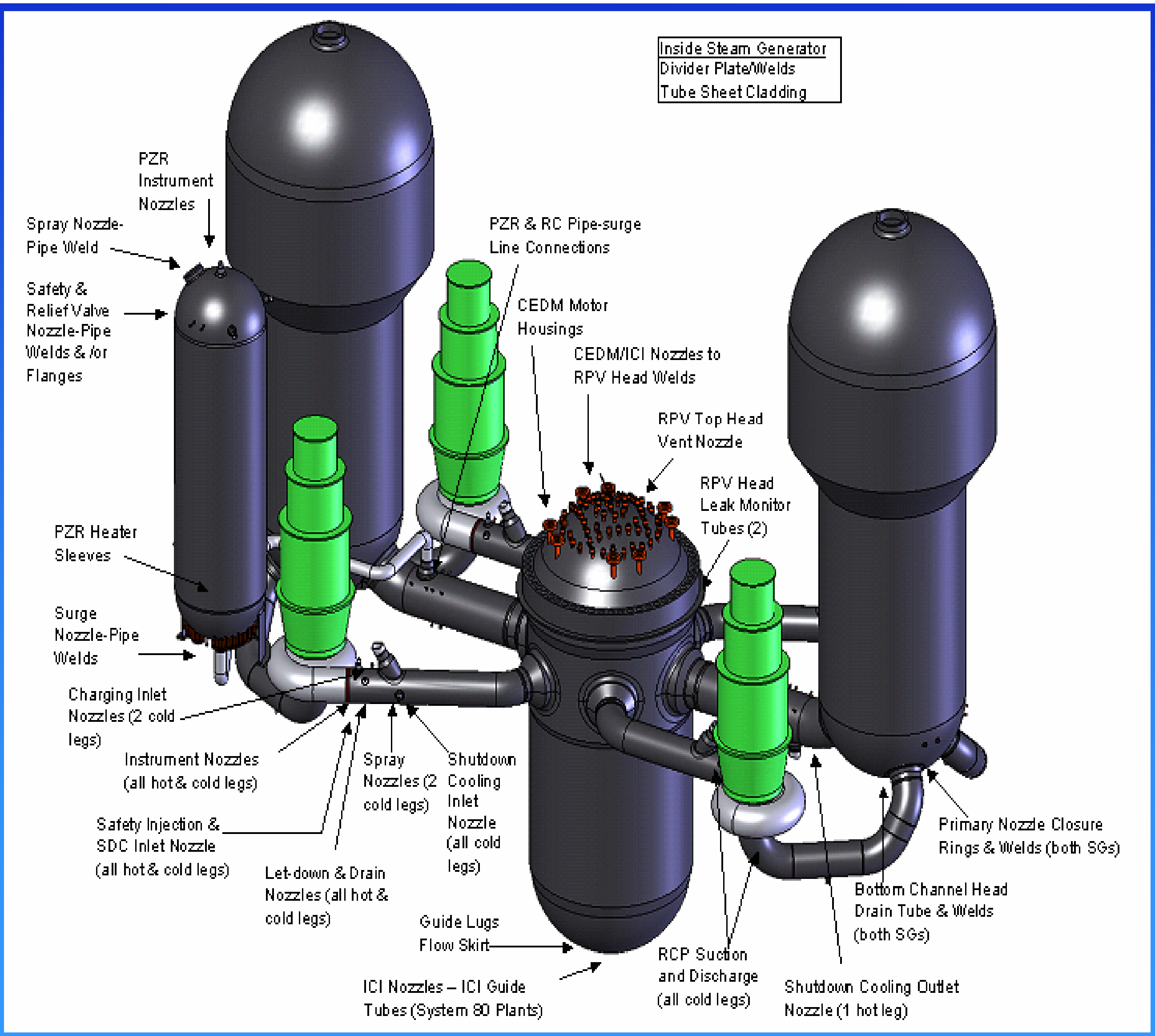
Locations of Alloys 600, 182 and 82 in Primary Circuit of PWRs



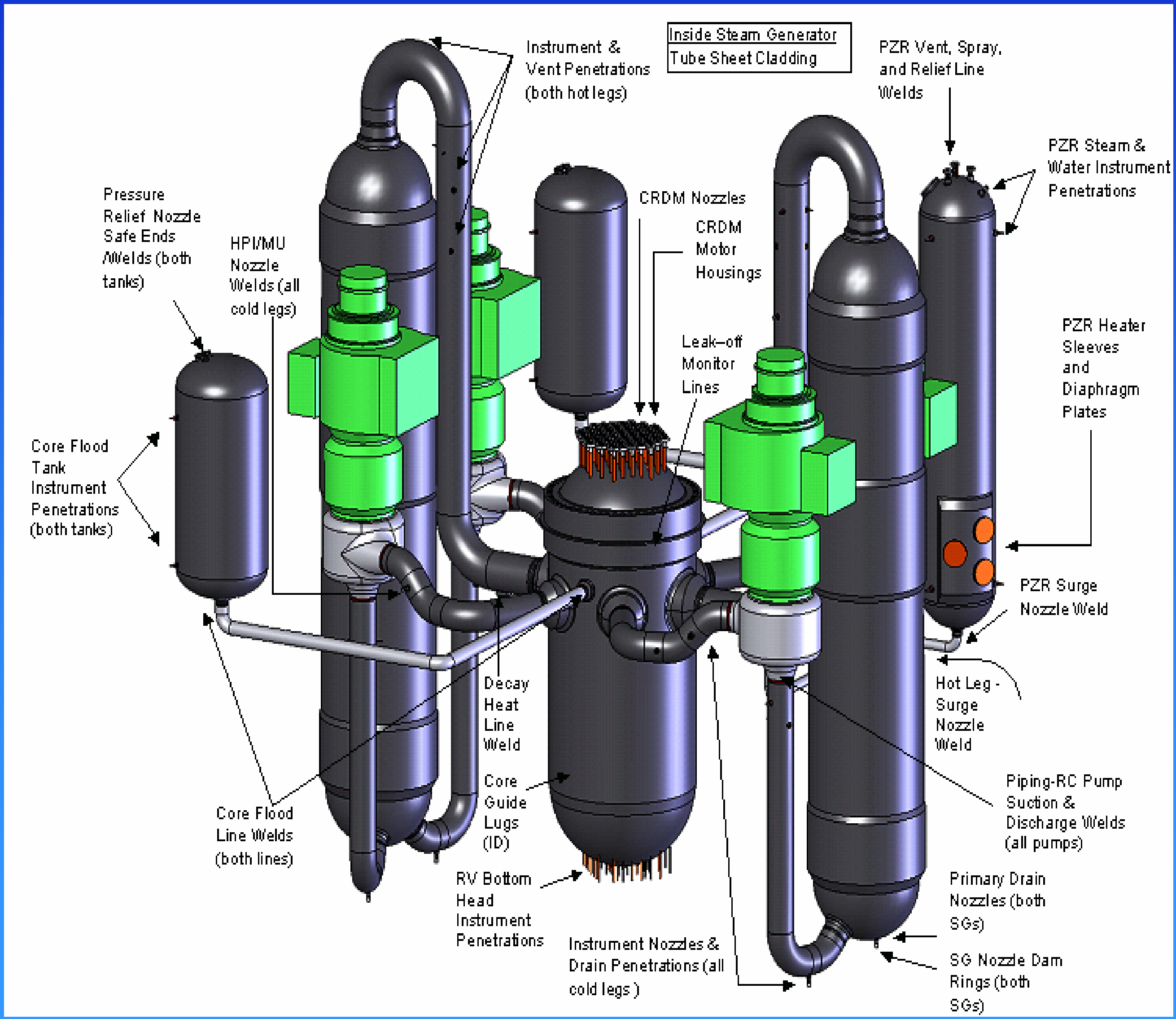
Alloy 600 in Westinghouse PWRs



Alloy 600 in CE PWRs



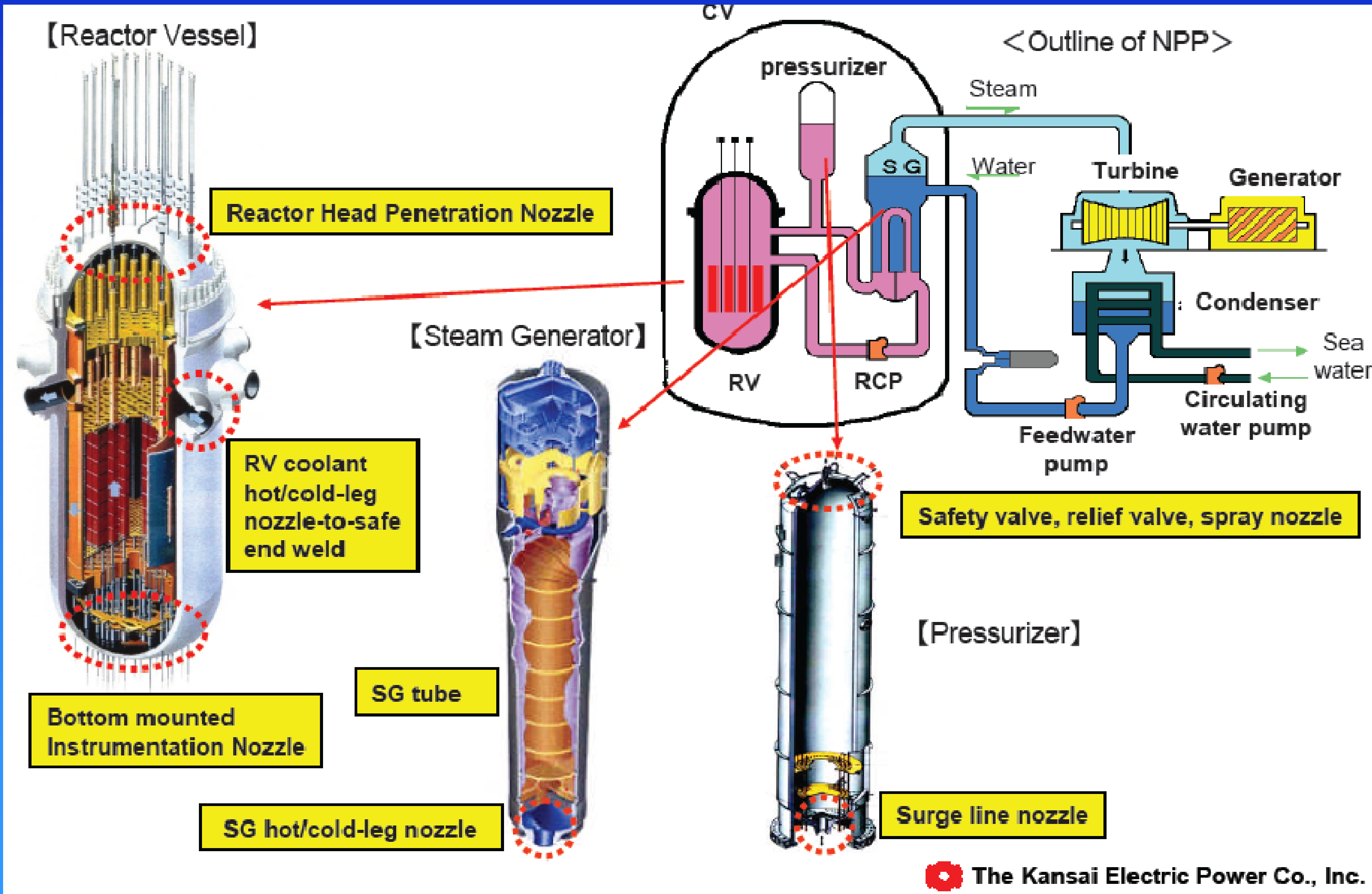
Alloy 600 in B&W PWRs



PWSCC Susceptible Components

- Steam generator tubing
- Small bore nozzle Alloy 600 J-groove welds
  - Pressurizer heater sleeves and instrument nozzles
  - Bottom mounted instrument (BMI) penetrations
  - Control rod drive mechanisms (CRDMs)
  - Other reactor coolant system (RCS) instrument locations
- CRDM canopy seal welds
- Large bore nozzle to pipe Alloy 600 butt welds
  - Pressurizer surge and spray line nozzles
  - RCS hot and cold leg nozzles
  - Other RCS nozzles

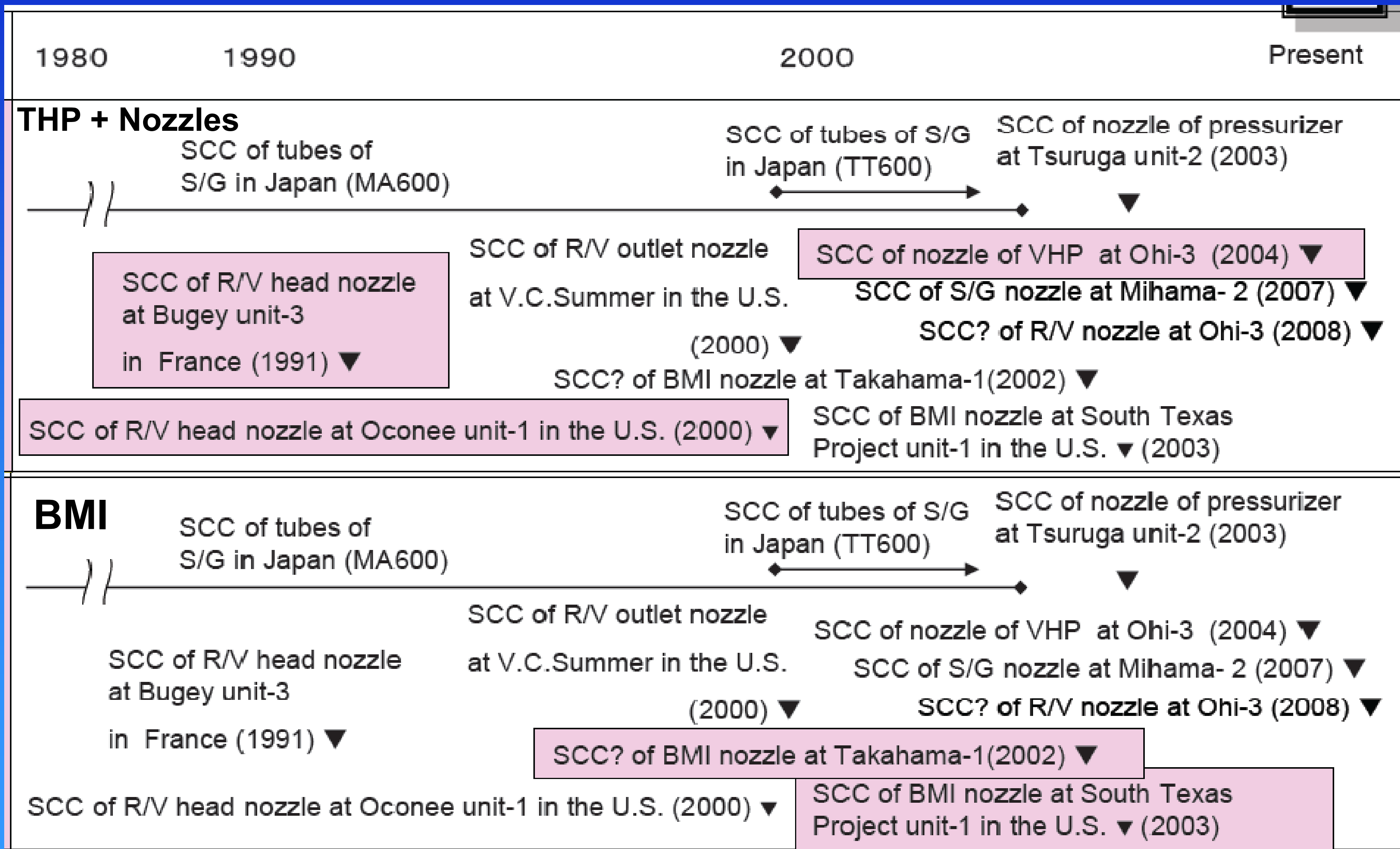
Japanese PWR PWSCC Components



Corrosion and Corrosion Control in LWRs

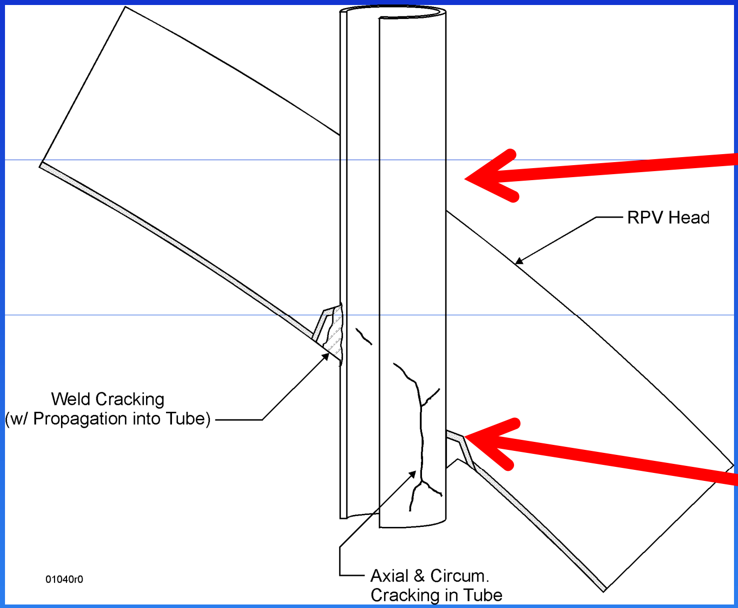
Structural Integrity Associates

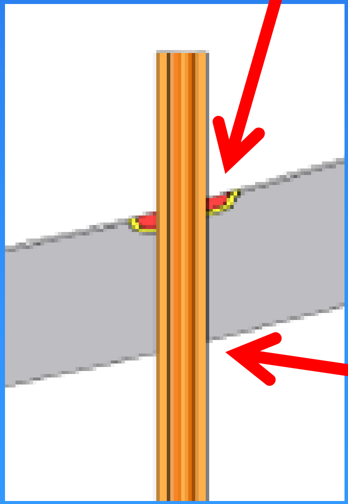
Japanese View of Key SCC Events in PWRs

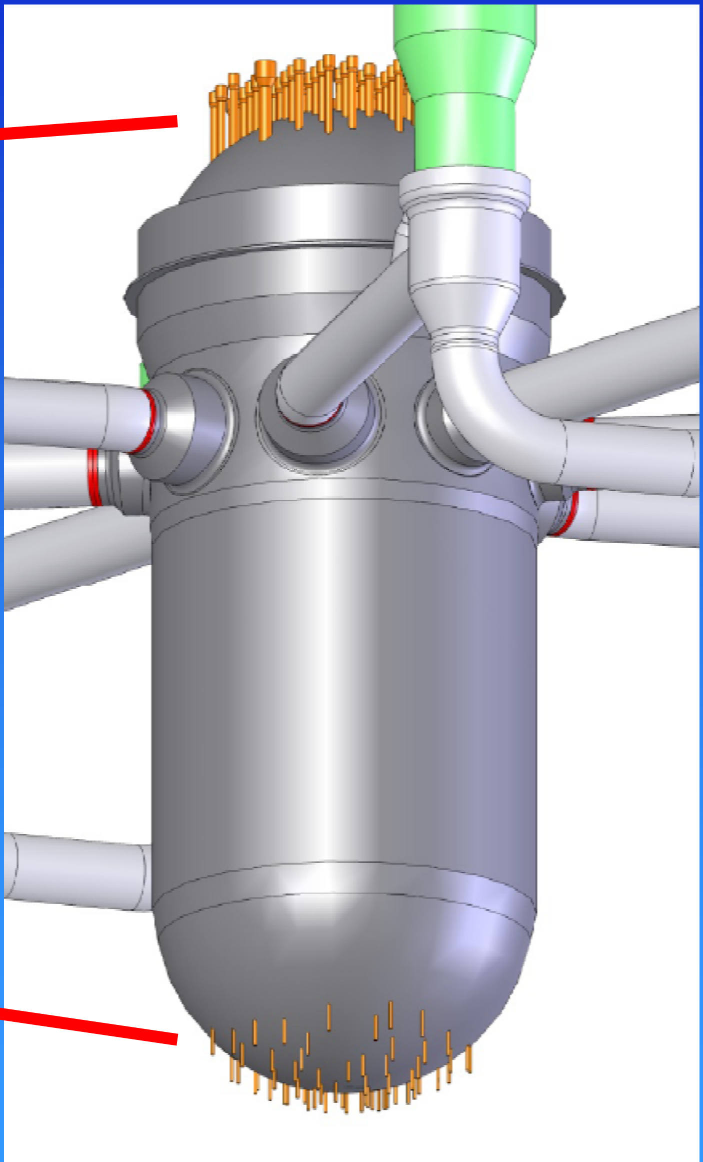


T. Kamada, Kansai, 7/07

CRDM Nozzle and BMI Locations







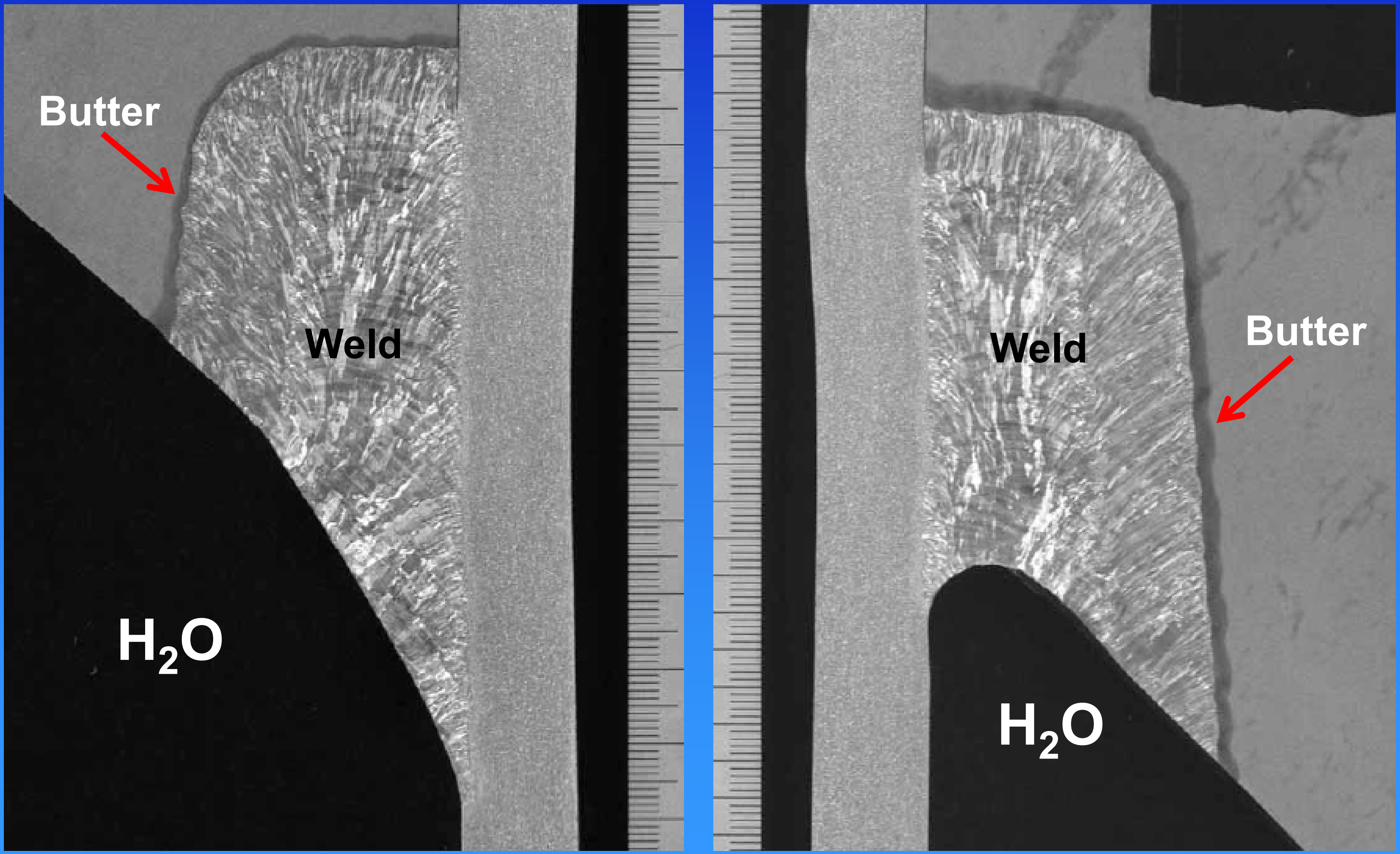
J-groove welds

<u>BMI vs. CRDM</u>

- Inverted geometry
- BMI 1/4 the size of the CRDM configuration
- Temperature

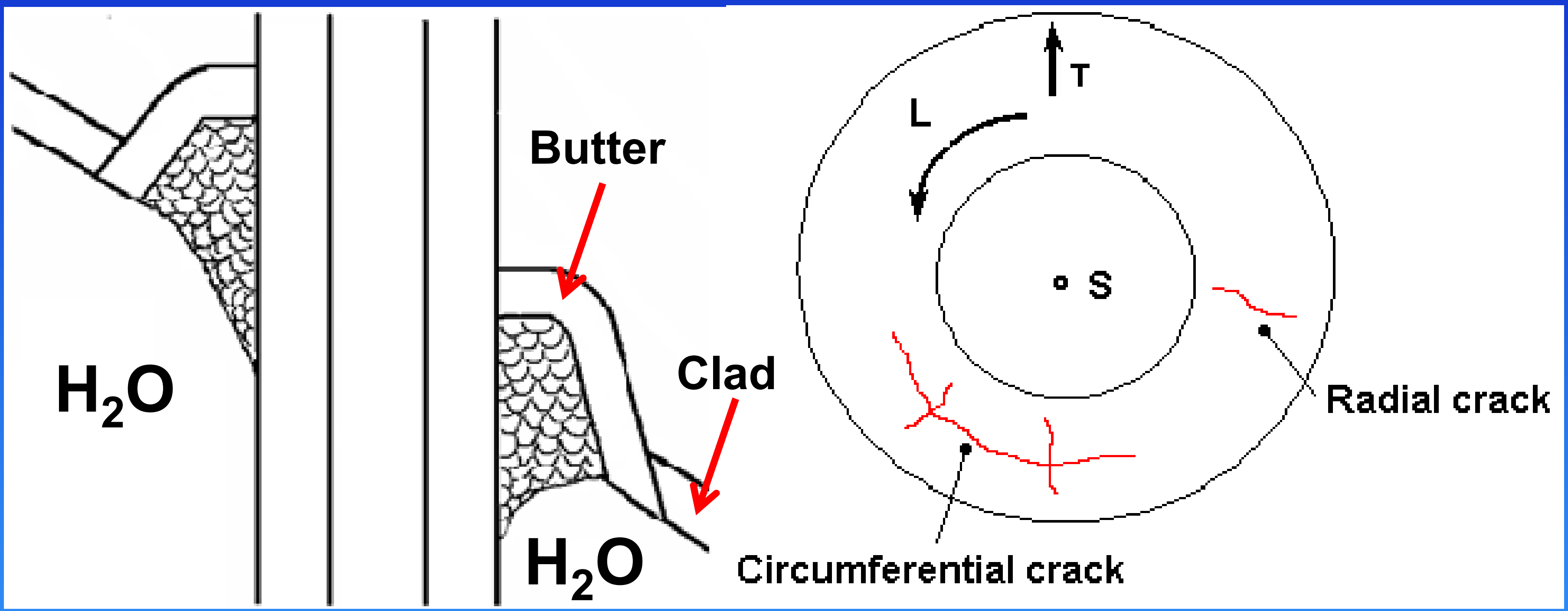
Structural Integrity Associates

Macrograph of a Diametral Cross-Section of a J-Groove Weld at CRDM



EPRI, MRP-220, 10/07 – Public Document

Orientation of Radial-Axial and Circumferential Cracking in J-Groove Welds

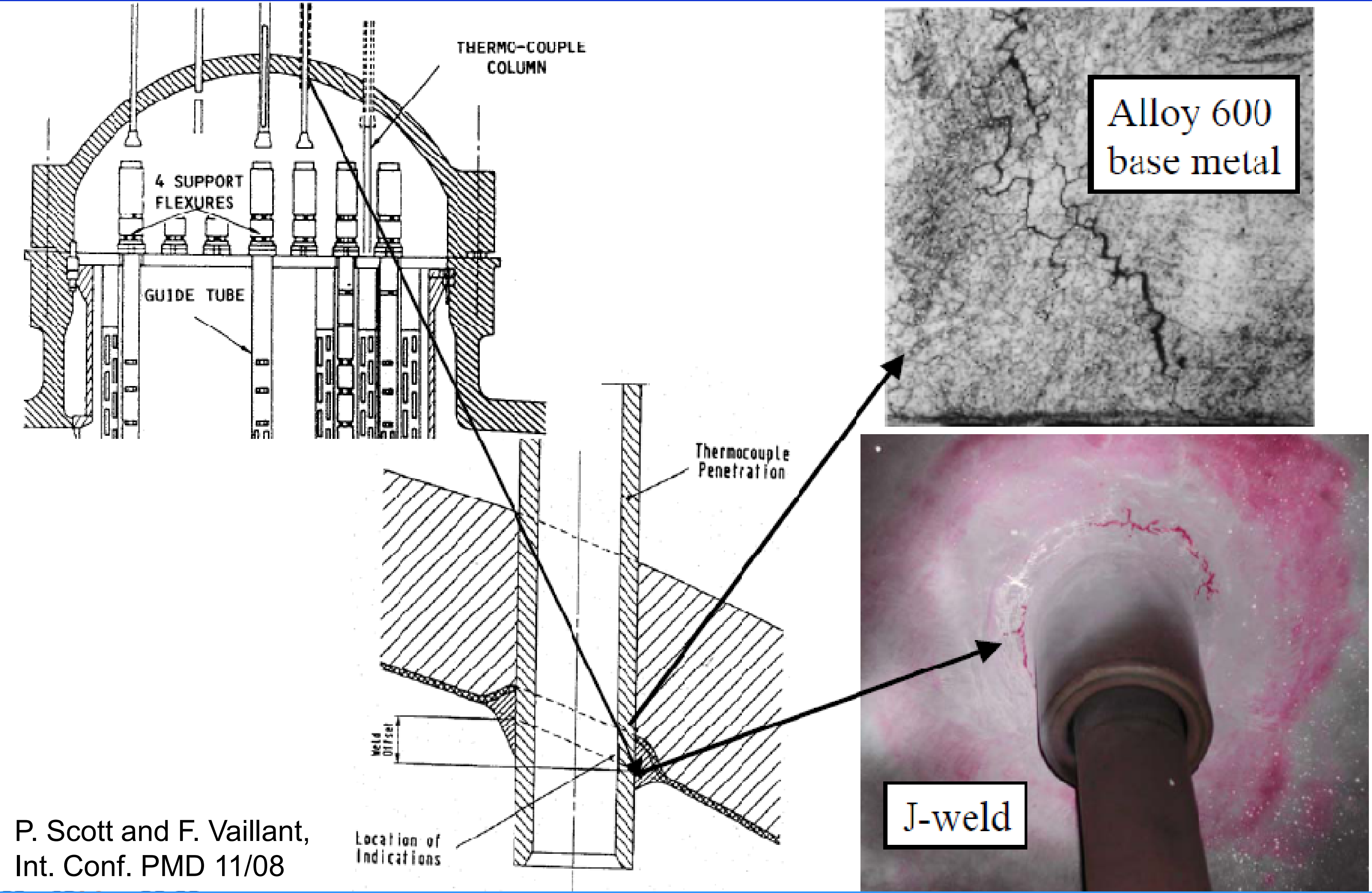


EPRI, MRP-220, 10/07 – Public Document

CRDM Nozzle Axial Crack at Bugey Unit 3

- Leakage of 22 l/d (0.004 gpm) found on the outside surface of the RVH during the 10-year hydrostatic test in September 1991
- Leak due to through-wall axial crack in an outer row CRDM nozzle that initiated at inside surface of the nozzle
- Subsequent inspections revealed several partial-wall axial cracks originating on the inner surface of the leaking nozzle near the elevation of the J-groove weld
- PWSCC caused by:
  - Stress concentration at a counter-bore on the nozzle inside surface
  - High hardness of the cold worked machined surface
  - High residual tensile stresses induced in the nozzle during welding
- Fix: New head with Alloy 690 head penetrations welded with Alloy 152

PWSCC of Upper Head Penetrations



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

CRDM Nozzle Circumferential Cracking Outbreak

- CRDM nozzle cracking in 10 PWR plants between November 2000 and November 2001
- NRC Bulletin 2001-1 (circumferential cracking)
- Newly discovered cracking is “more safety significant” because of a potential for cracks to be oriented circumferentially around the nozzle
- Location for the circumferential crack is associated with the root of the J-weld that forms the pressure boundary between the vessel head and the CRDM nozzle
- Majority of the degradation has taken the form of leaks identified by qualified visual exams

CRDM Nozzle Leak at Oconee Unit 1

- Leakage at CRDM nozzle 21 at the beginning of refueling outage in 11/00
- Leak due to a single axial crack that originated in the J-groove weld on the inner head surface
- Leak path was created as the crack grew upward through the weld and nozzle base material until it penetrated to the annulus region between the nozzle and the LAS head
- Crack extended radially from 1 cm (0.40 in.) deep in the OD of the nozzle through the Alloy 182 butter to the LAS base metal where it was blunted
- As the crack extended into the weld butter, the crack branched and turned circumferentially for 9.5 mm (3/8 in)

Boric Acid Deposits
Oconee Unit 1 Reactor Vessel Head

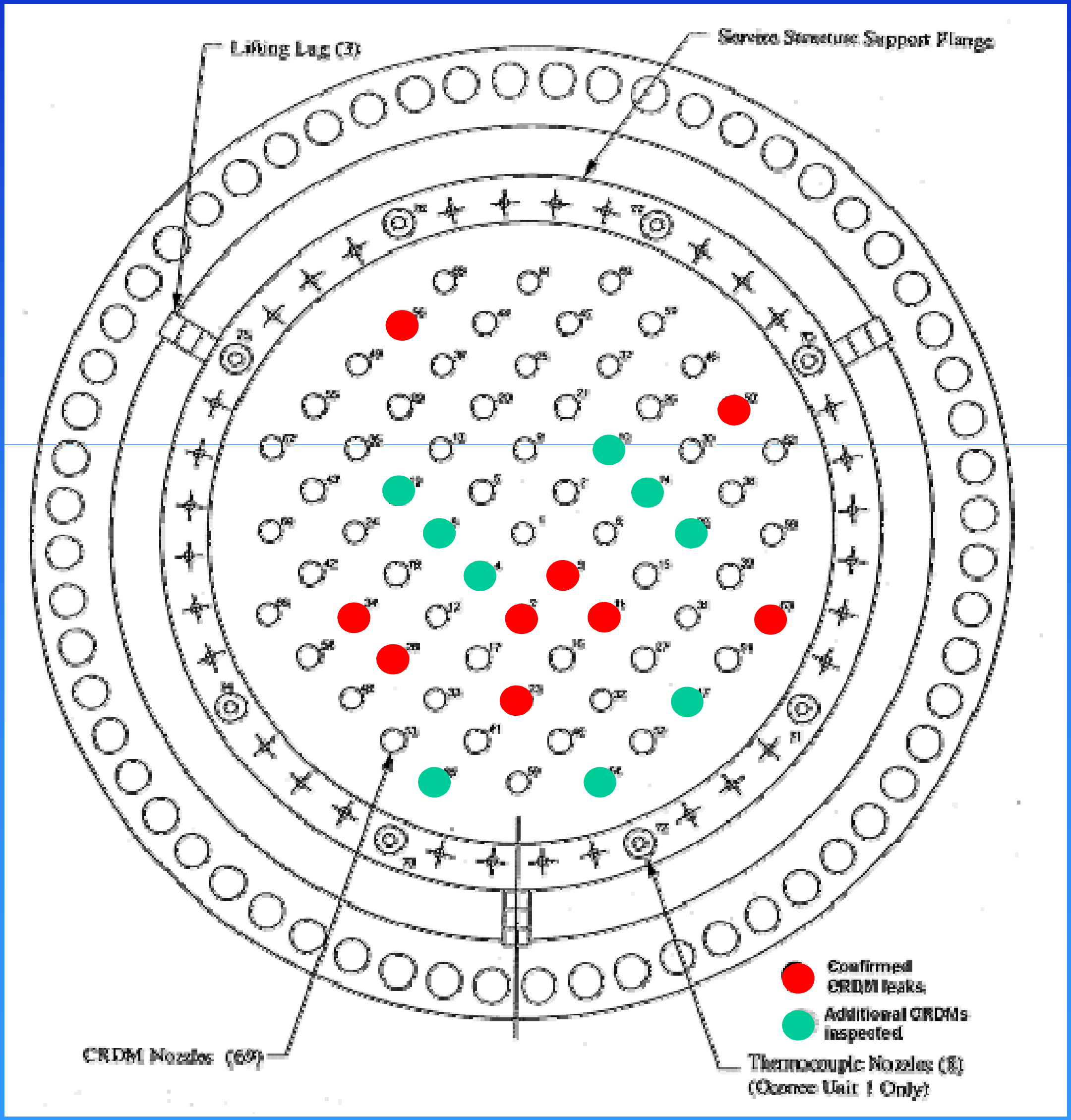
D. Jackson, ICONE109-22740, 4/02

CRDM Nozzle Leak at Oconee Unit 3

- Visual inspection reactor vessel head 2/01 showed boric acid deposits around nine CRDM nozzles (# 3, 7, 11, 23, 28, 34, 50, 56 and 63)
- PT of underside of the head on each of the 9 suspected leaking nozzles revealed multiple rejectable indications on each nozzle
- ET of 9 leaking nozzles indicated clusters of shallow axial cracks located either above the weld or below the weld, or, in some cases, both
- Nozzles 50 and 56 had non-typical clusters above the weld with circumferential cracks extending 165° around the nozzle

Leaking CRDM Nozzle at Oconee Unit 3

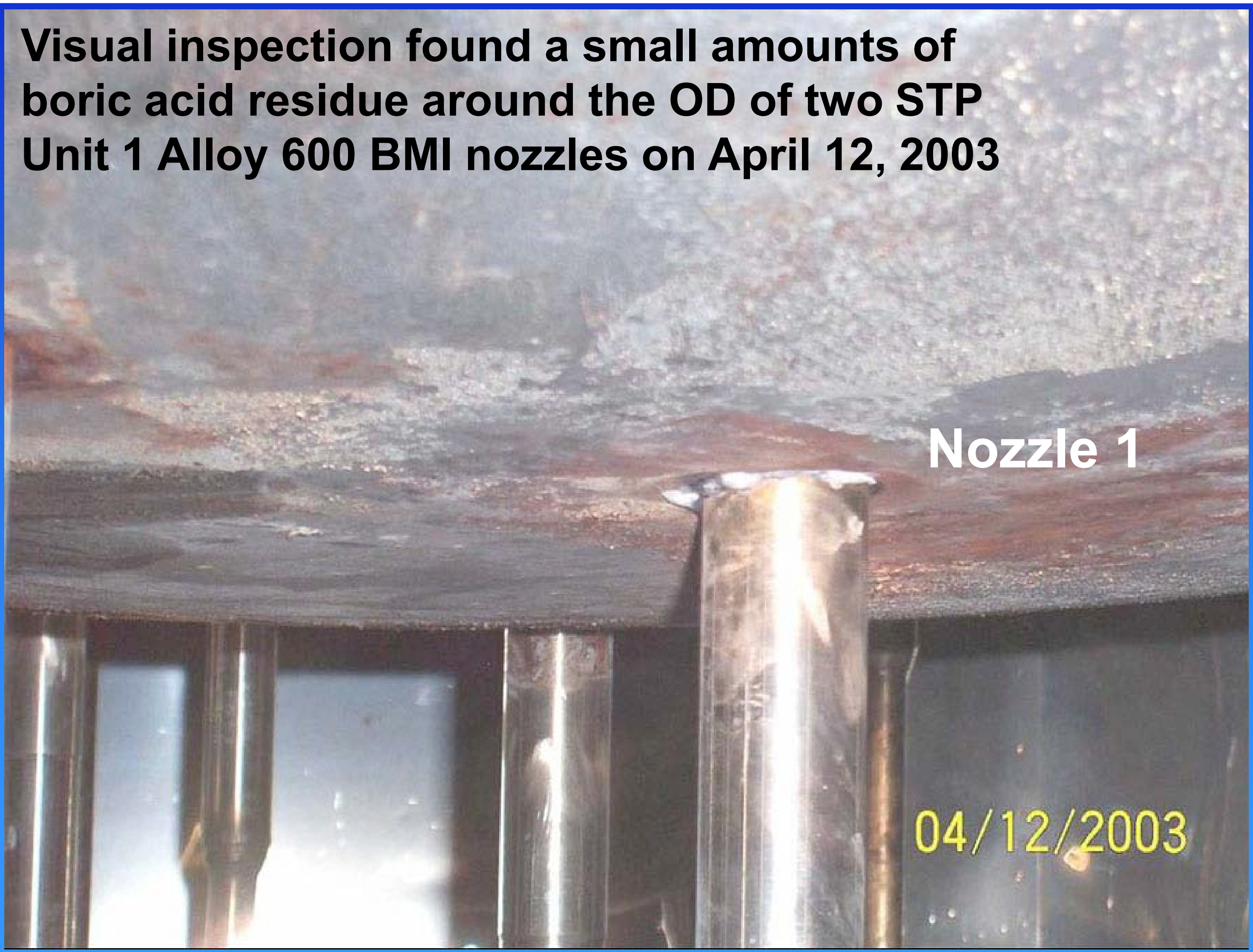
Boric Acid Residue on 9 of 69 CRDMs at Oconee 3



CRDM Nozzle Leak at ANO 1

- **Bare metal visual examination of the THPs during the 1R16 outage 3/01**
- **BA crystals were 360° around nozzle 56**
- **PT revealed the presence of a linear <u>circumferential</u> flaw on the downhill OD surface of the nozzle below the J-weld**
- **Circumferential crack linked with an axial crack that propagated along the fusion interface between the nozzle and the Alloy 182 and extended 3.3 cm (1.3 in) beyond the root of the J-weld**

STP Unit 1 Leaking BMI Alloy 600 Penetrations – Nozzle 1

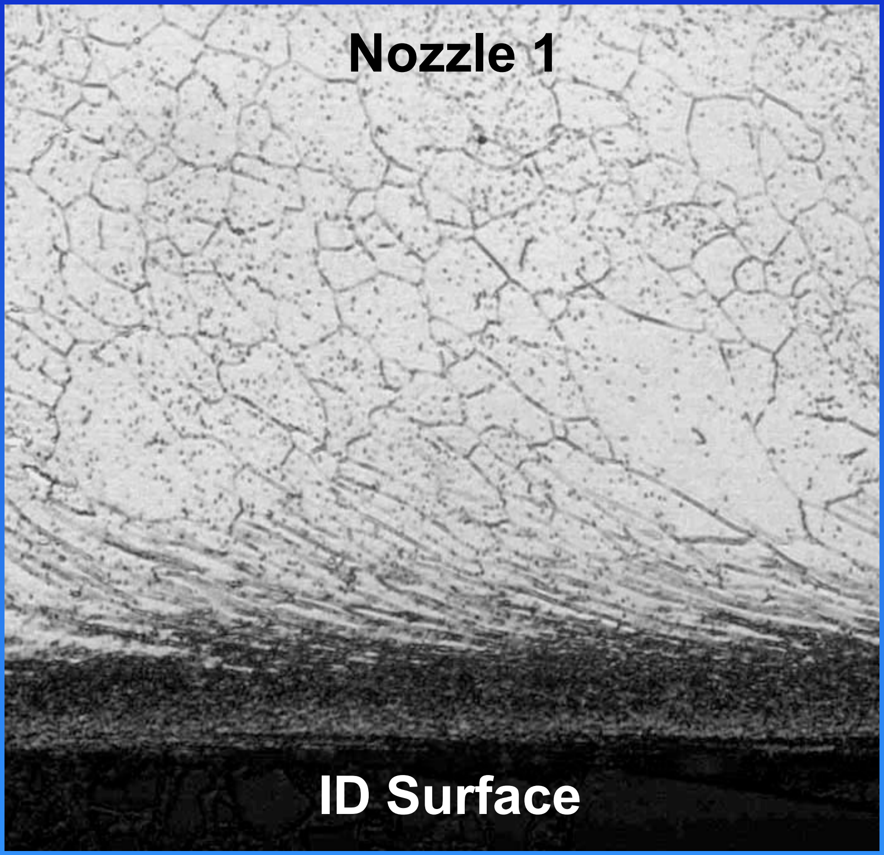


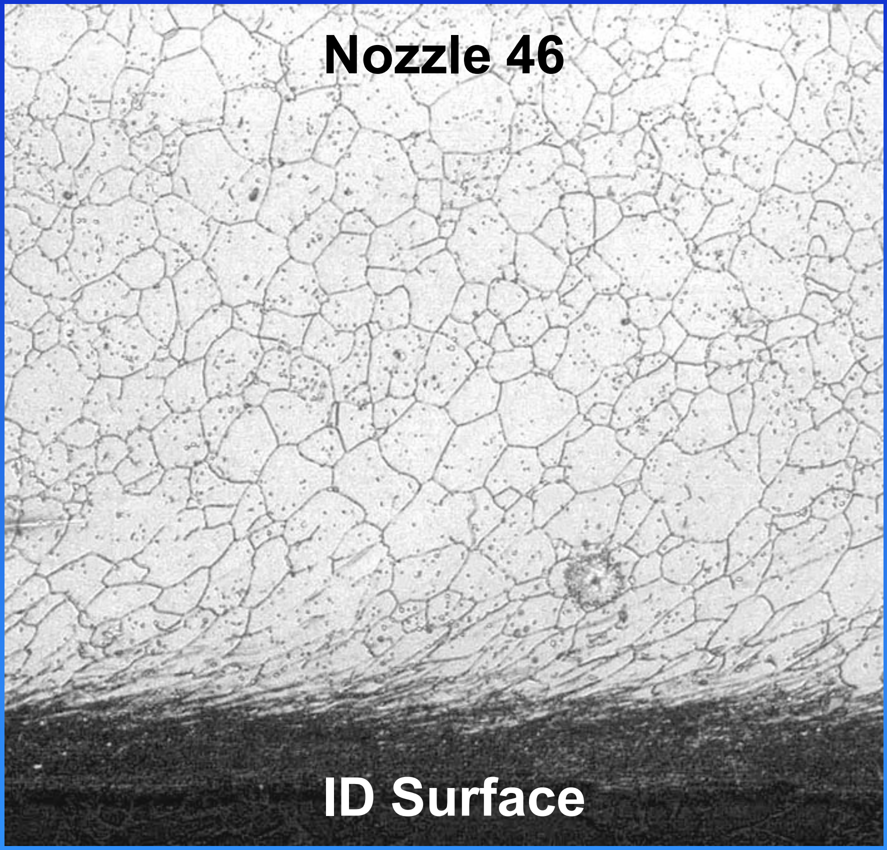
A. McIlree, Cold Work Workshop, 6/07

STP Unit 1 Leaking BMI Alloy 600 Penetrations – Nozzle 46

A. McIlree, Cold Work Workshop, 6/07

STP Alloy 600 Cold Work

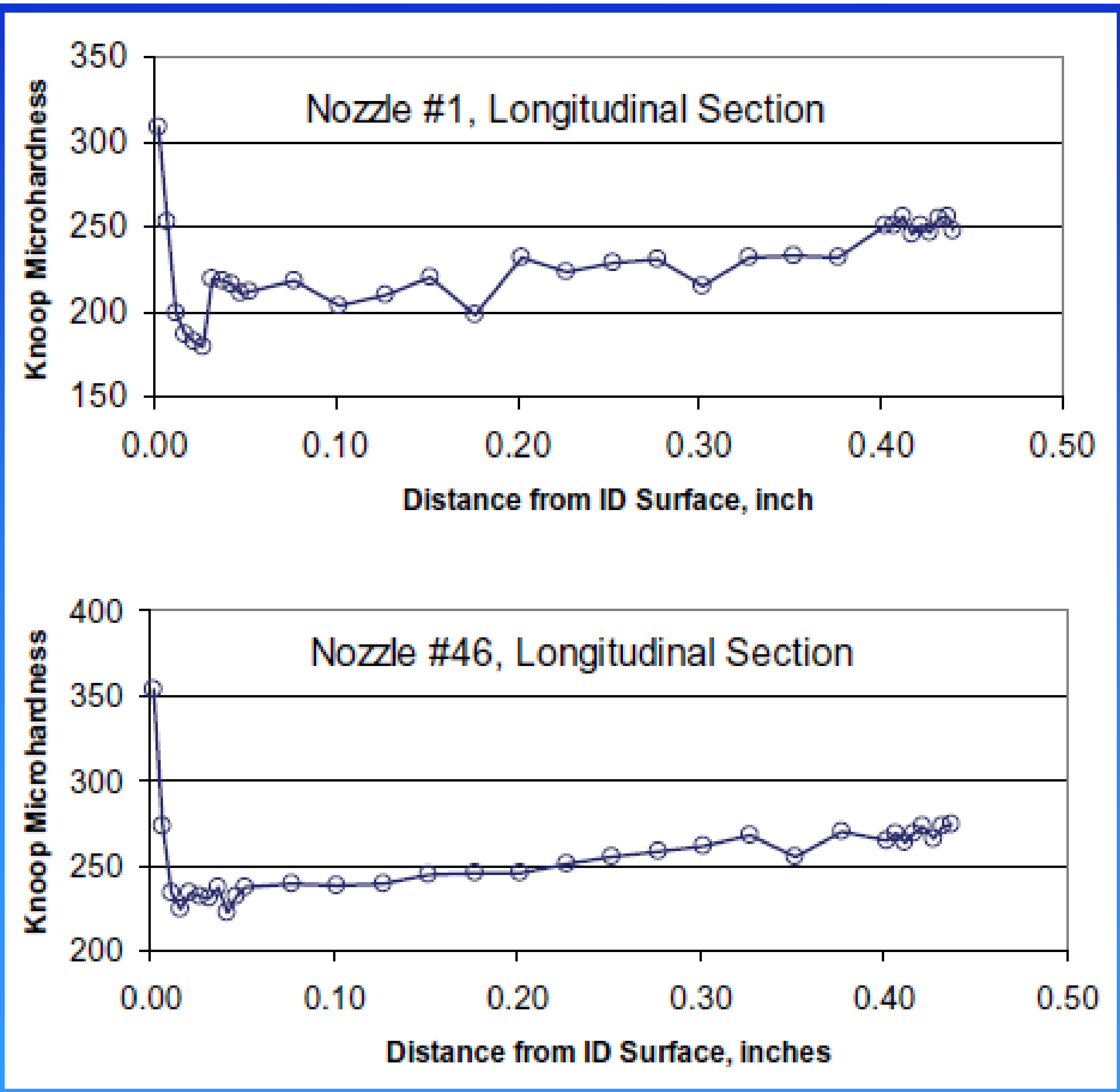




A cold-worked layer was found on the ID surface of both nozzles. This was consistent with the deep gun-drilling process used during BMI nozzle manufacturing.

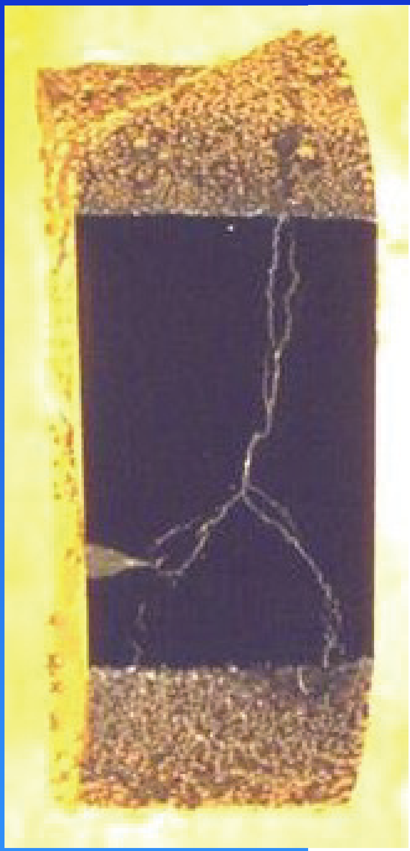
A. McIlree, Cold Work Workshop, 6/07

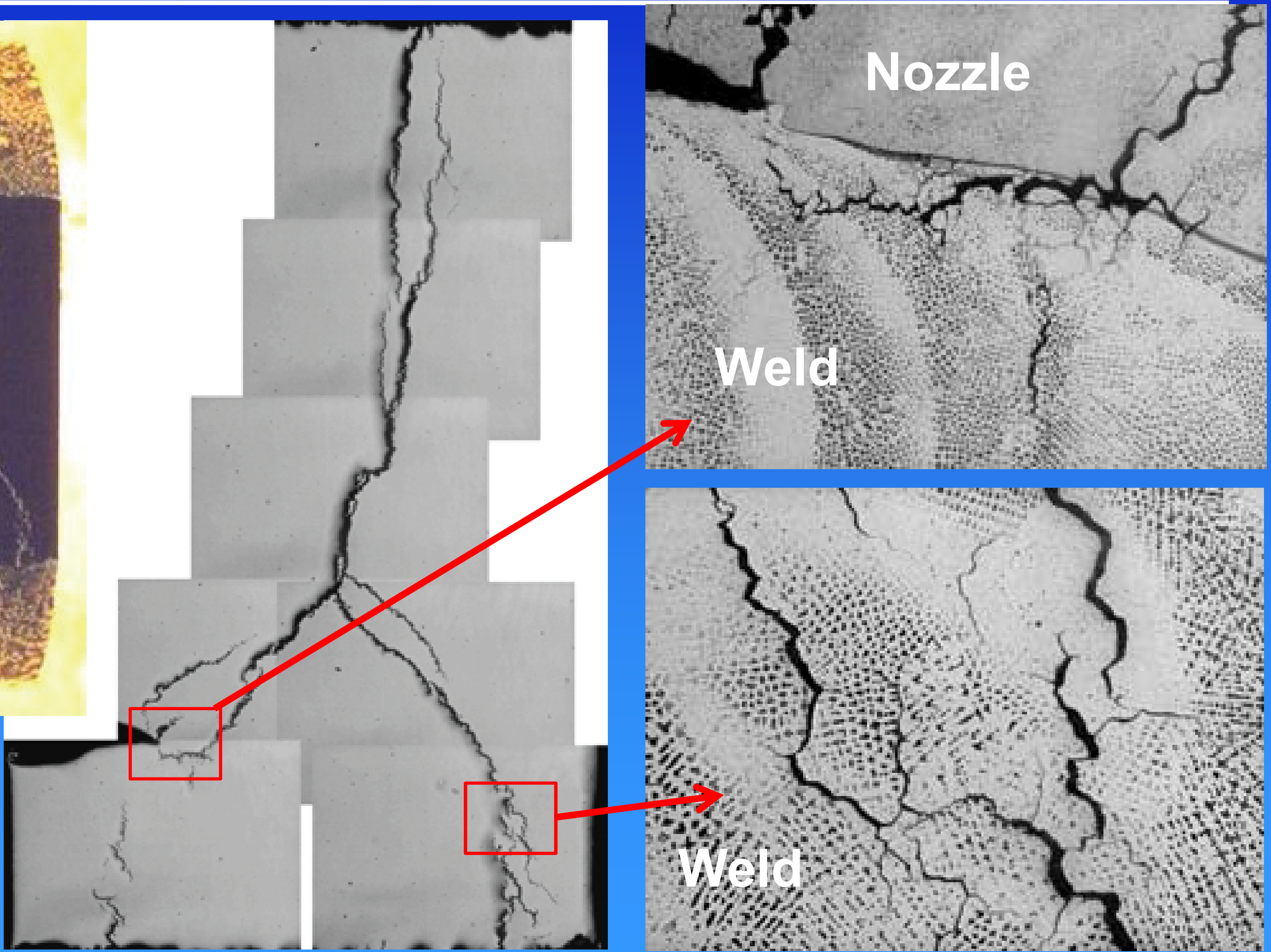
Knoop Microhardness of STP Unit 1 Nozzles #1 and #46



H. Xu, et al. 12th Env. Deg., 2005

Y-shaped Axial Crack in Nozzle 1

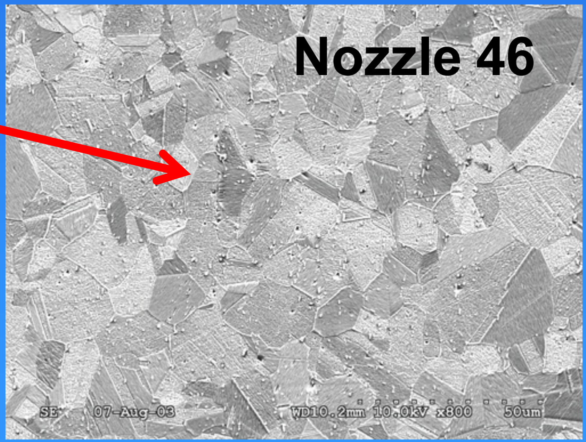




H. Xu, et al. 12th Env. Deg., 2005

STP Unit 1 Leaking BMI Alloy 600 Penetrations Summary

- 1st reported PWSCC in Alloy 600 BMI nozzles located at the reactor vessel bottom head
  - Alloy 182 J-groove welds at the reactor vessel inlet temperature (T_{cold}) of 293°C (560°F)
- PWSCC contributing factors:
  - Intragranular carbides with little carbide coverage on the grain boundaries
  - Very fine grain size
  - High bulk yield strength
  - Cold-worked ID surface
  - High residual stresses (no PWHT)

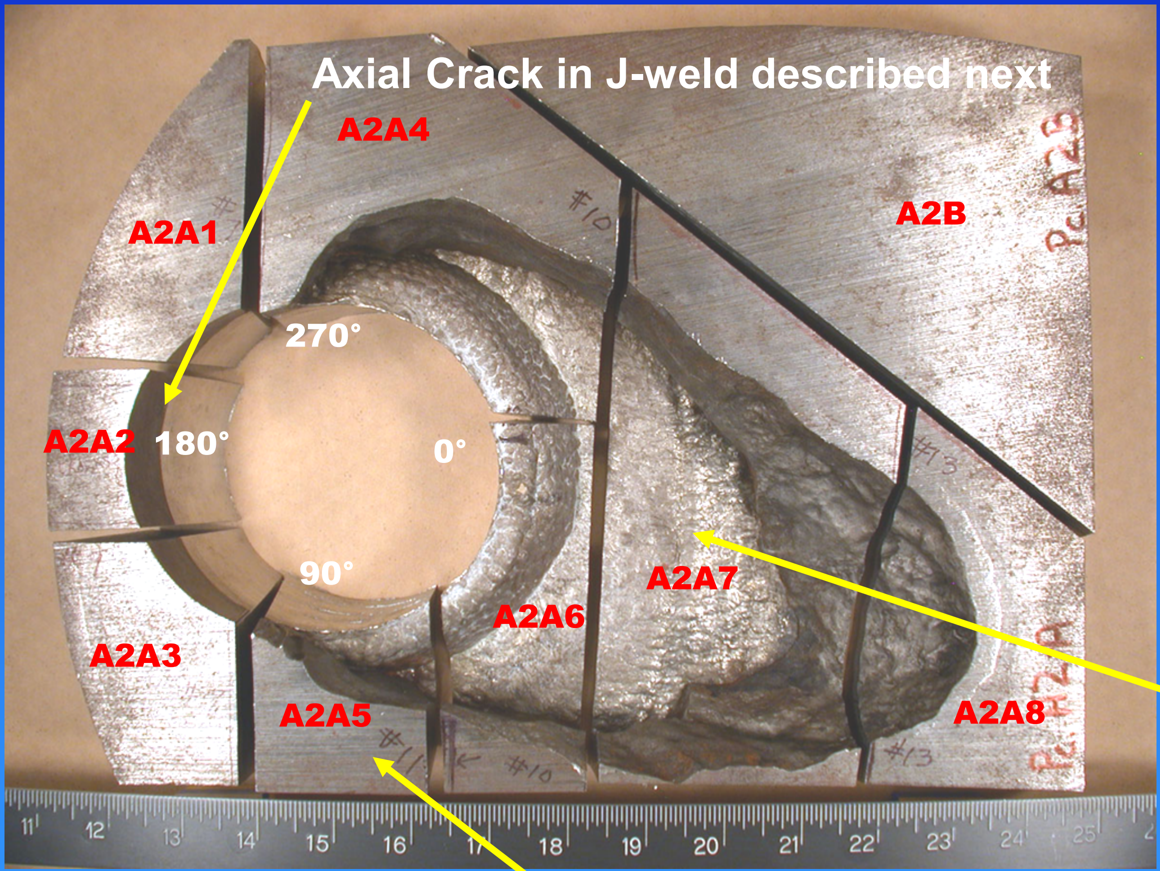


H. Xu, et al. 12th Env. Deg., 2005

Davis-Besse PWSCC Investigation

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

Sectioning of Davis-Besse Cavity



Major cuts made in preparation for cavity exam. Most sections were further reduced for metallographic and fractographic exams. Largest cracks were near ~10° (major leak) and 180° (non-leaking).

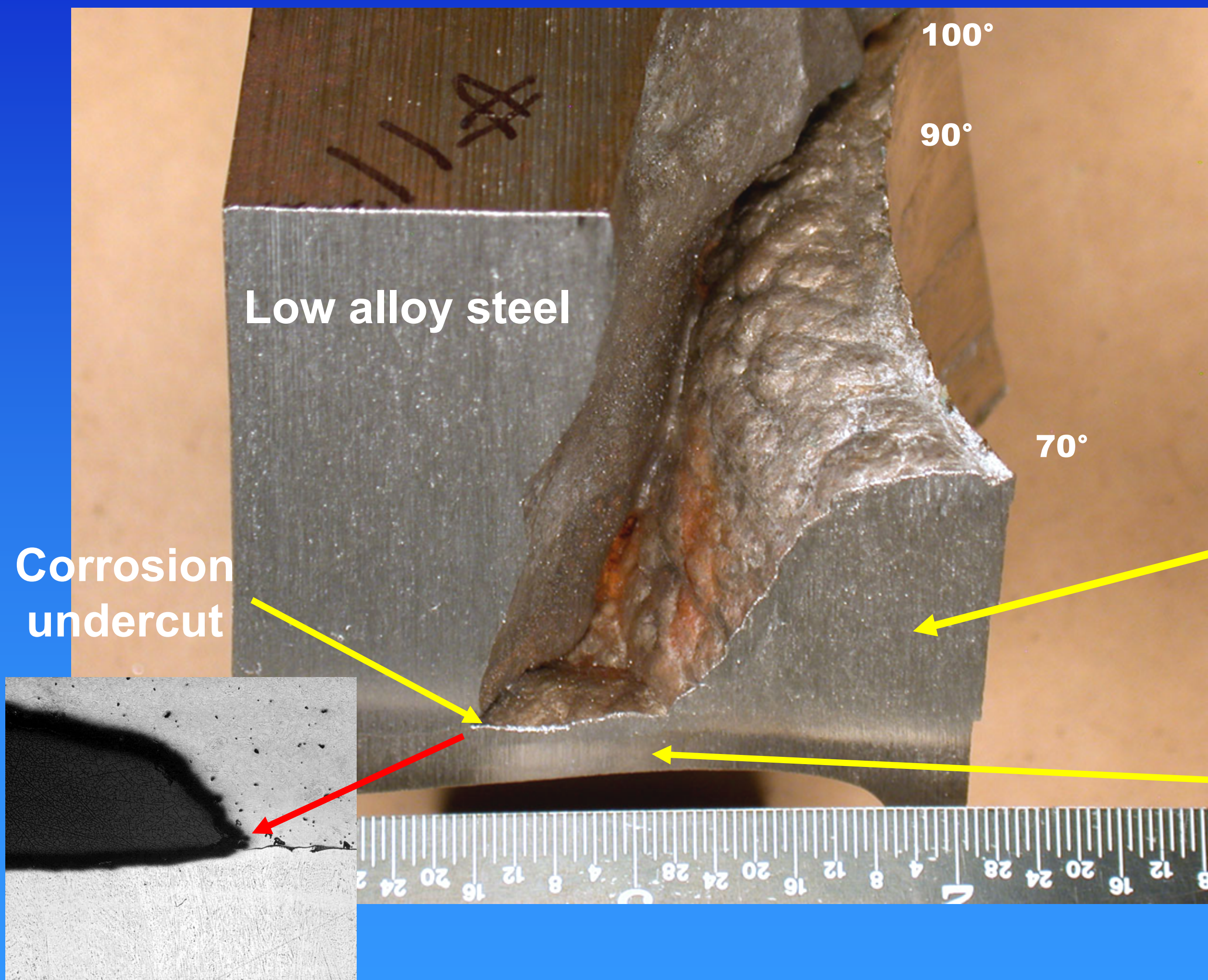
Cracks in clad described later

Piece A2A5 shown on subsequent slide

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

Structural Integrity Associates

Examination of Davis-Besse Cavity Characteristics Near J-weld



Exposed J-weld/LAS fusion surface, exposed cladding and corroded LAS near Nozzle #3.

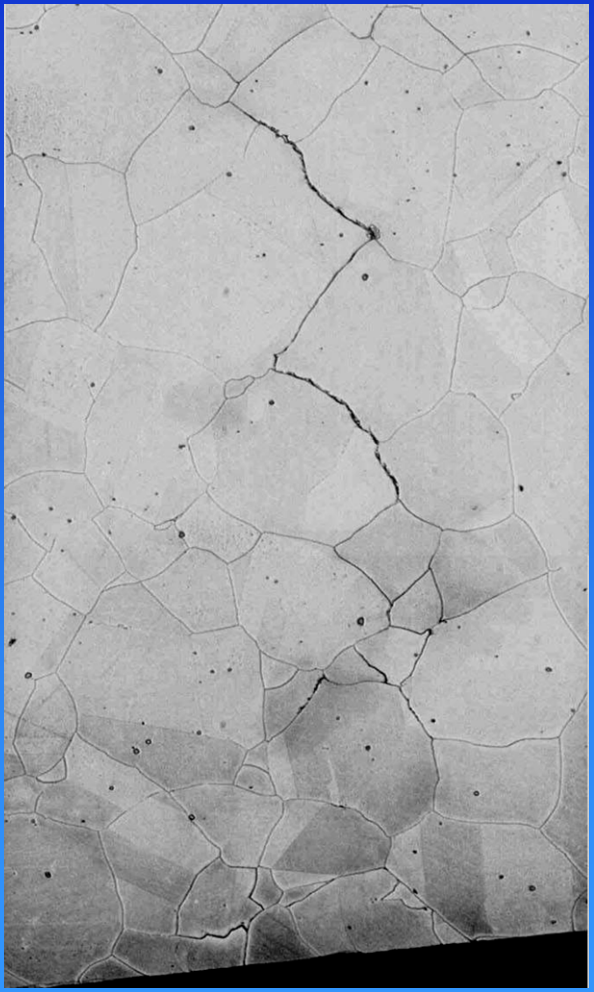
Exposed J-weld

Exposed clad (thinnest location)

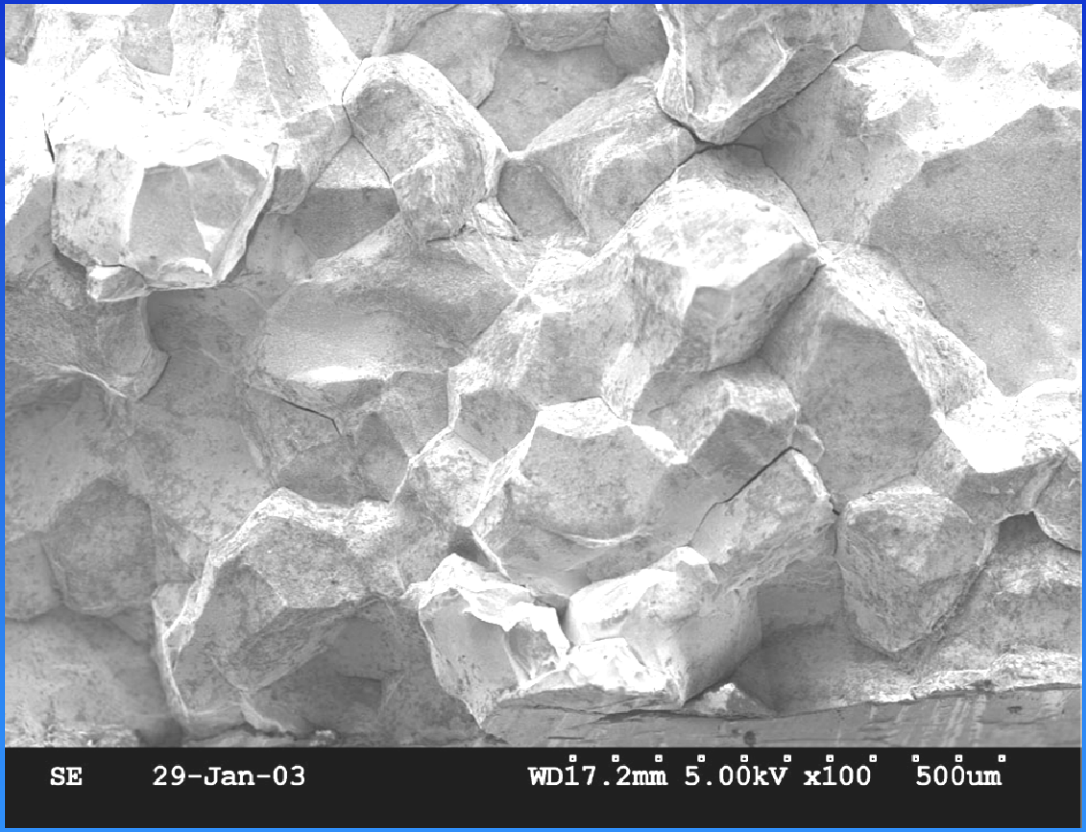
W. Cullen, ACRS Mtg., 4/22/03

Structural Integrity Associates

PWSCC in Davis-Besse CRDM Nozzle #3



IGSCC crack in Alloy 600 of Nozzle #3, 170° location, near upper end

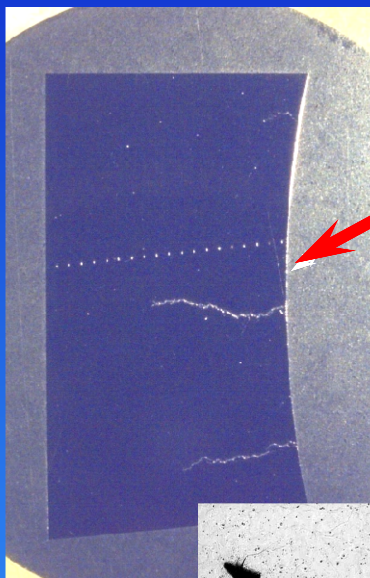


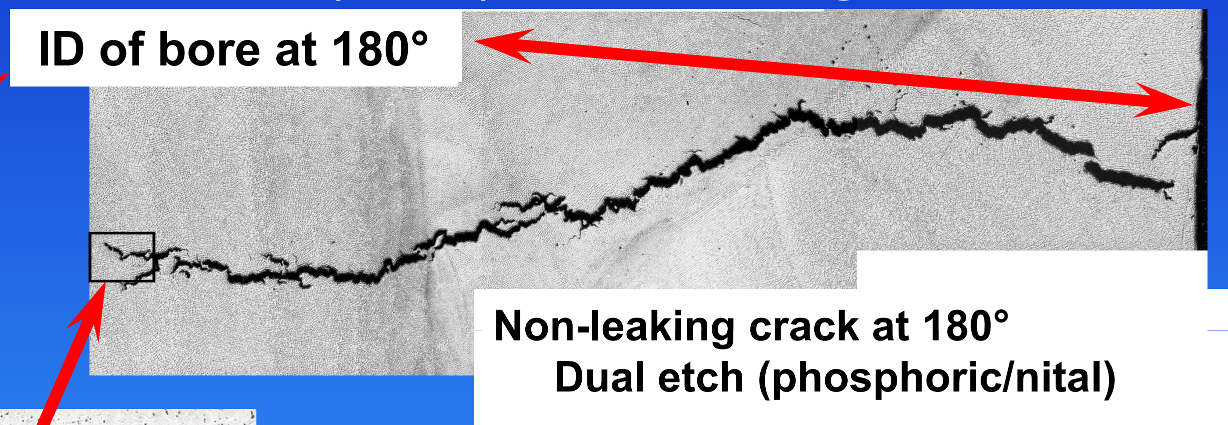
IGSCC surface from A600 of Nozzle #3. Surface 100% IGSCC with lots of O_2 and C

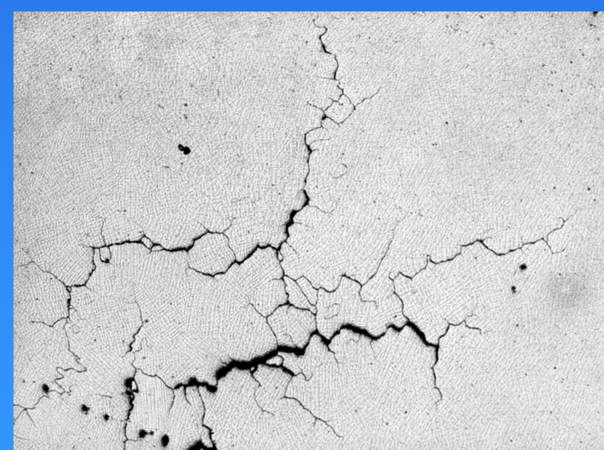
W. Cullen, ACRS Mtg., 4/22/03

Character of PWSCC Cracks in J-weld of Davis-Besse Nozzle #3

Optical image (left) and metallographs (below) are mirror images of each other.





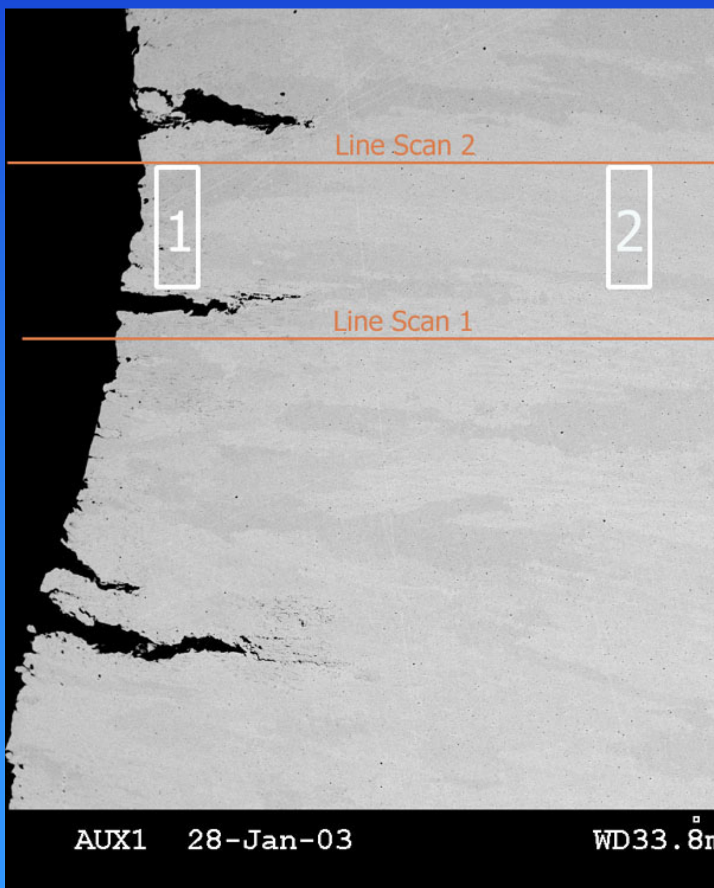


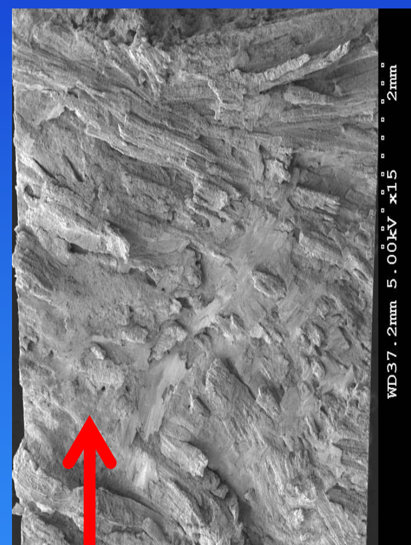
Tip of one of many branches of the leaking crack at 10°

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

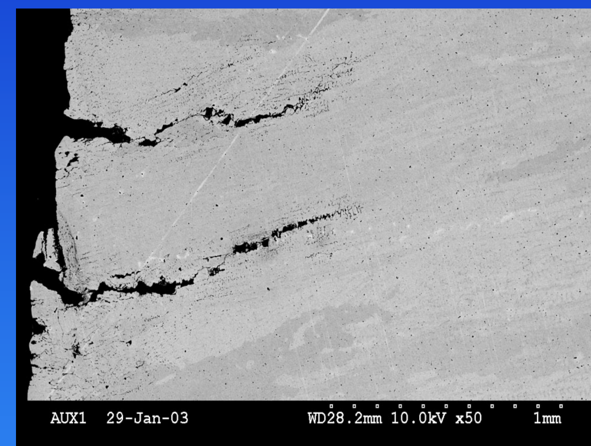
PWSCC in Davis-Besse SS Cladding

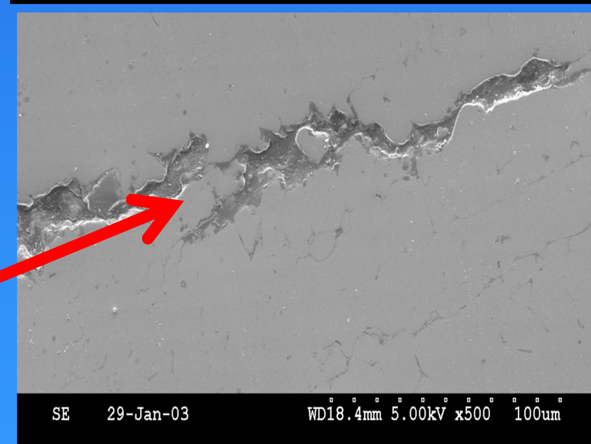
Opened crack in cladding shows interdendritic growth morphology (IDSCC) – all IDSCC, no tearing, even near the bulge





SEM shows ID crack

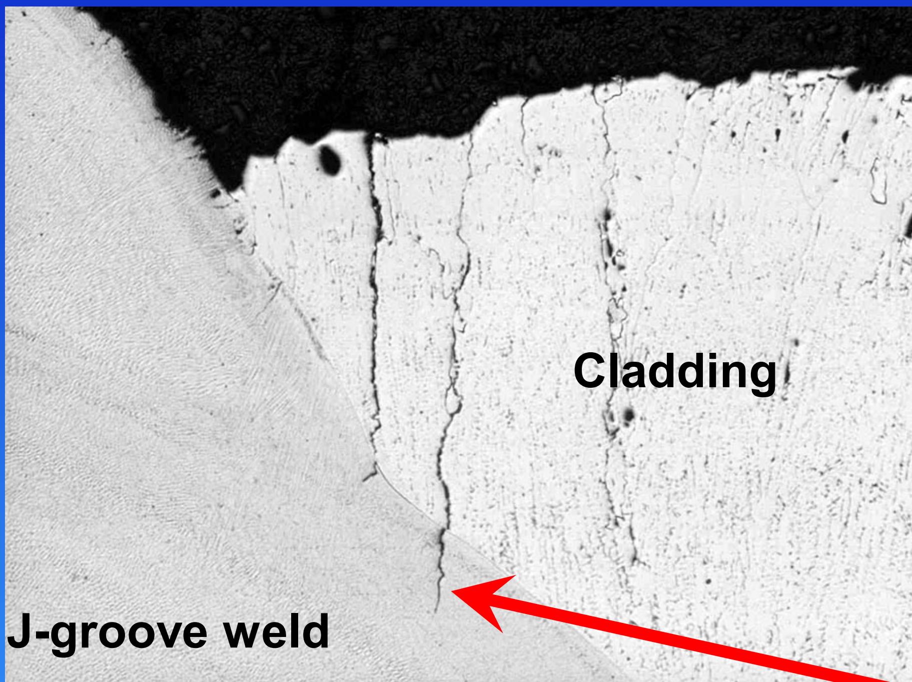


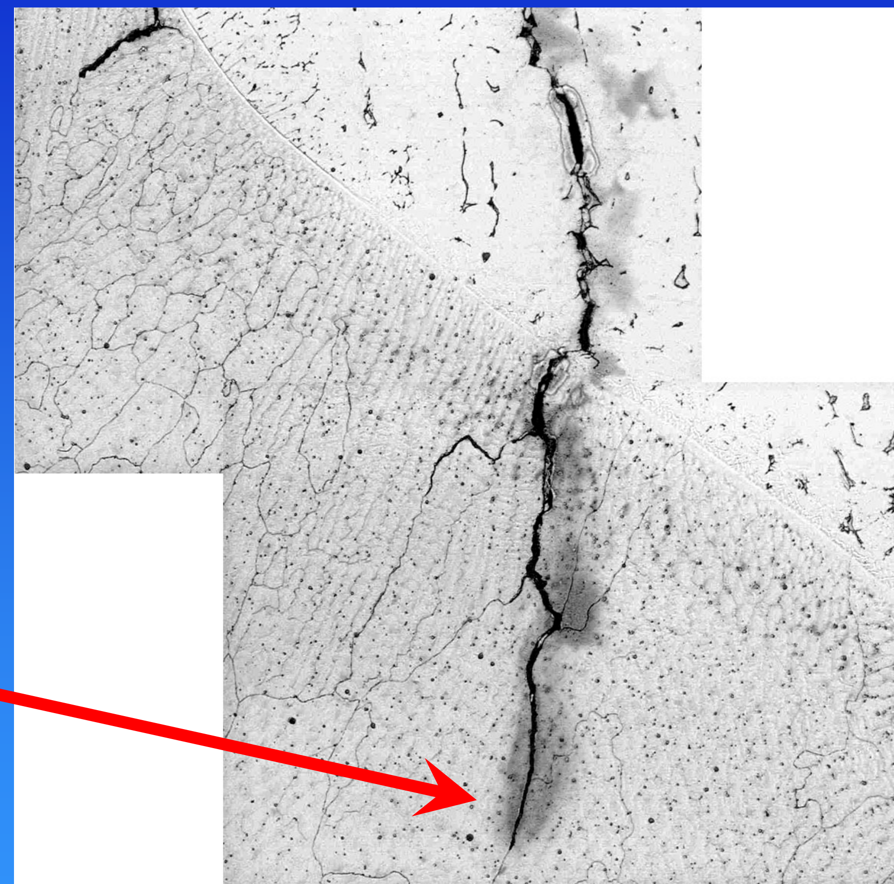


SEM shows preferential dissolution of ferrite in crack path

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

PWSCC in Davis-Besse SS Cladding





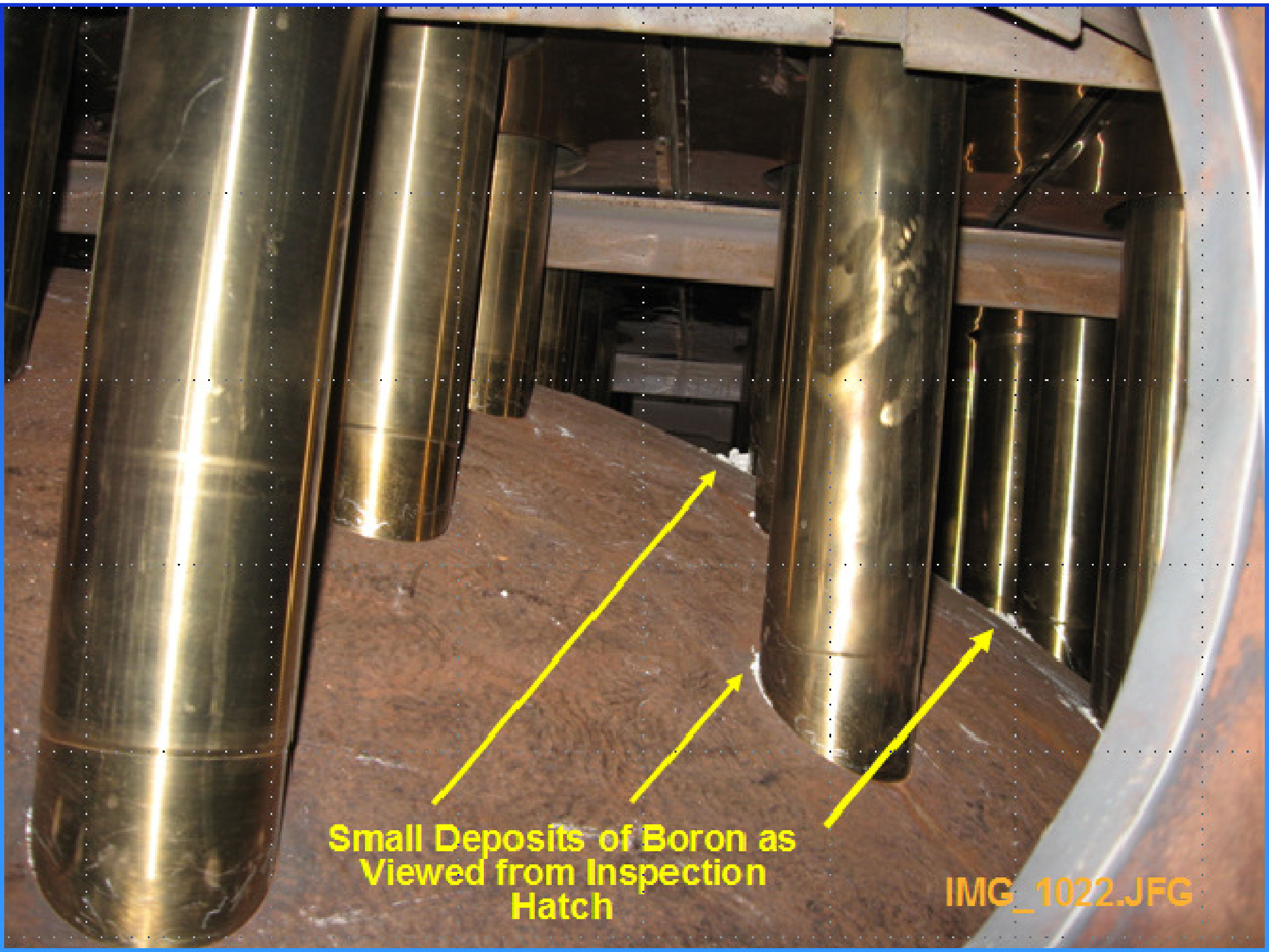
Close-up of clad crack penetrating fusion line into J-weld

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

2010 Davis-Besse Part 2

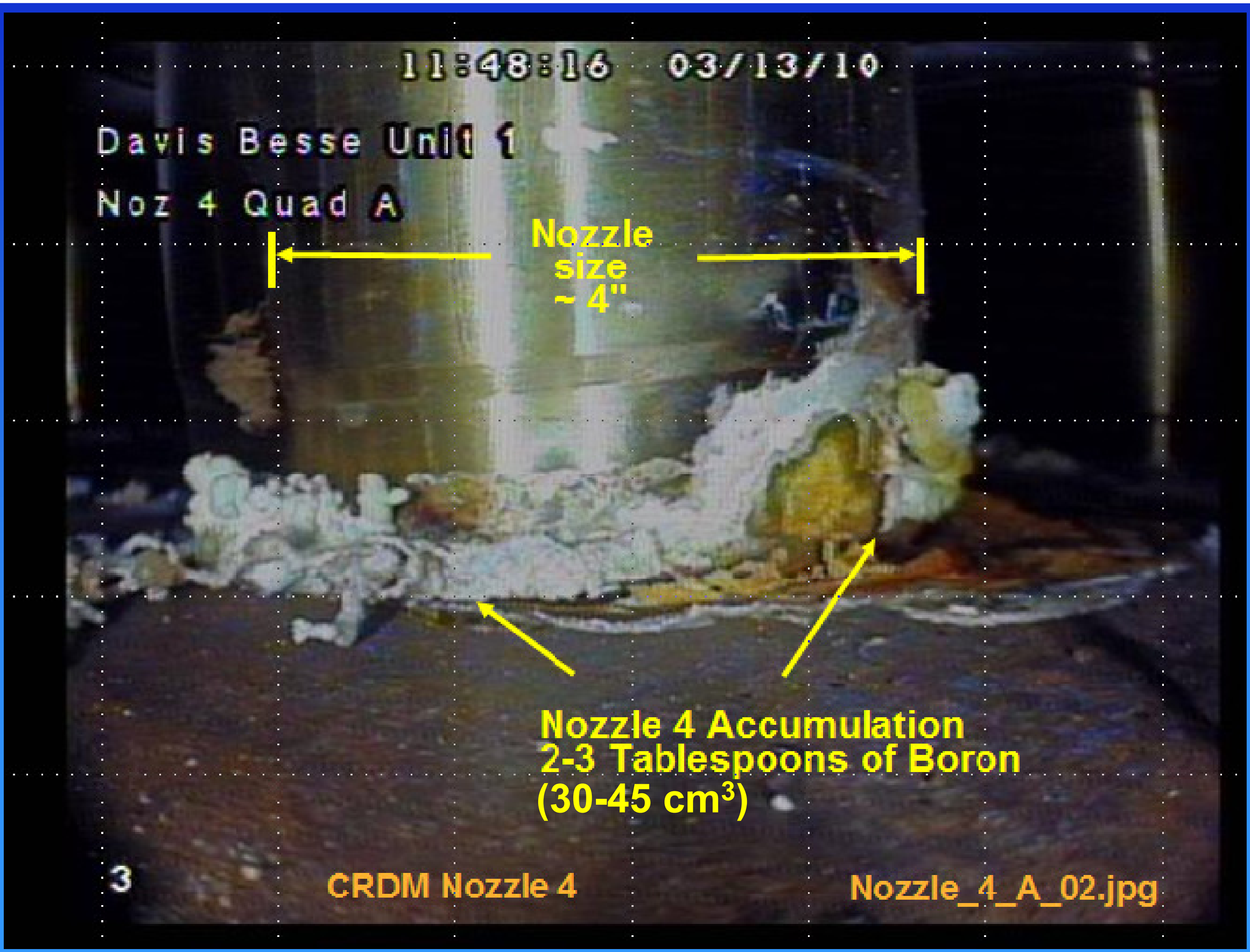
- **Bare metal visual inspections performed:**
  - **2003, 2005, 2006 and 2008 with no identifiable boron leakage**
- **March 12, 2010 – Identified indications in CRDM penetration nozzles during axial UT scans – initiated 8 hour report to the NRC**
- **March 13, 2010 - Bare metal visual examinations reveal boron deposits on the RVH – updated 8 hour report to the NRC**

2010 Davis-Besse Inspection Results



FENOC NRC Public Meeting 6/10

2010 Davis-Besse Inspection Results

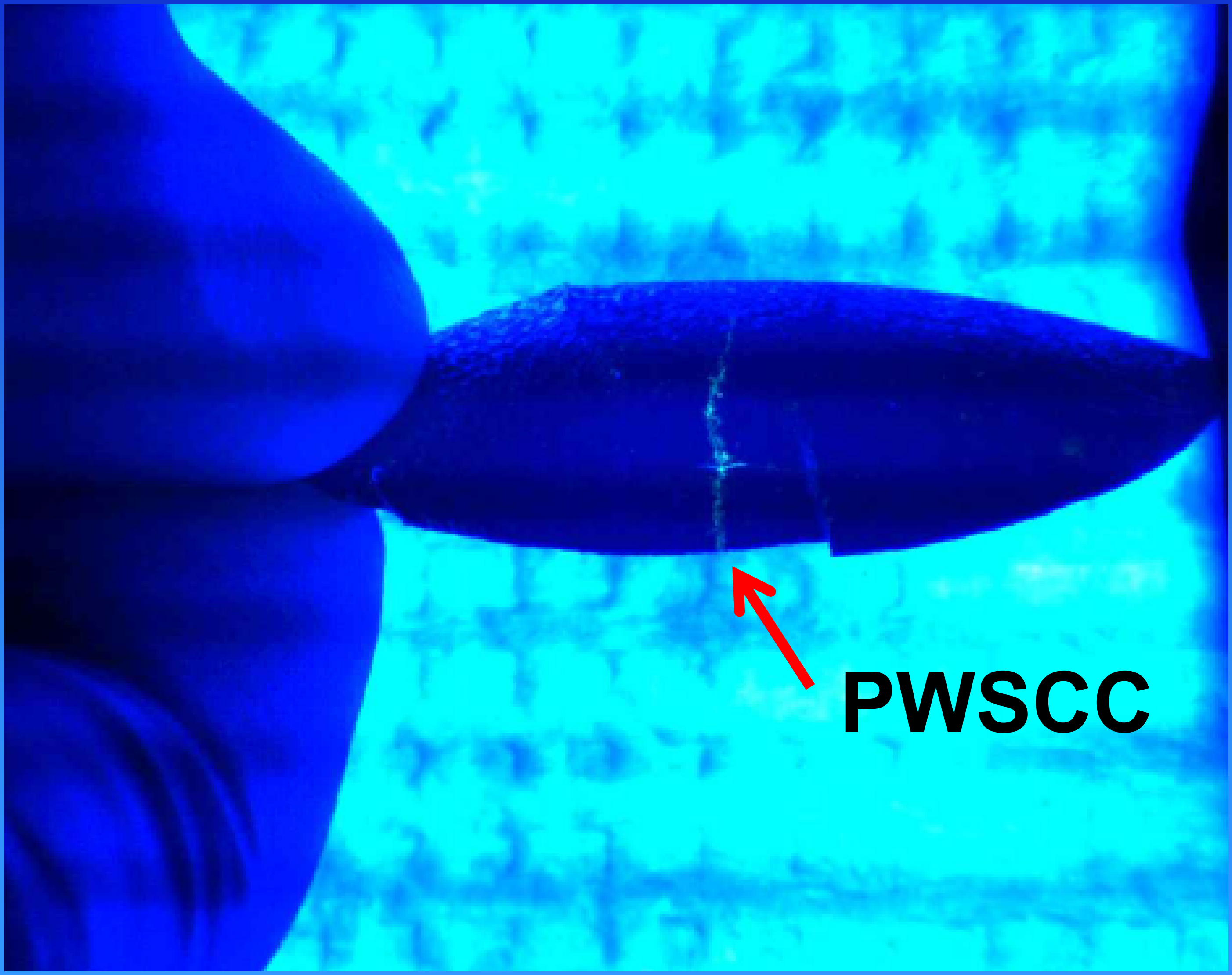


2010 Davis-Besse Inspection Results

- 24 of 69 nozzles identified for modification
- Samples taken of weld and nozzle metal for lab analysis
  - Indications cut out of nozzles 4 and 10 for analysis
  - Nozzle 4 and 10 ends removed for lab analysis

Davis-Besse Boat and Ring Specimens

Davis-Besse Boat Specimen Examined by Fluorescent PT



2010 Davis-Besse Root Cause Evaluation

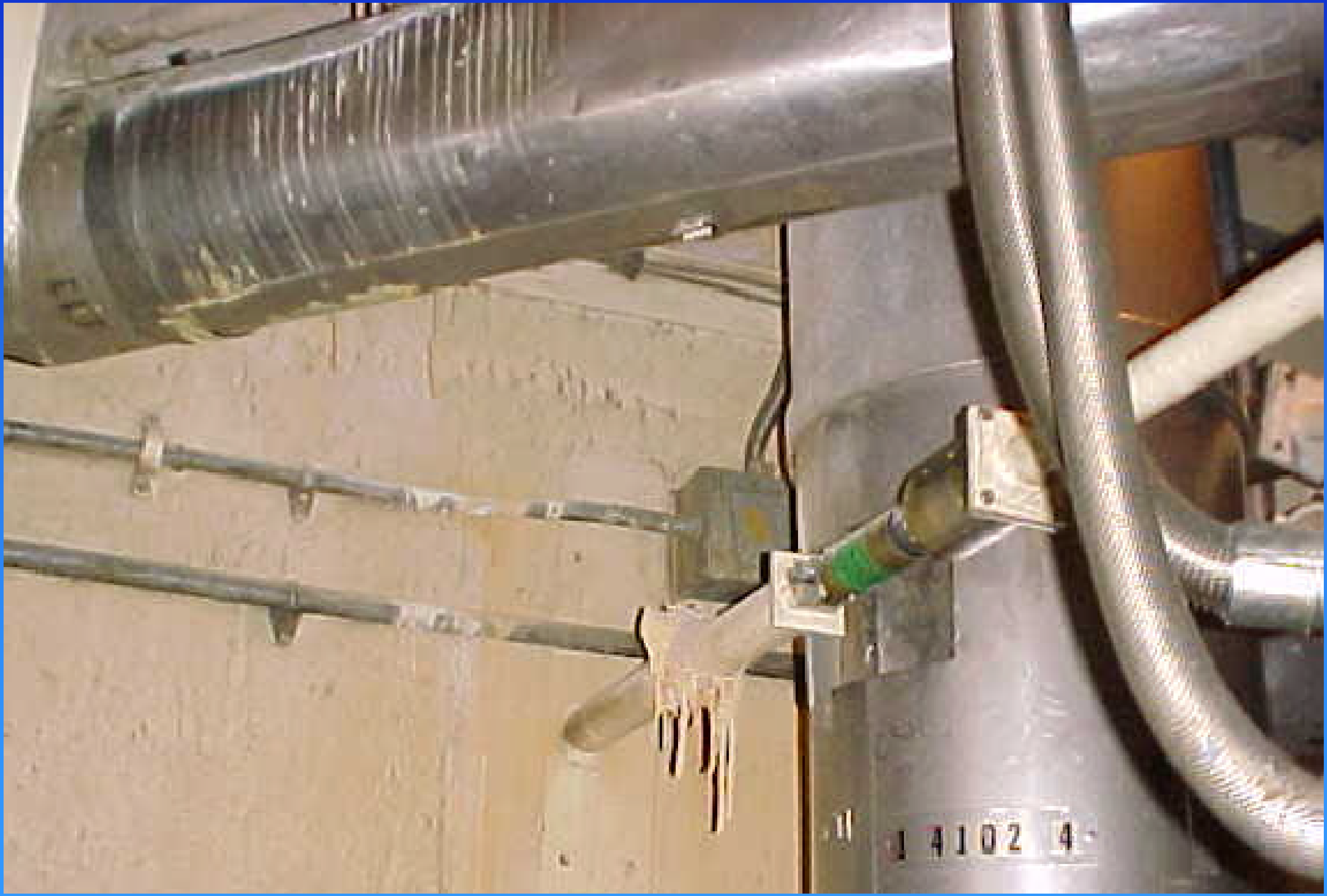
- Accelerated (greater than expected, i.e., after only 3 cycles) PWSCC due to elevated RPV head temperatures
  - RPV was operating nominally at 319.1°C (606.4°F), but new head was ~324.4°C (616°F) - 5.3°C (9.6°F) too hot!
- PWSCC Mitigation
  - Reconfiguring the core to reduce the head temperature to 322.7°C (613°F)
    - FENOC believes ~1.7°C (~3°F) reduction plus repairs will keep new cracks from forming until RFO 2012
  - Shortening the next operating cycle
- New head installation with Alloy 690 CRDMs moved up to 2011 from 2014 to avoid mid-service inspection

FENOC NRC Public Meeting 6/10

V. C. Summer Hot Leg PWSCC

- >91 kg (>200 lbs) of H_3BO_3 near the reactor vessel "A" loop hot leg outside the primary shield wall in 10/7/00
- Type 304 SS RCS piping was welded (many repairs) to Alloys 82 and 182 buttered LAS nozzle
  - Weld essentially became a "double V" design because welding/grinding were on both the ID and OD
- Multiple crack initiation sites on the ID in the original Alloy 182 butter
- Axial crack was contained entirely within the Alloy 82 and the Alloy 182 nozzle butter with small ligaments that reached the pipe OD surface as a single small weep hole

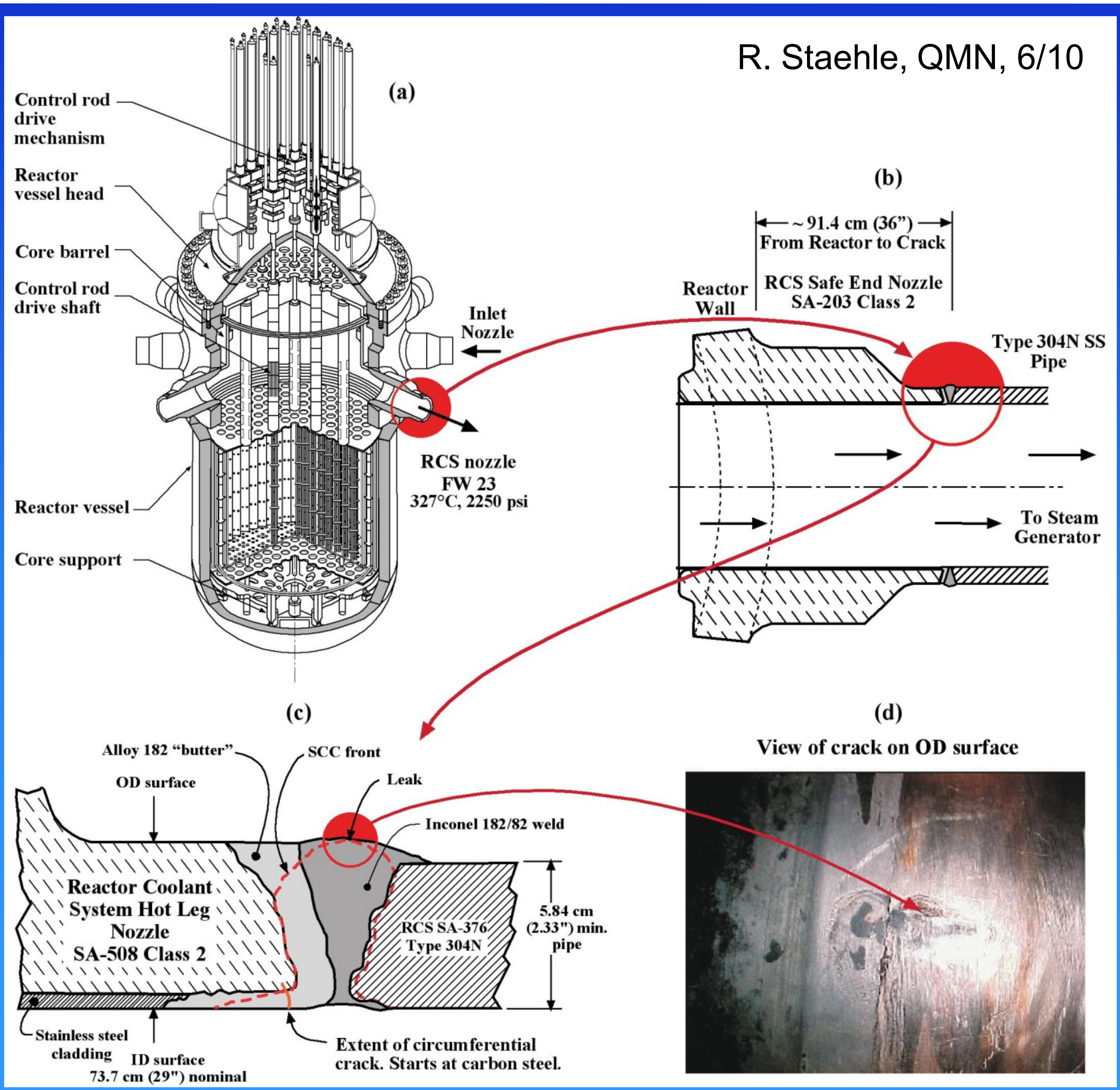
Boric Acid Deposits at V. C. Summer



SCE&G to NRC 1/18/01

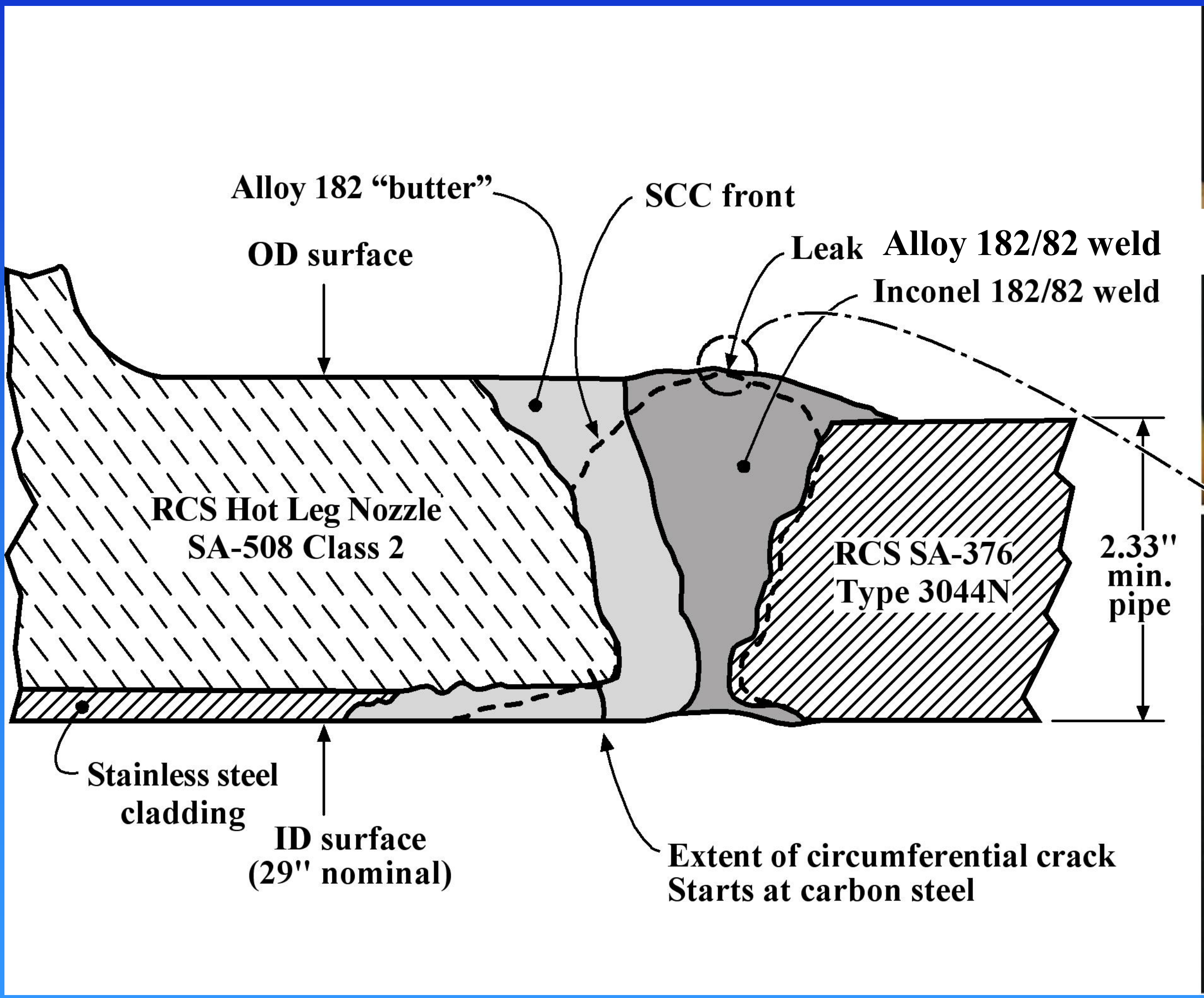
Structural Integrity Associates

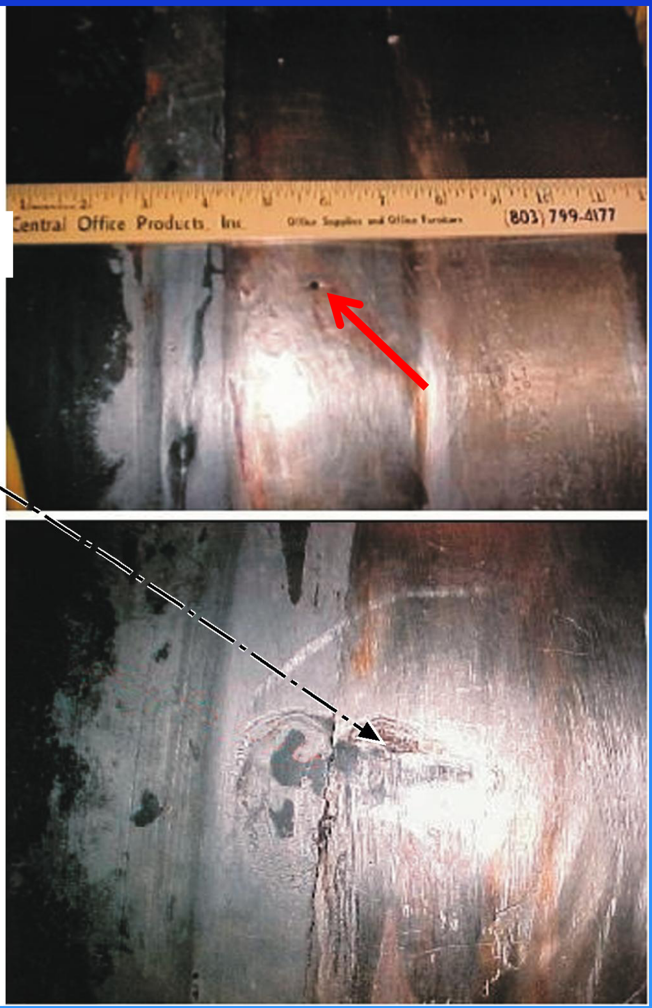
V. C. Summer Hot Leg PWSCC



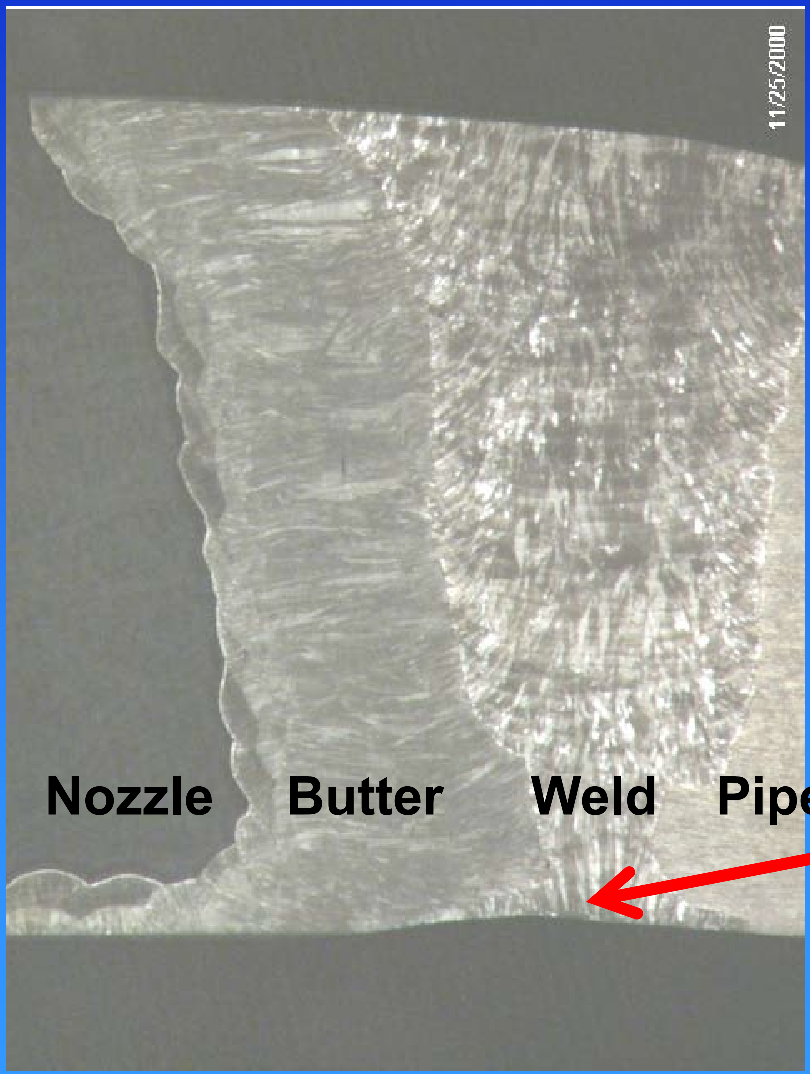
Structural Integrity Associates

V. C. Summer Hot Leg PWSCC of Alloys 82 and 182

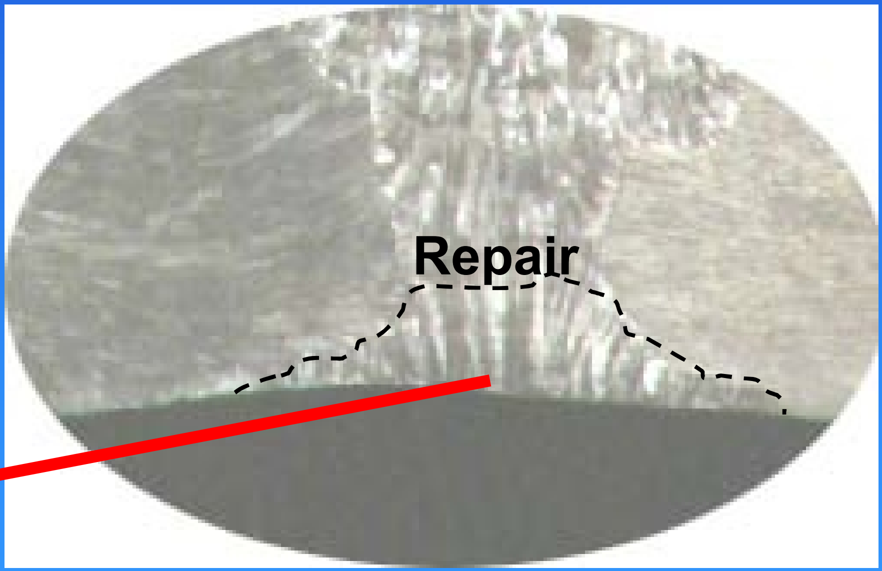




Cross Section of V. C. Summer Weld/Butter

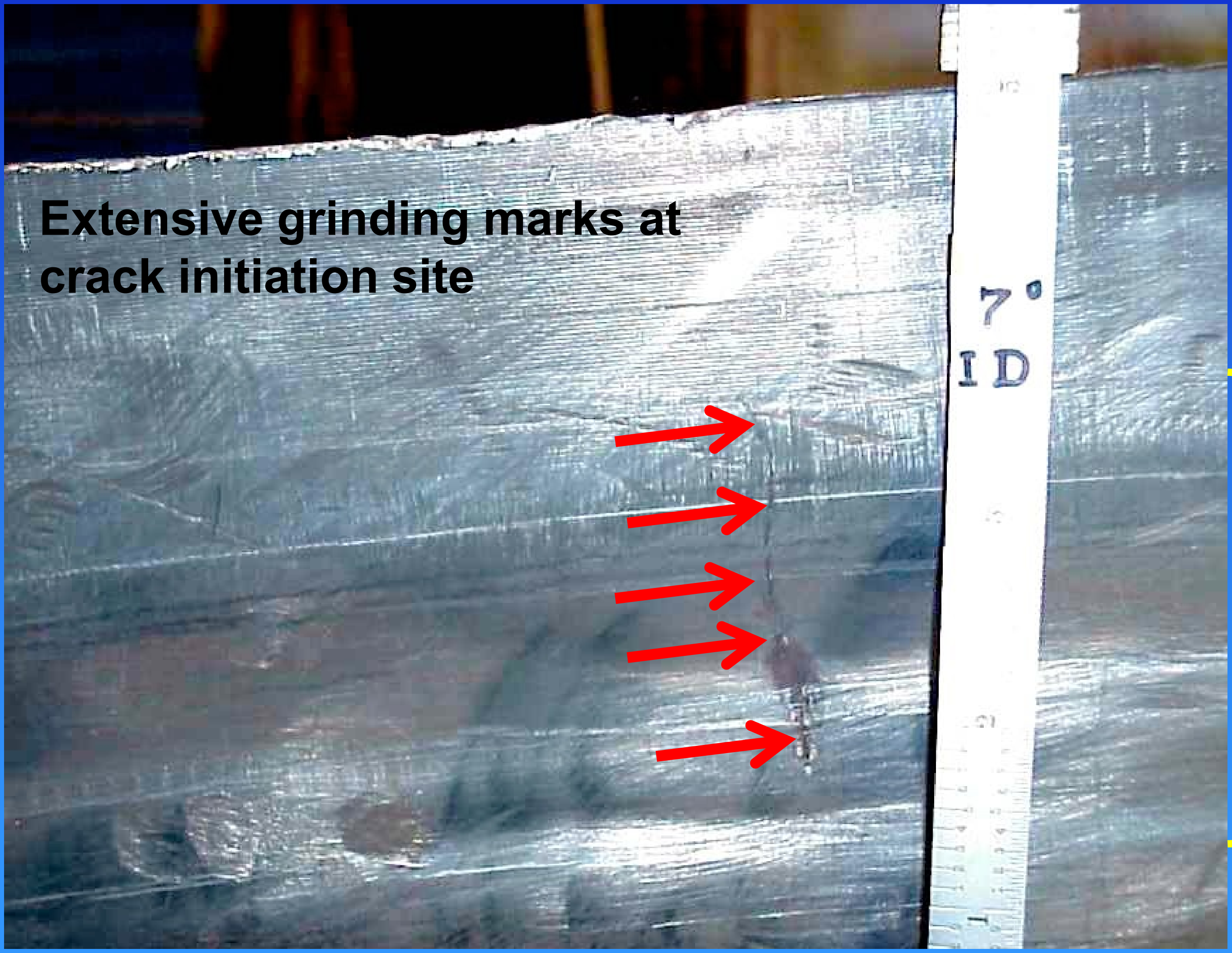


Weld had an ID Repair with extensive surface grinding (cold work) shown in next slide



A. McIlree, Cold Work Workshop, 6/07

Surface of VC Summer Butt-Weld



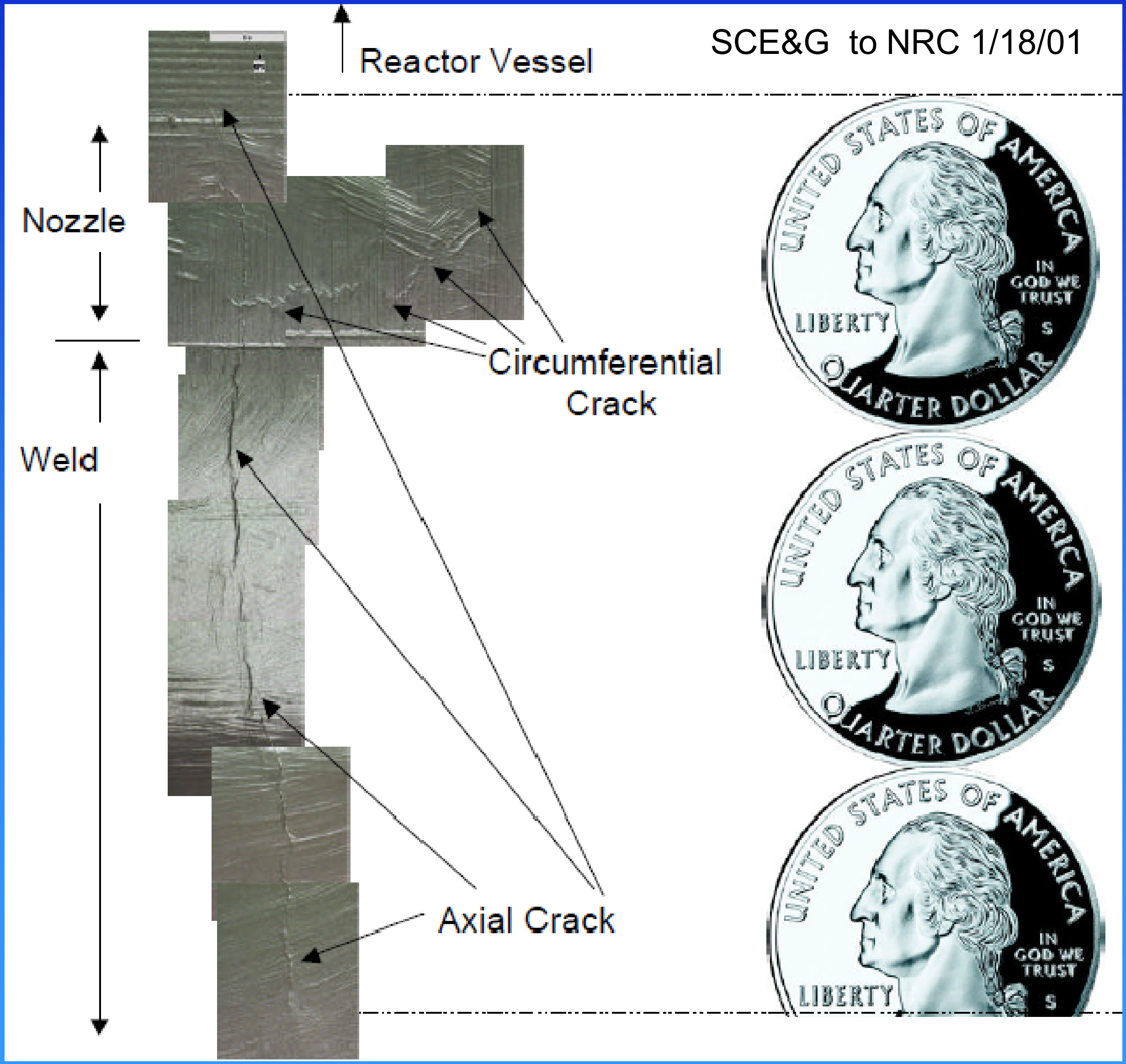
Nozzle

Weld

Pipe

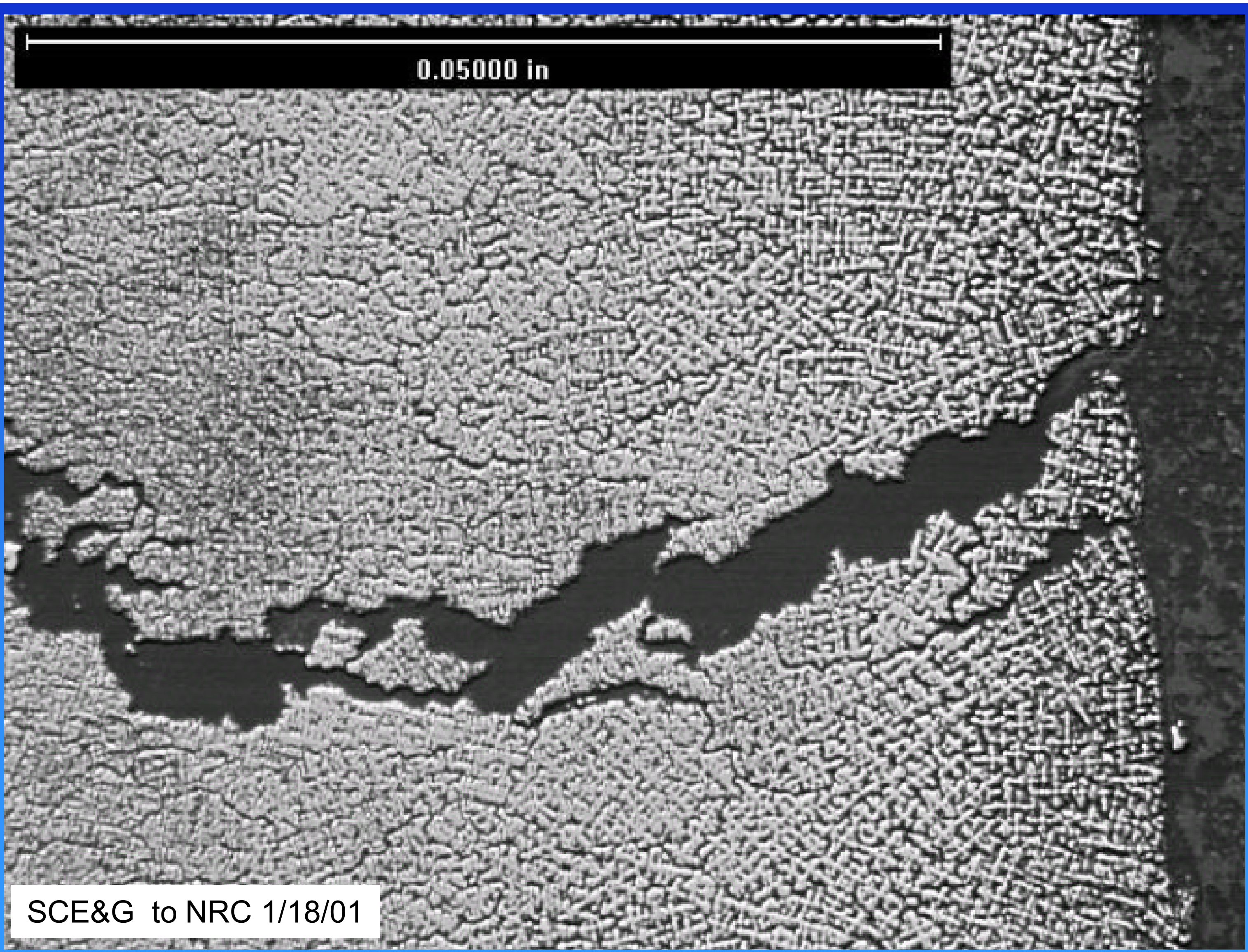
A. McIlree, Cold Work Workshop, 6/07

Surface View and Cross Section of V. C. Summer Crack



Structural Integrity Associates

Metallography of Through-wall IDSCC Crack at the ID Surface (7º)



Ringhals 3 and 4 PWSCC – 2000

- Ringhals 3
  - Two indications recorded in one safe end, first evaluated as sub surface planar flaws
- Ringhals 4
  - Several indications recorded in one safe end, evaluated as volumetric defects
  - Planar flaws removed by boat samples to
    - Stop further growth
    - Metallographic examination
- No leakage

L. Skånberg, SMiRT 2001

Metallographic Exam Results

- IDSCC in weld repaired Alloy 182
- Significant branching of some cracks
- Very tight crack tips and also tight crack sections connected to inner surfaces
- Some hot cracking and small lack of fusion
- No IDSCC propagation into RPV steel or stainless steel

L. Skånberg, SMiRT 2001

Summary of Operating Experience of PWSCC of Alloy 182 and 82

- >300 Ni-base welds are known to have had PWSCC reportable indications (2008)
  - Only two Alloy 82 PWSCC
- Shortest time before detection of SCC non-stress relieved welds is 13 years (97,297 EFPH) and 12 years (77,000 EFPH) for a SG tube sheet impacted by a loose part
- In only 4 cases of PWSCC linked to fabrication defects; the dominant variable controlling crack initiation is surface residual stress, which depends strongly on surface finish
- Most cases due to high residual stresses associated with repairs or localized high cold work and/or not stress relieved

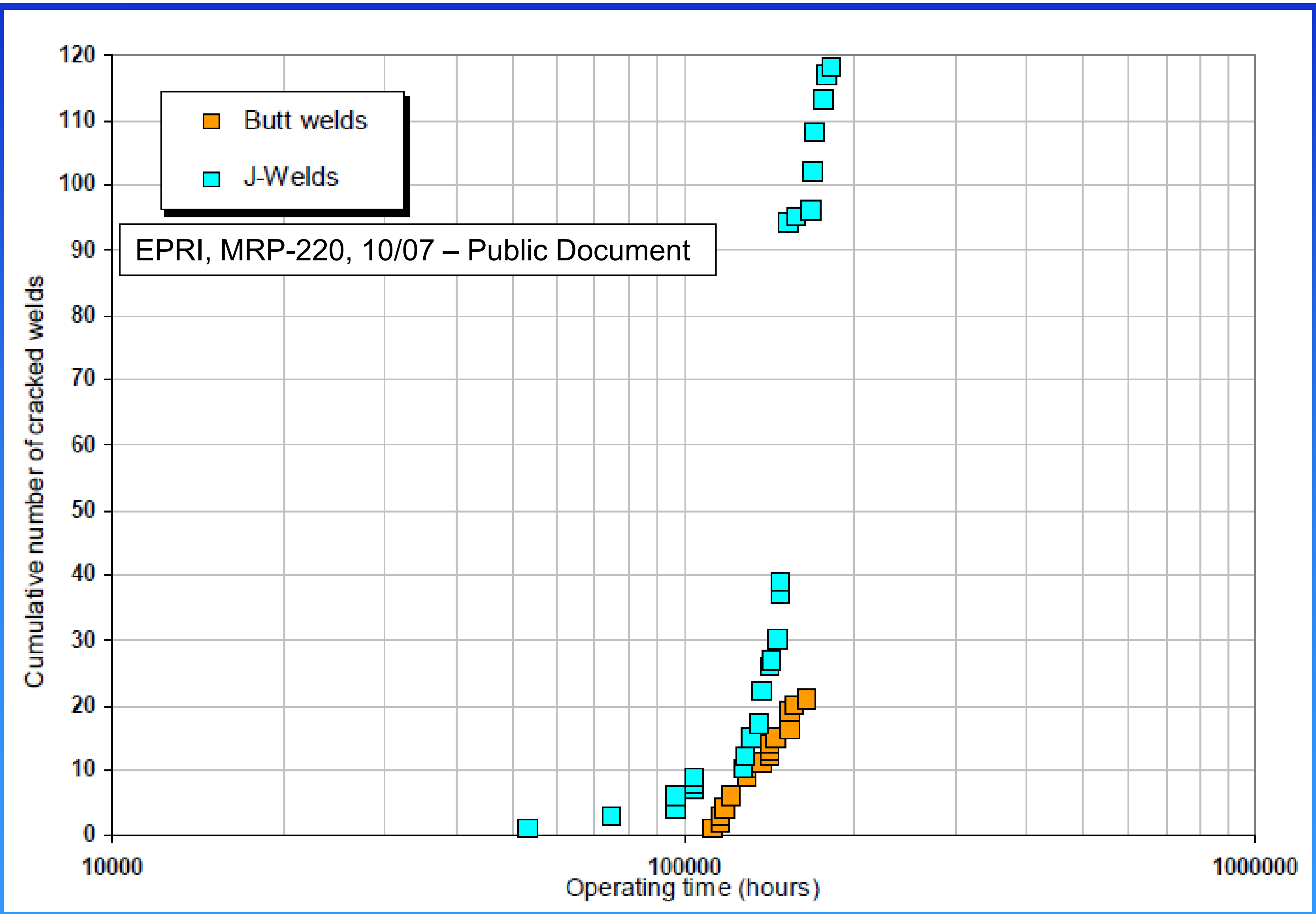
P. Scott and F. Vaillant, Int. Conf. PMD 11/08

Incidence of PWSCC in Ni-base Alloys in PWRs

- Only cold worked and/or as-welded Alloy 600/182/82 components have been affected
- Components subjected to heat treatment due to stress relief of adjacent LAS components (~610°C [~1130/°F]/10 h) have not cracked to date:
  - Mockup studies show that the surface residual stress is significantly reduced even though the stress relief temperature is not optimized for Ni-base alloys
  - Microscopic examination shows that stress relief occurs due to recrystallization during heat treatment of heavily cold worked surface layers due to grinding

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

Operating Times to Weld Cracking as a Function of Weld Type



PWSCC Parameters

Nickel Alloys and PWSCC

- Susceptibility of Ni-base alloys to PWSCC are strongly affected by their microstructure
- Very complex due to:
  - Grain boundary precipitates
  - 2nd phases
  - Defects such as dislocations, interstitial atoms, vacancies, stacking faults, etc.
  - Cold work

Nickel-base Weld Metal and PWSCC

- Weld metal microstructure is even more complex than wrought materials
  - Solidification of weld metal leads to dendrites growing in the direction of the heat flow, i.e., perpendicular to the solid material on which the weld is deposited
  - Since all welds are multiple pass welds, the grain structure of dendrites in subsequent passes is affected by the previous passes. The dendrites are thus being modified by several weld passes
  - Creates a very intricate and complex microstructure
  - Relative orientation of the dendrites in the weld metal has a significant effect on SCC propagation rates

PWSCC Factoids

- PWSCC occurs in wrought Alloy 600, Alloy 182 and 82 weld metals plus Alloy 600's high strength version, Alloy X-750 plus Alloy 718
- Secondary side SCC – Alloy 600
- Unlike BWR IGSCC, no consensus cracking mechanism has been identified
  - Only various models and correlations exist
- Remedies to date rely on empirical and phenomenological correlations

Essential Corrosion Features of PWSCC

- Strong influence of corrosion potential – worst case at Ni-NiO equilibrium
- Continuous failure mechanism between 286°C (546°F) water and 400°C (752°F) steam
- Highly temperature dependent – Arrhenius relationship
- Activation energy of ~50 kcal/mole for initiation and ~30 kcal/mole for propagation
- Favorable influence of grain boundary carbides (M_7C_3) – completely opposite of stainless steel carbides ($M_{23}C_6$) in BWRs in NWC
- Cold work very detrimental
- High heat-to-heat PWSCC variability with a factor up to 50 between "best" and "worst" heats

P. Scott and P. Combrade 11th Env. Deg., 2003

Mill Annealed Alloy 600

- Mill annealing:
  - Dissolve all the carbides (Cr_3C_7)
  - Enlarge the grain size
  - Cover the gb with carbides during slow cooling in air
- Alloy 600 with insufficient carbides at the grain boundaries is more susceptible to PWSCC
- Undissolved intragranular carbides are undesirable because they provide nucleation sites for the dissolved C and prevent precipitation of the carbides on the gbs
- Undissolved carbides prevent the grain growth
- Smaller grains have a much larger gb area per unit of volume and the carbides do not properly cover the gbs

NUREG 1771, 4/03

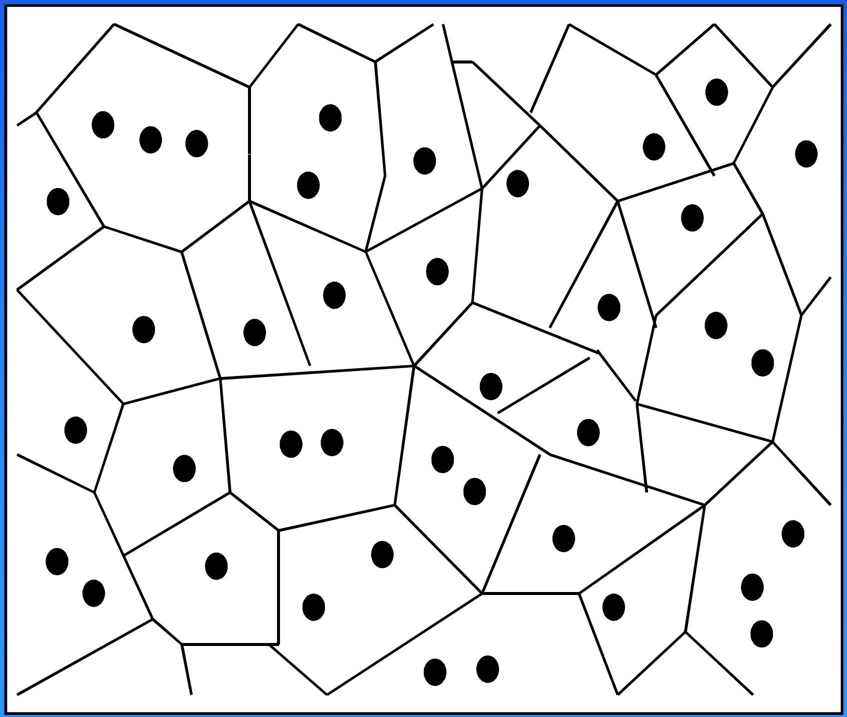
Alloy 600 Microstructures and PWSCC

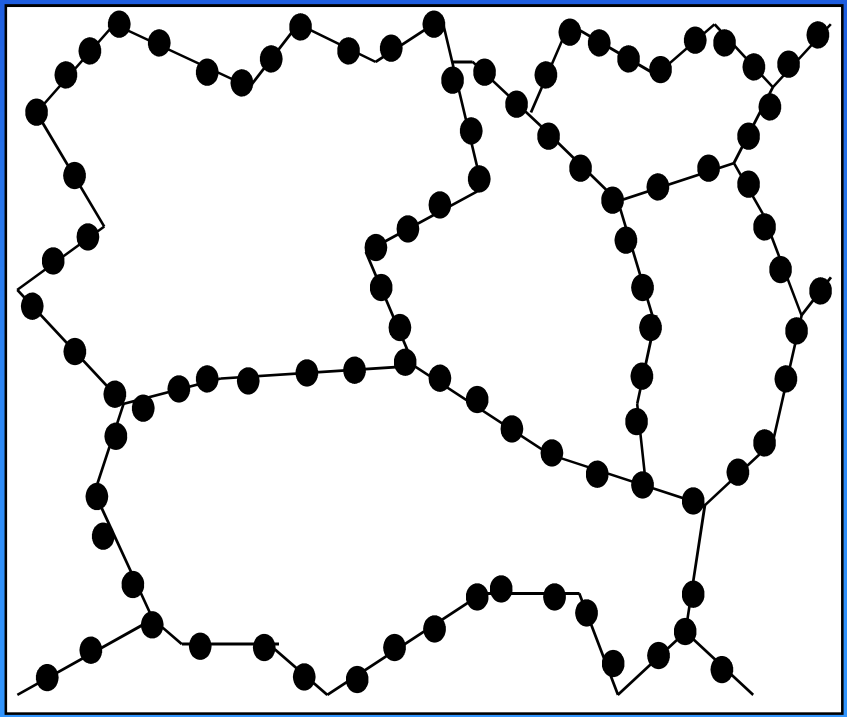
PWSCC Susceptible

Few grain boundary carbides
Many intragranular carbides
Small grain size

PWSCC Resistant

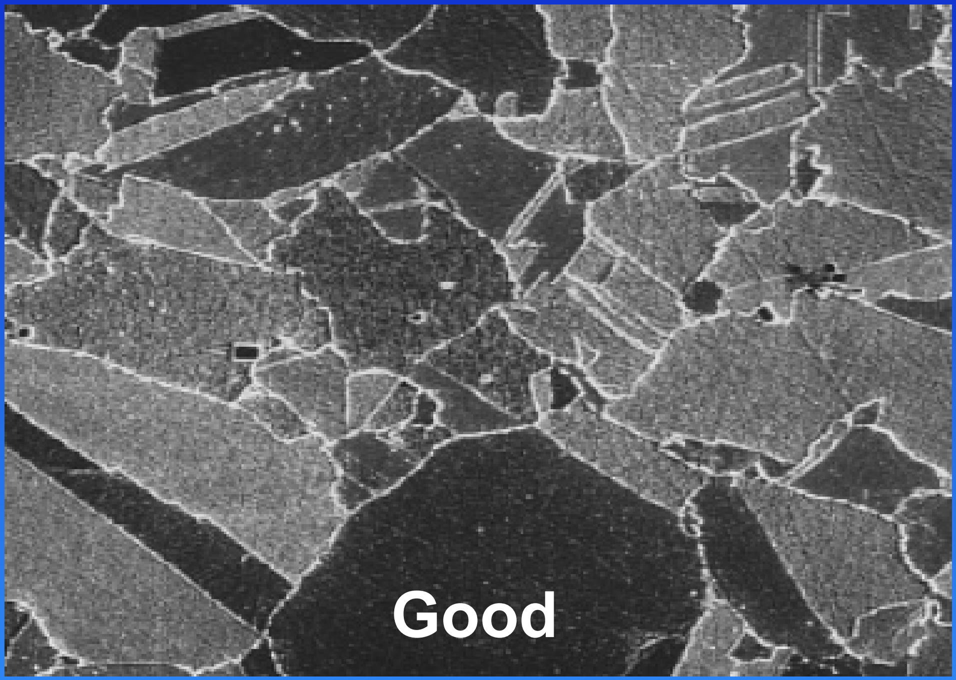
Many grain boundary carbides
Few intragranular carbides
Large grain size

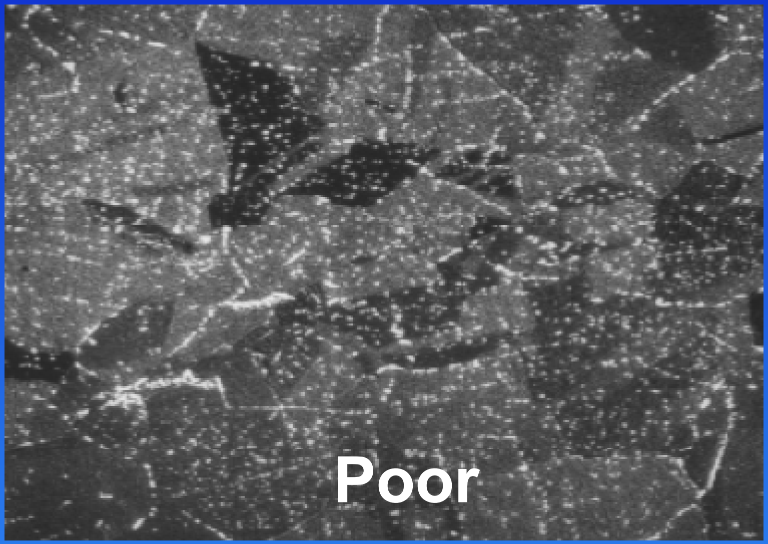


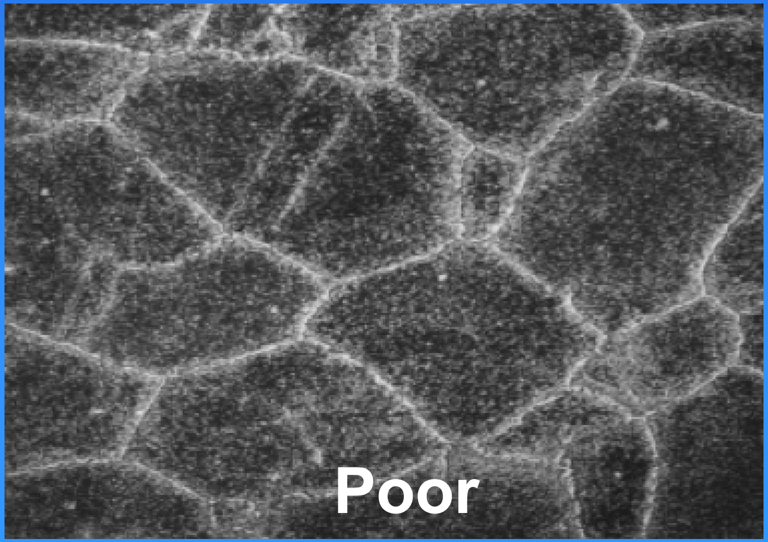


The metallurgical antithesis of BWR IGSCC in NWC!

Microstructural Factors



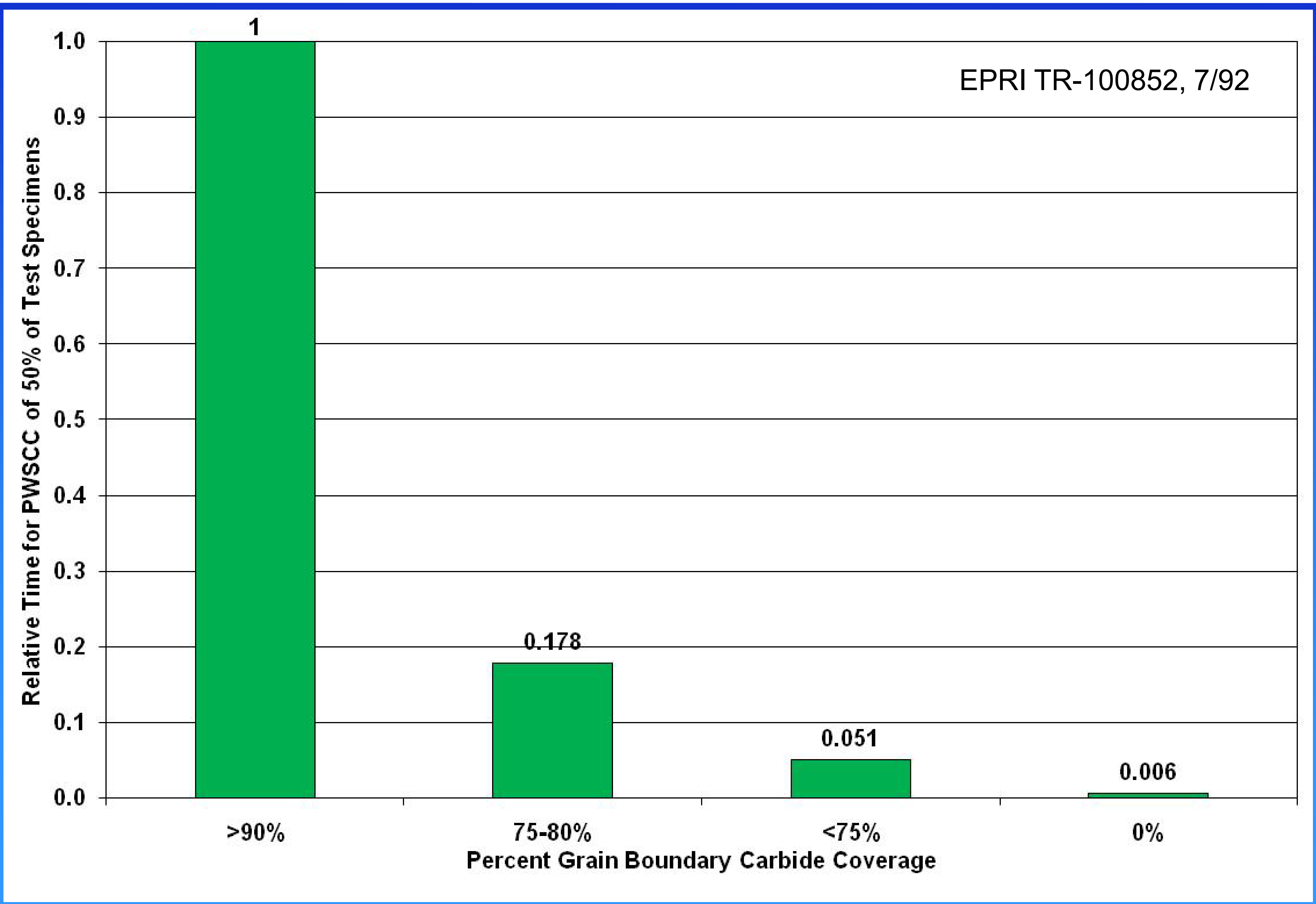




- IG carbides are beneficial
- TG carbides are detrimental
- Sensitization is not detrimental
- Cold work is detrimental
- Strong influence of manufacturing process, but not yet understood

P. Comrade, et al, EDF, 11/08

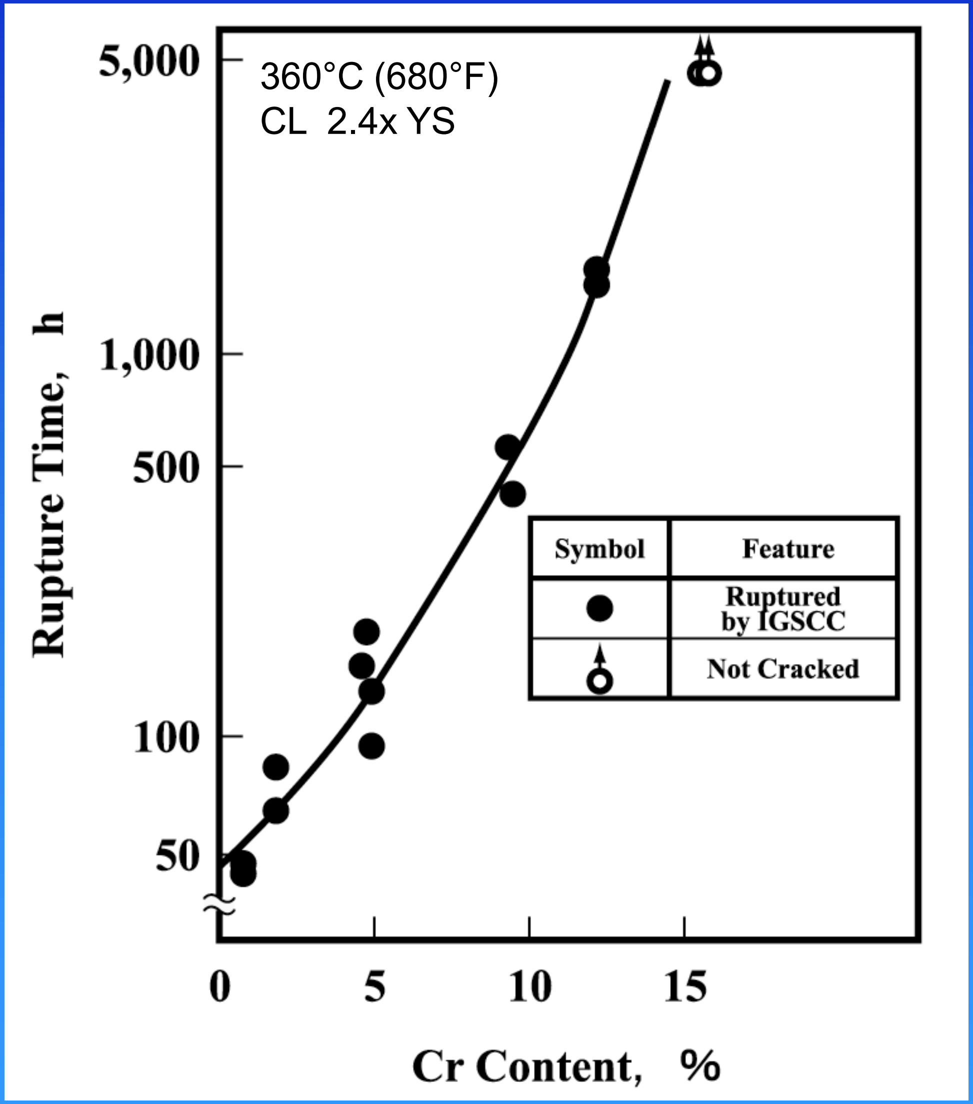
Effect of GB Carbide Coverage on PWSCC Susceptibility



Effect of Carbon Content on PWSCC

- Higher the C content, the higher the annealing temperature required to obtain desired microstructure
- Combination of higher C and lower annealing temperature can lead to PWSCC
- C > 0.018% or small grain size < 0.033 mm (0.87 mils) diameter can promote PWSCC
- Thermal Treatment – Alloy 600 heated to just below the recrystallization range and held for 10-15 hours allowing Cr to diffuse back into Cr depleted zones at the gbs. (Alloy 690 receives a similar treatment.)

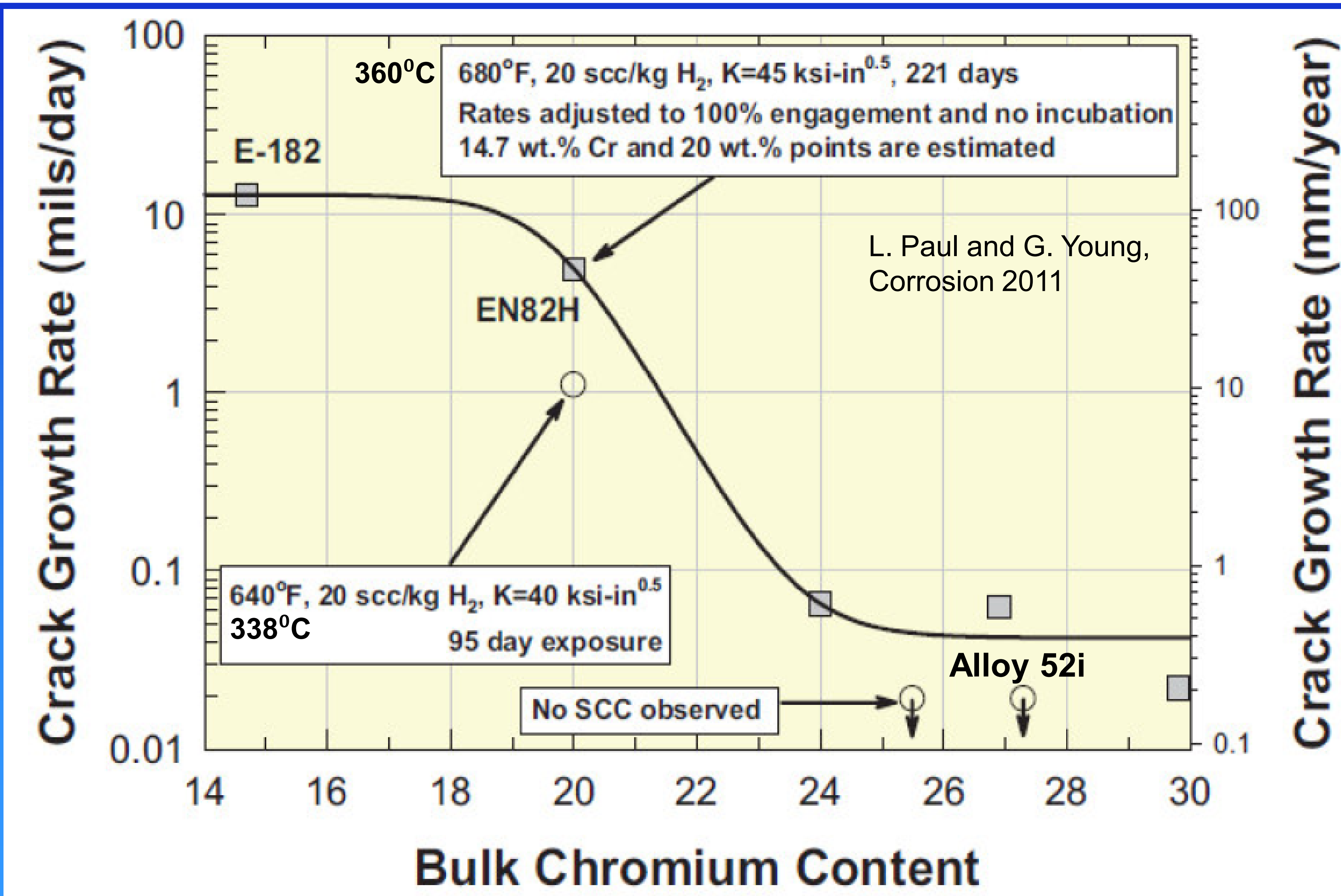
Effect of Cr Content on PWSCC



Old data suggests that Alloy 600 with 14-17% Cr is good stuff!

T. Yonezawa, et, al., JAIF 1988

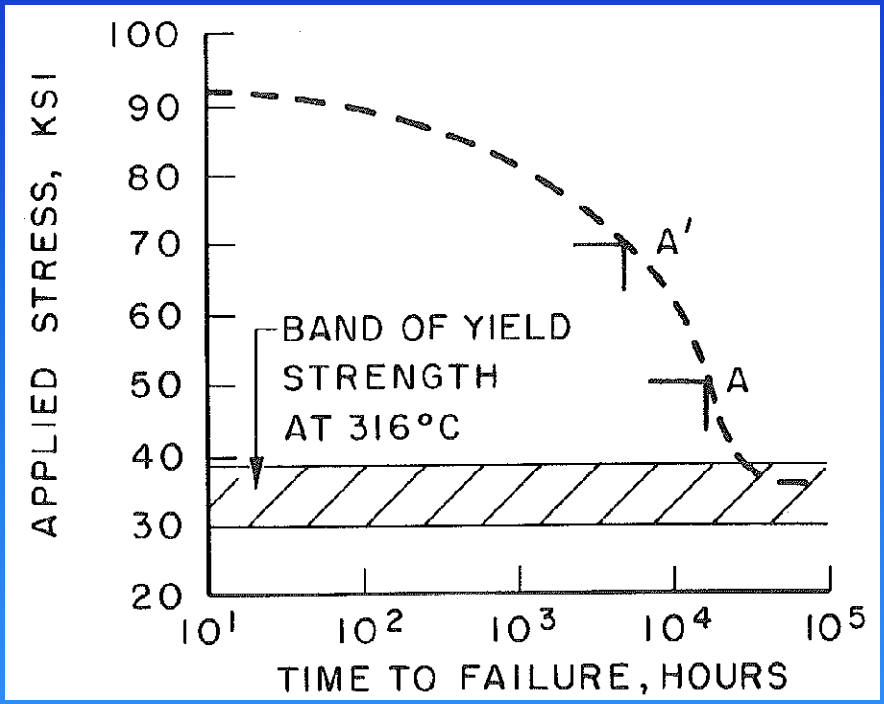
Effect of Cr Content on PWSCC



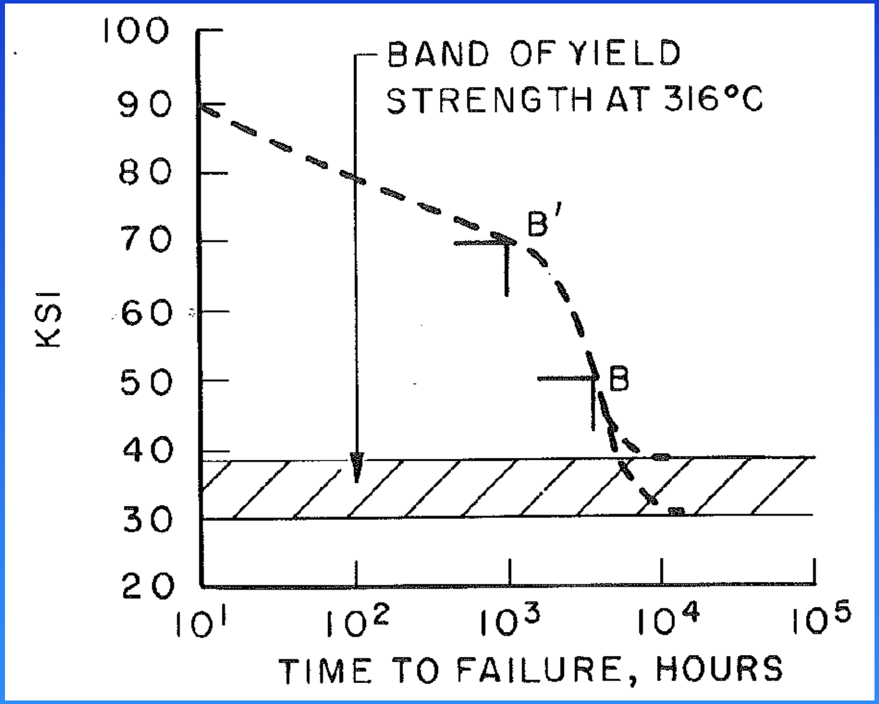
Effect of Stress on PWSCC

- PWSCC should not occur if tensile stress <207-241 MPa (<30-35 ksi) (σ_y 207-310 MPa [35-45 ksi])
- Since design stresses permitted by the ASME code are <207-241 MPa (<30-35 ksi), PWSCC should not occur under applied pressure/thermal loadings alone
- Higher tensile residual stresses needed for PWSCC!
  - During fabrication (e.g., expansion transitions and inner row U-bends)
  - High strains induced during operation (e.g., dented tube support plate intersections and U-bends deformed by tube support plate deformation)
  - Geometric abnormalities (e.g., excessive tube ovality and oversized tube sheet holes)

Effect of Stress on Alloy 600 PWSCC Time to Failure



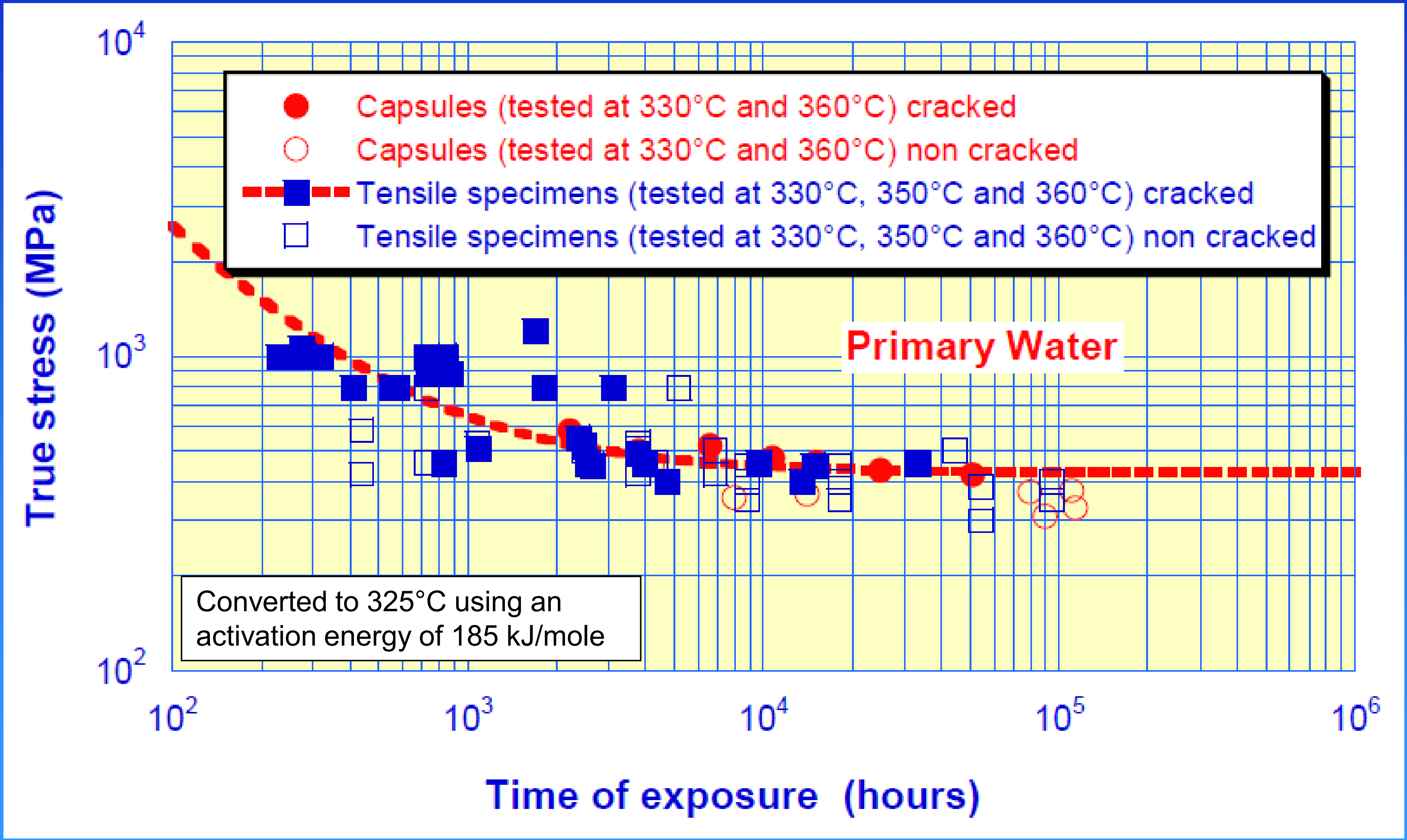
290ºC (554ºF)



340ºC (644ºF)

D. Van Rooyen, Corrosion, Vol. 31, No. 9, 9/75

Effect of Stress on Alloy 182 PWSCC Time to Failure



C. Amzallag, et al., 10th Env. Deg., 2001

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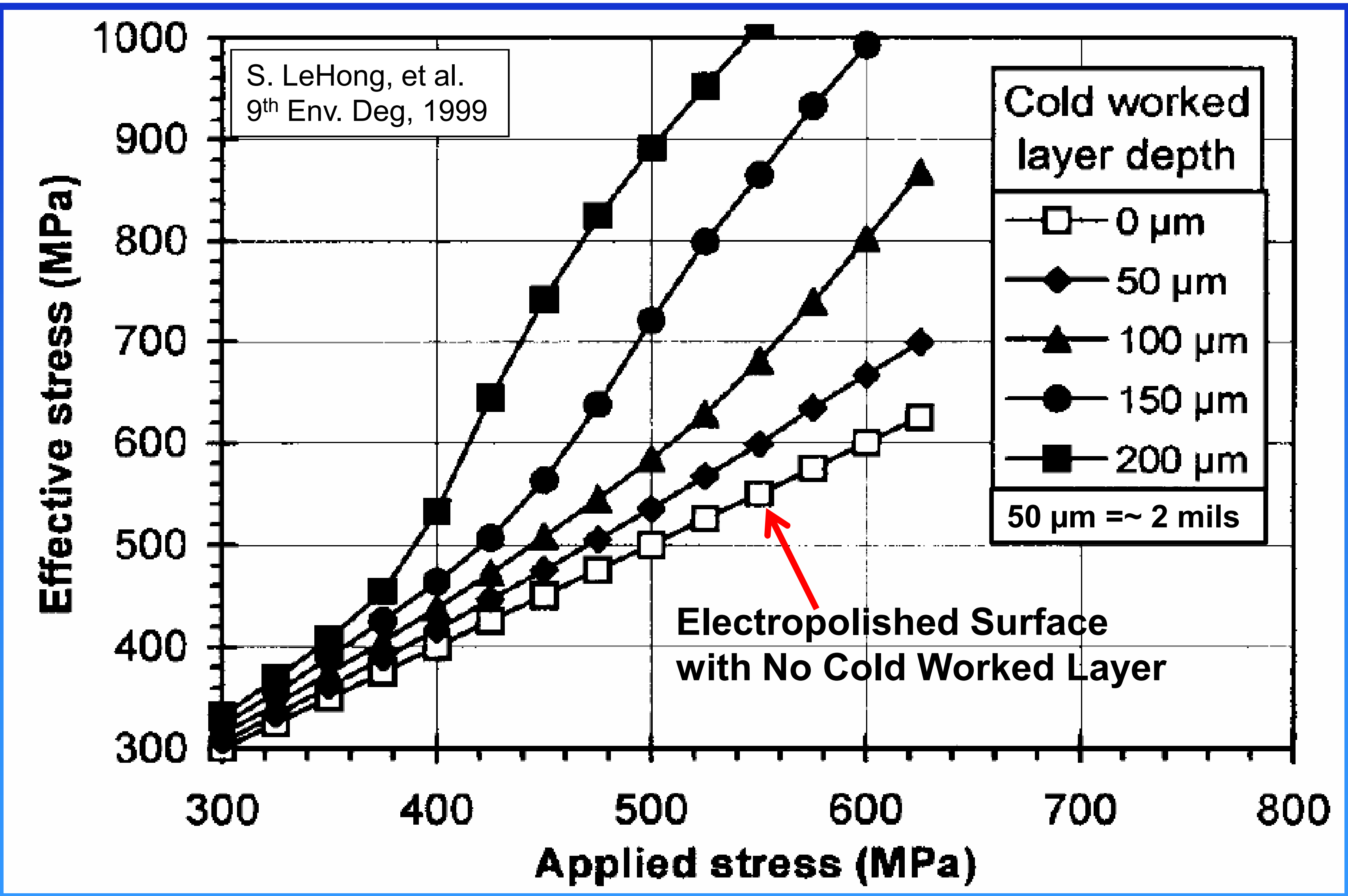
Equivalent Stress for PWSCC vs. Applied Stress and Thickness of a CW Layer on Alloy 600

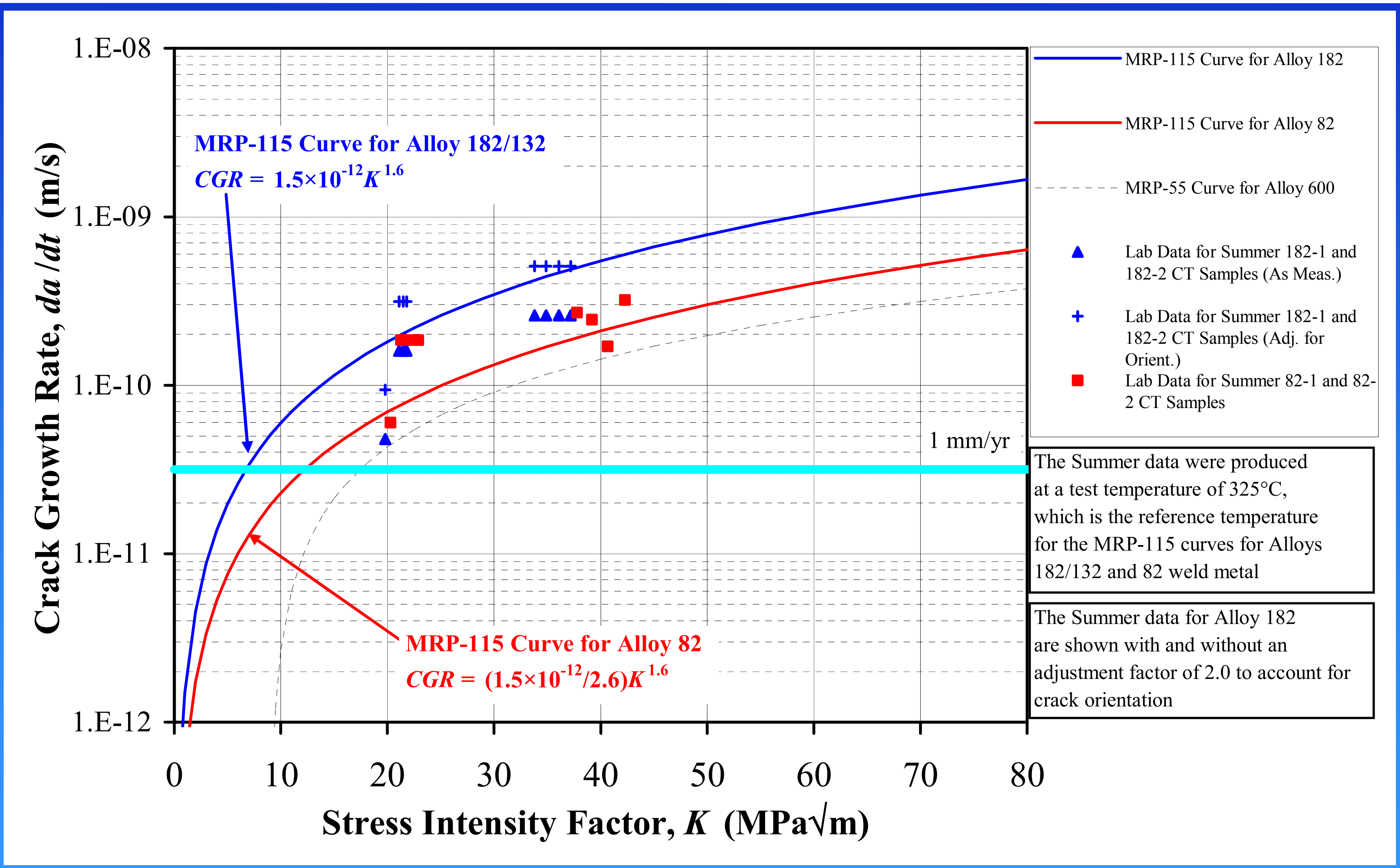


PWSCC Initiation vs. Propagation

- Very different behaviors of Alloys 600, 690 and 718
  - Alloy 600: initiation somewhat difficult , but “easy” propagation
    - High stress level required σ> σy
    - “Easy” propagation – low K_{1SCC}< 10 MPa√m (<9 ksi√in)
  - Alloy 690: Initiation very difficult, but sometimes possible – CERT on non optimized structures
    - Propagation very difficult – requires high cold work
  - Alloy 718: Initiation very difficult – usually requires surface defects
    - “Easy” propagation
- Are initiation and propagation controlled by the same process(es)?
  - No clear answer

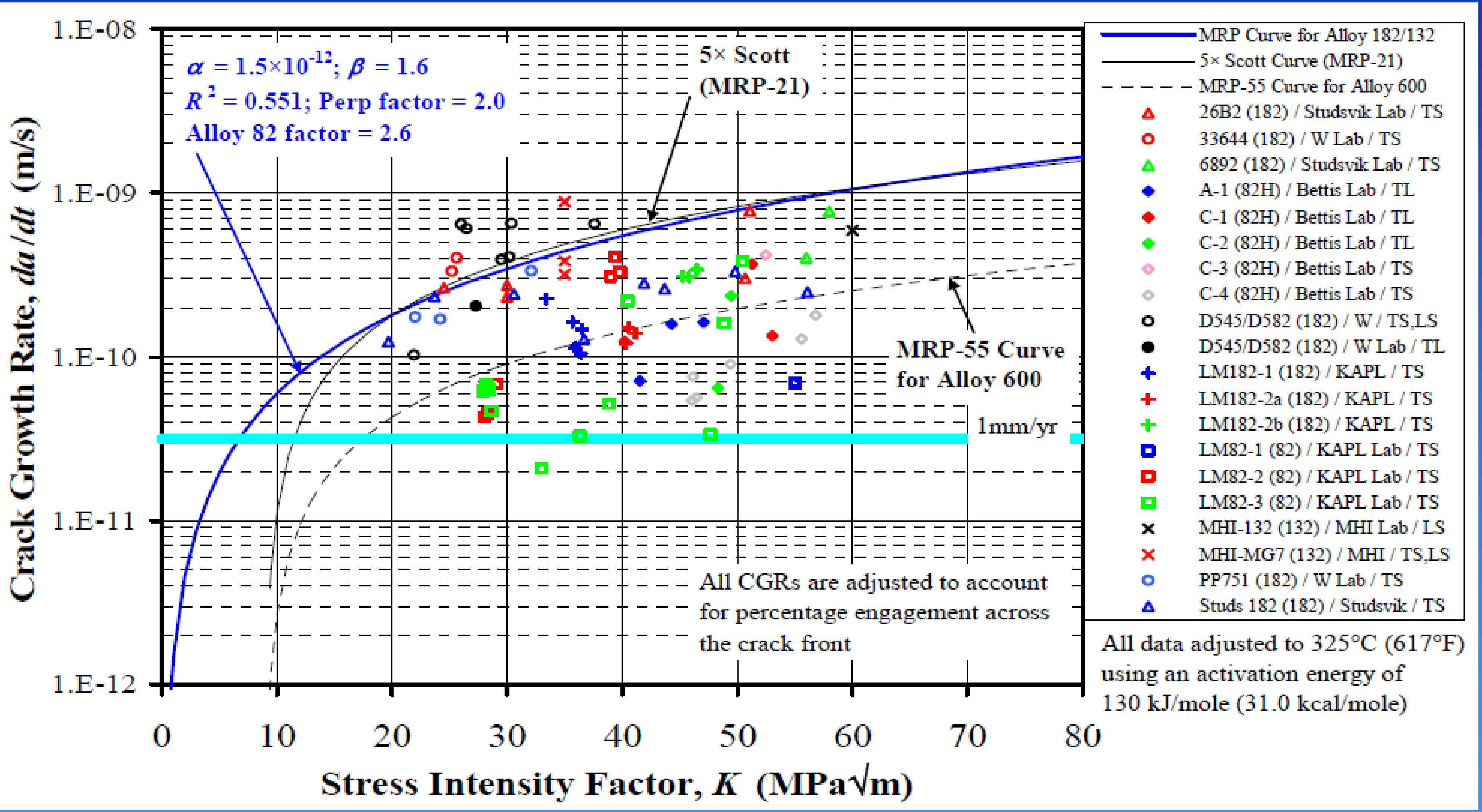
P. Comrade, et al, EDF, 11/08

Effect of K on Alloy 600 CGR



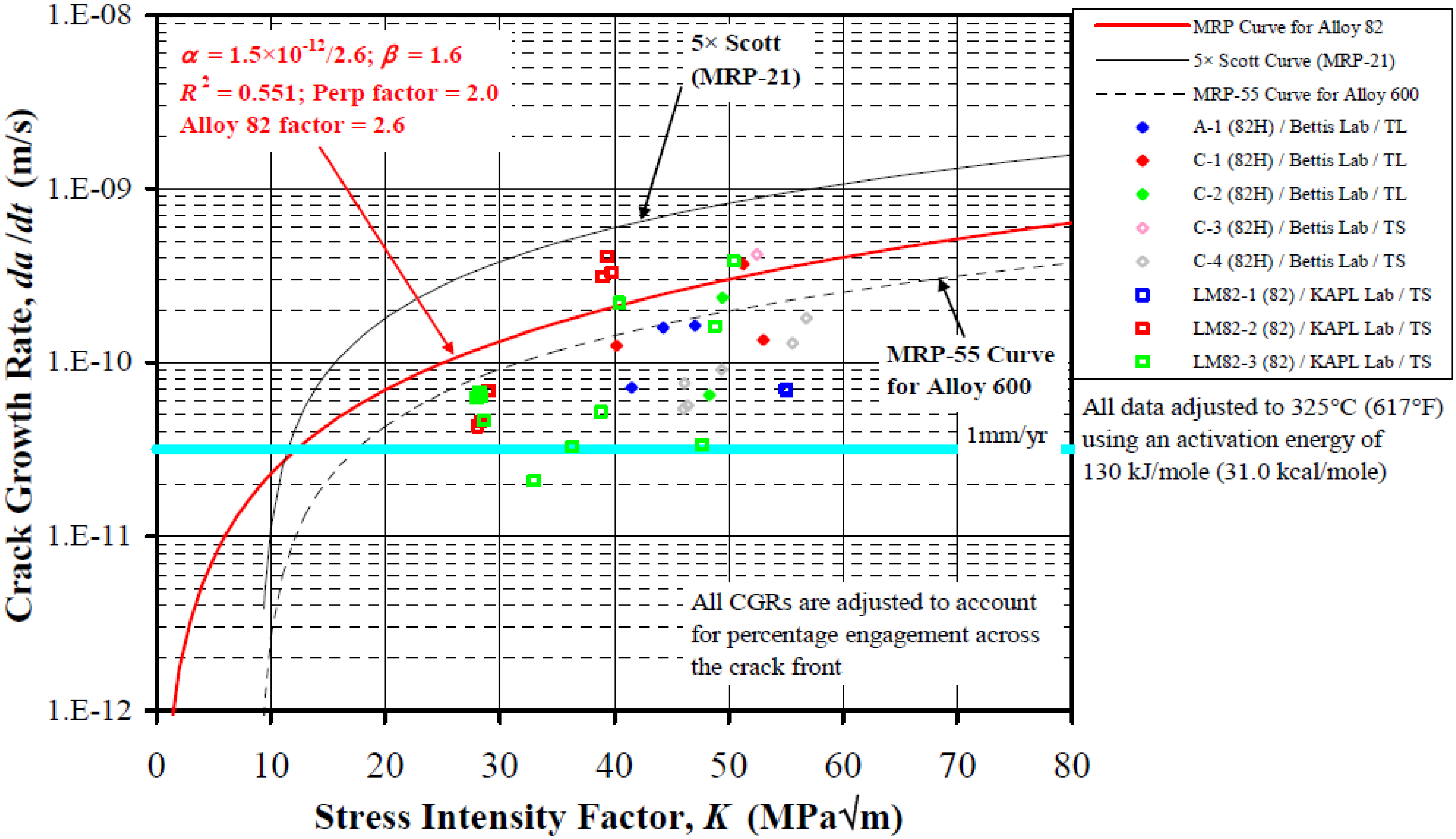
R. Jacko, et al., NRC-ANL Conf. Vessel Penetration Inspection, Cracking, and Repairs, 9/03

Effect of K on Alloy 182/132 CGR



EPRI, MRP-220, 10/07 – Public Document

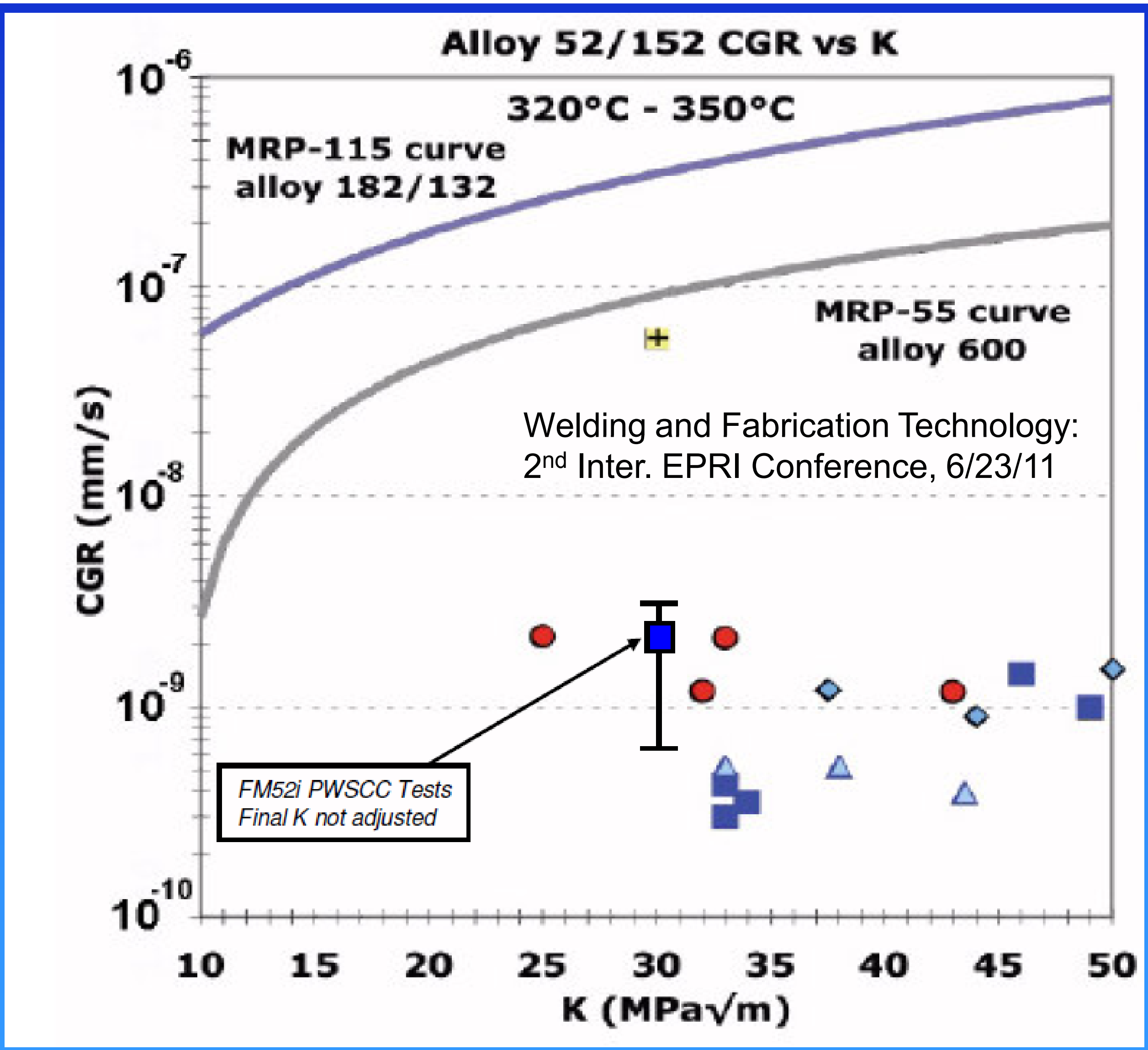
Effect of K on Alloy 82 CGR



All data adjusted to 325°C (617°F) using an activation energy of 130 kJ/mole (31.0 kcal/mole)

EPRI, MRP-220, 10/07 – Public Document

Effect of K on Alloy 52/152 CGR



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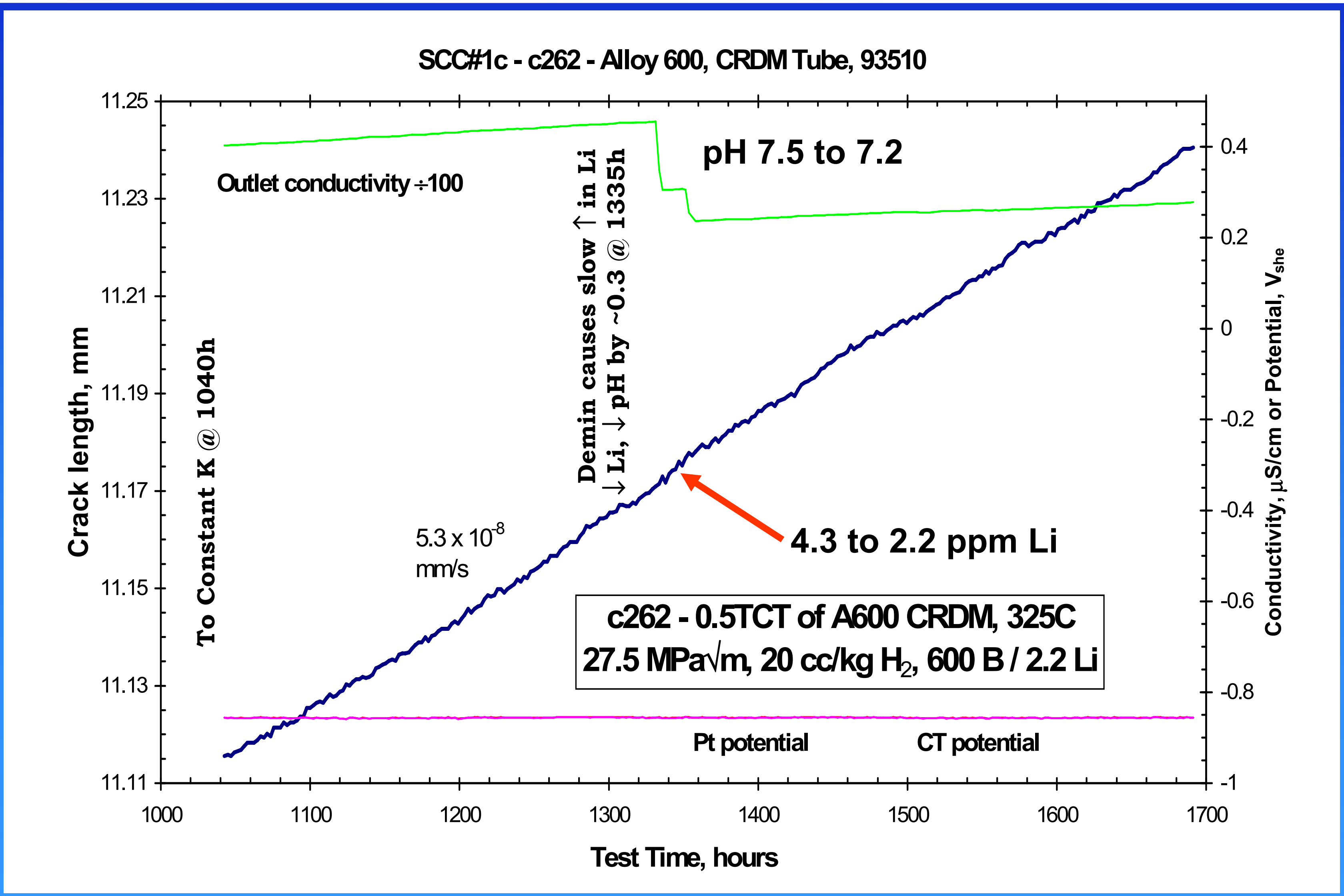
Key PWSCC Environmental Factors

- Effects of environmental parameters on PWSCC initiation and growth
  - ♦ Lithium Hydroxide – little effect
  - ♦ Boric Acid – little effect
  - ♦ LiOK + B – little effect
  - ♦ pH – little effect
  - ♦ Hydrogen
  - ♦ Oxygen (as an impurity)
  - ♦ Temperature
  - ♦ Zinc

Effect of Li on Alloy 600 CGR at 325ºC



P. Andresen, paper 05592, Corrosion 2005

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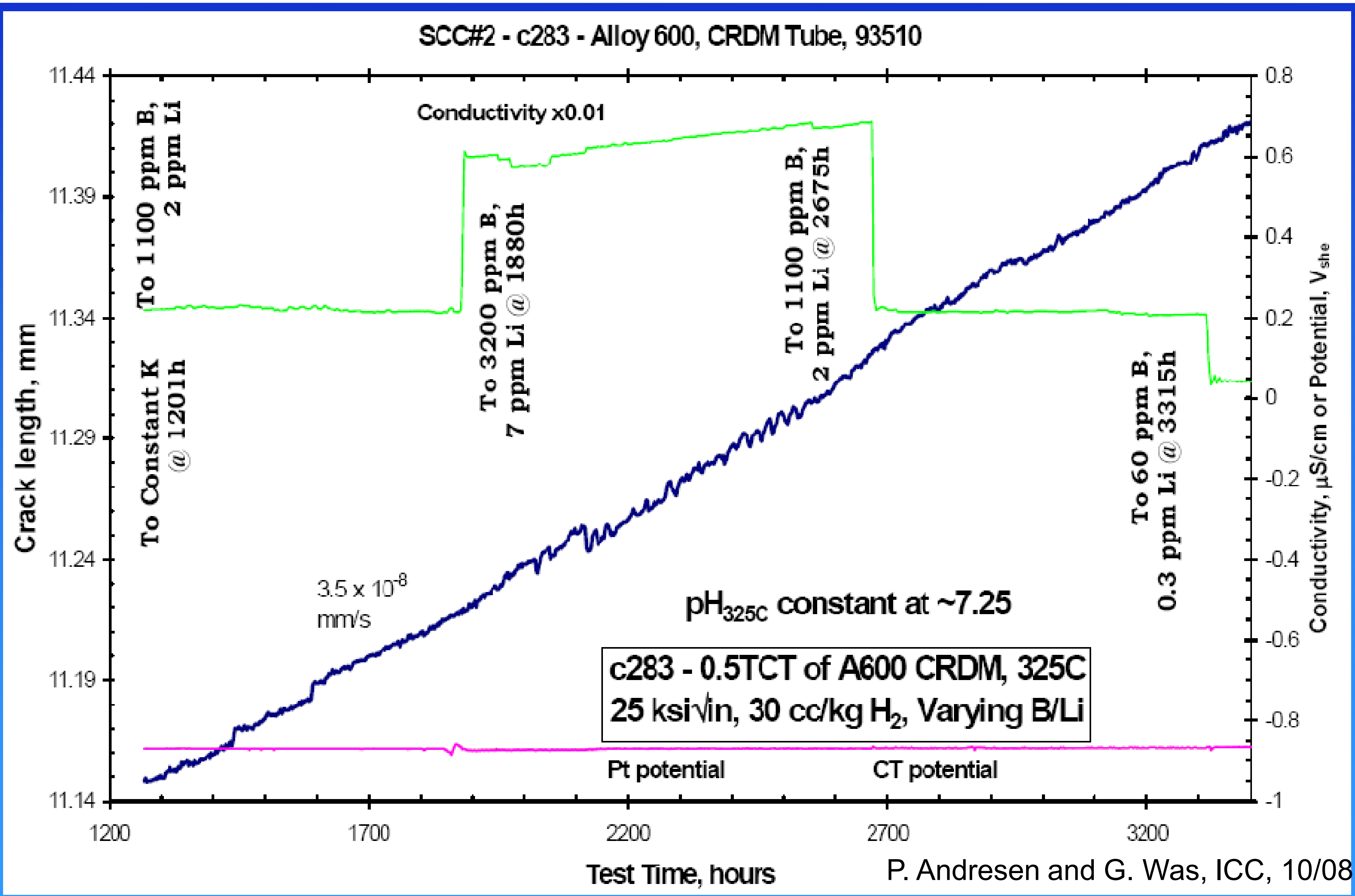
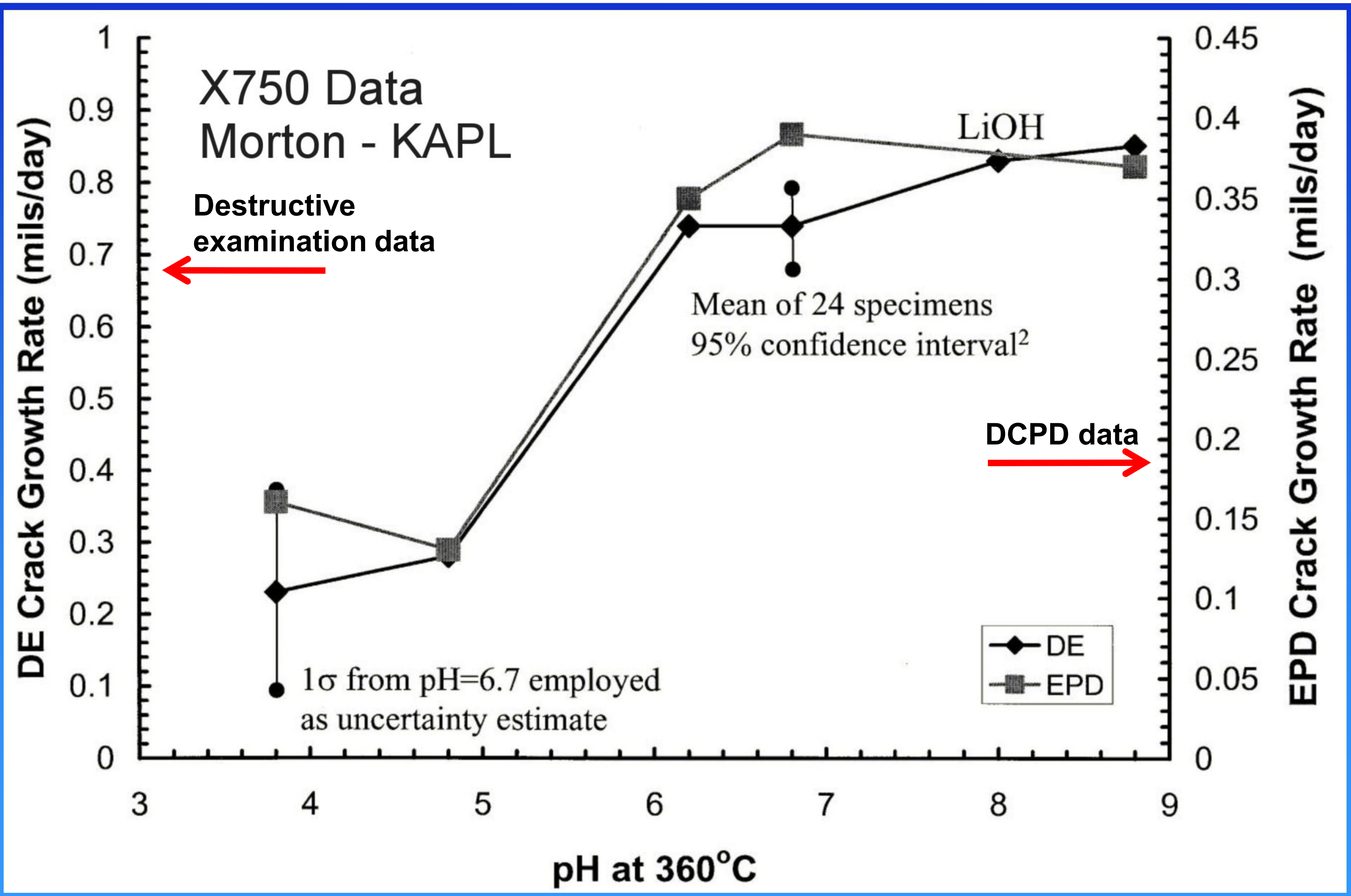
Effect of Li and B on Alloy 600 CGR at 325ºC



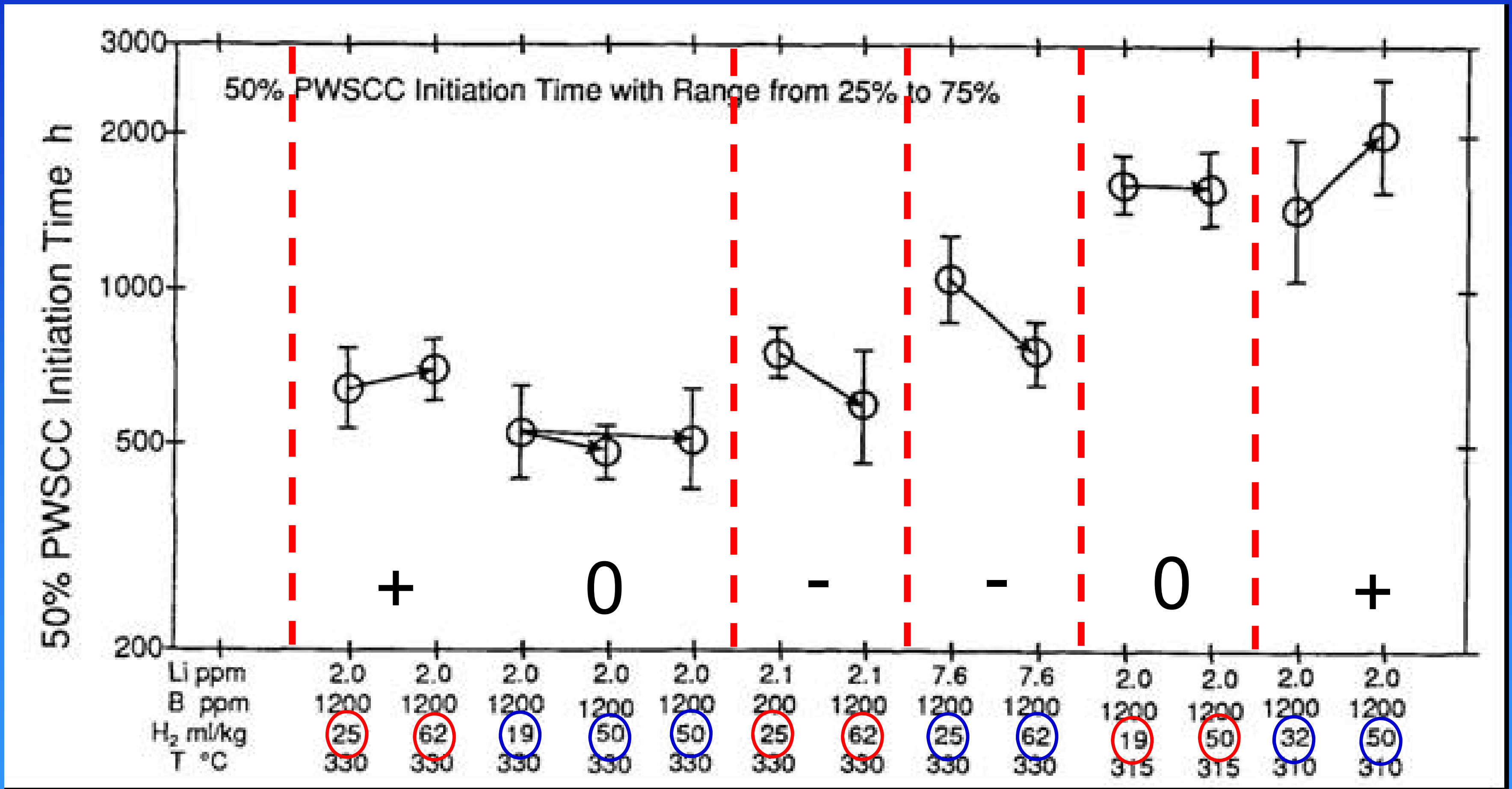
P. Andresen and G. Was, ICC, 10/08

Effect of pH_T on Alloy X-750 PWSCC Propagation at 360°C



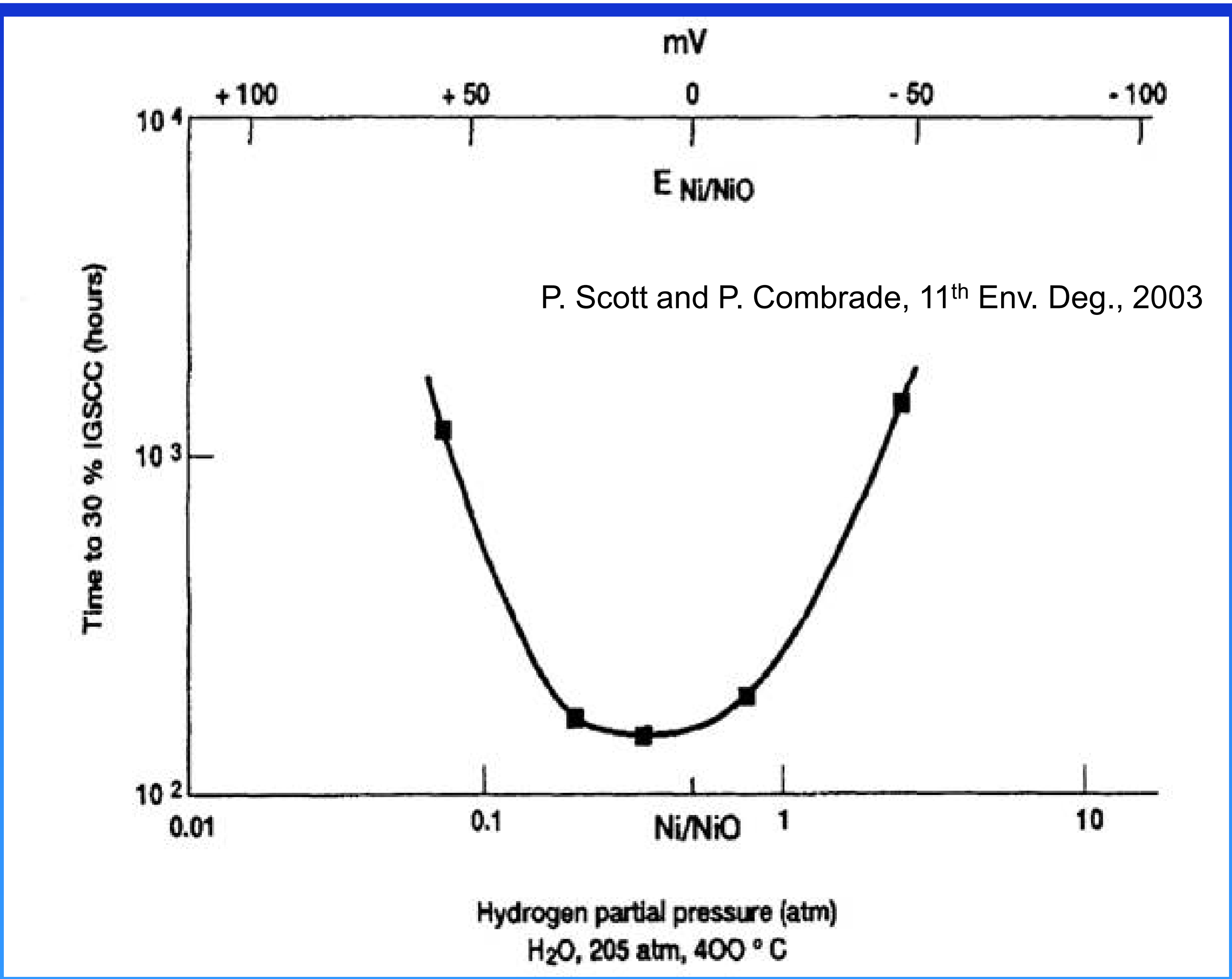
D. Morton and M. Hansen, paper 03675, Corrosion 2003

Effect of H_2 on PWSCC Initiation of Alloy 600 RUBs at 310 to 330ºC



R. Jacko, et al., 5th Env. Deg., 1991

Effect of H_2 on PWSCC Initiation of Alloy 600 RUBs at 400ºC



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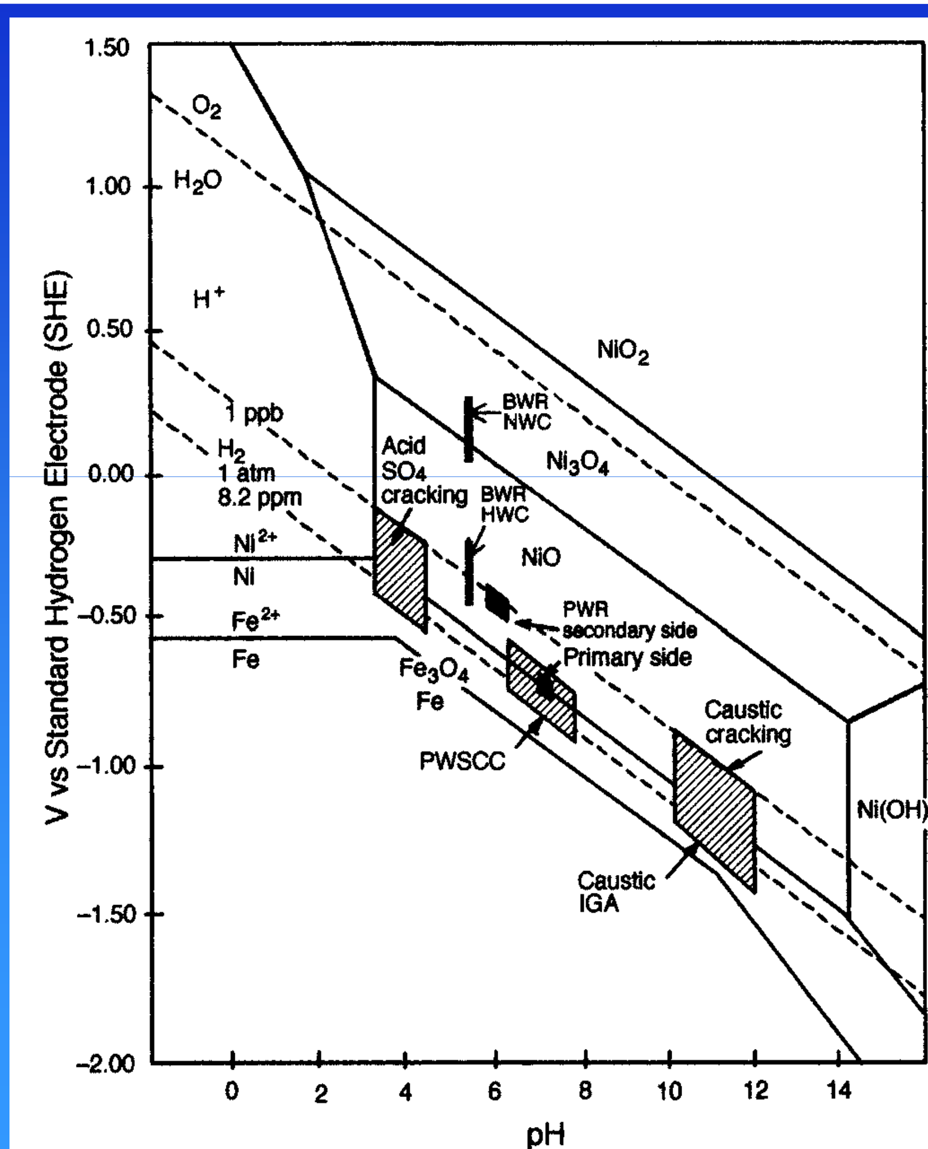
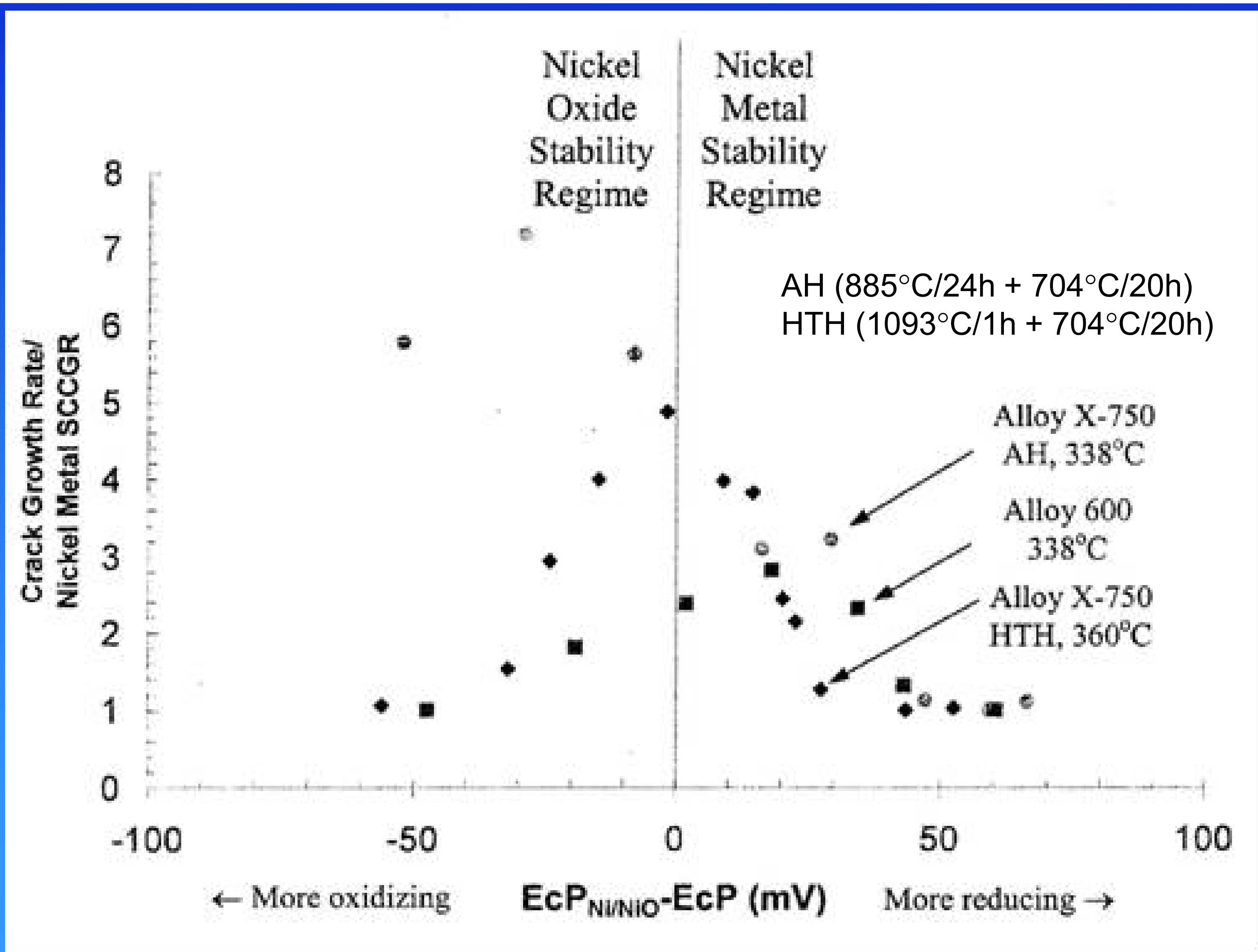
Pourbaix Diagram for Ni Alloys in LWRs

Peter Scott



P. M. Scott, Corrosion, Vol. 56, No. 8, 2000

PWSCC Growth Rate vs. Corrosion Potential Difference from Ni/NiO



T. Cassagne, et al, 8th Env. Deg., 1997

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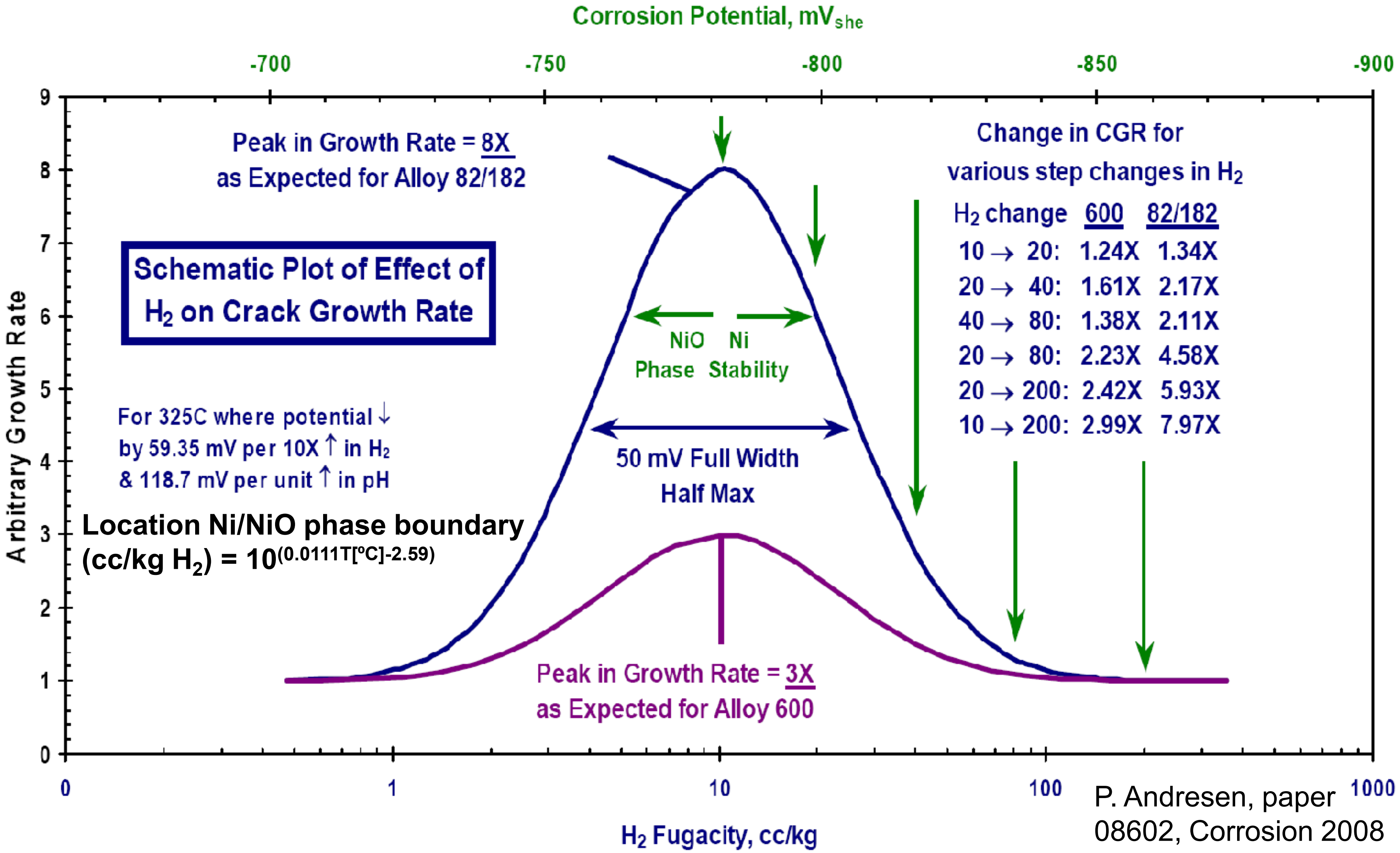
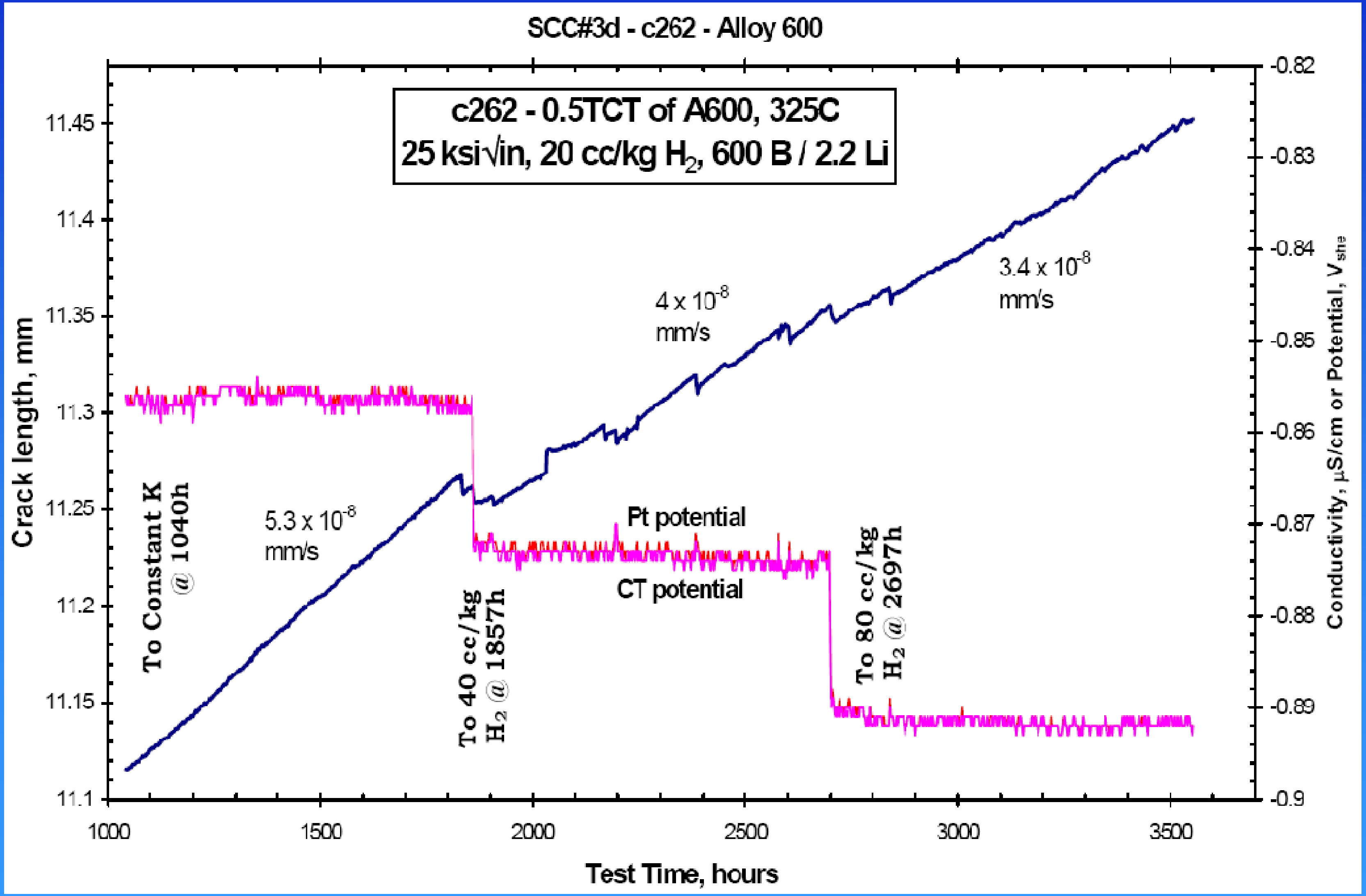
Schematic Effect of H_2 on Alloy 600/182/82 Crack Growth Rate at 325ºC



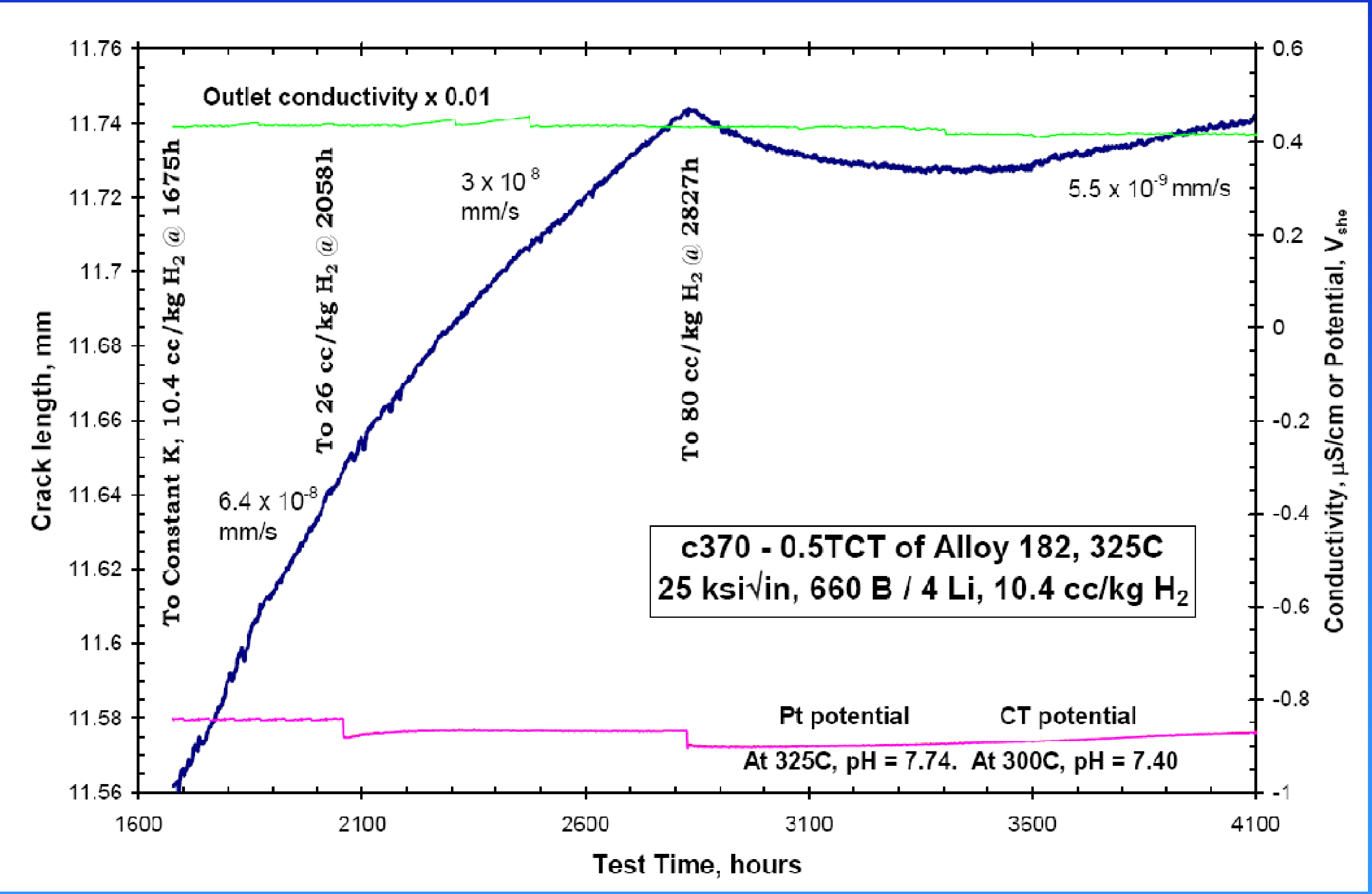
P. Andresen, paper 08602, Corrosion 2008

Effect of H_2 on Alloy 600 Crack Growth Rate at 325ºC



P. Andresen, et al., Corrosion 2008

Effect of H_2 on Alloy 182 Crack Growth Rate at 325ºC



P. Andresen and G. Was, ICC, 10/08

Effect of H_2 on PWSCC of Alloy 182

c385, 10.4 cc/kg H_2 – more crack advance

c386, 80 cc/kg H_2 – less less crack advance (Note Ni-metal stability gives shiny fracture surface)

P. Andresen, MRP/PWROG Briefing to NRC, 7/08

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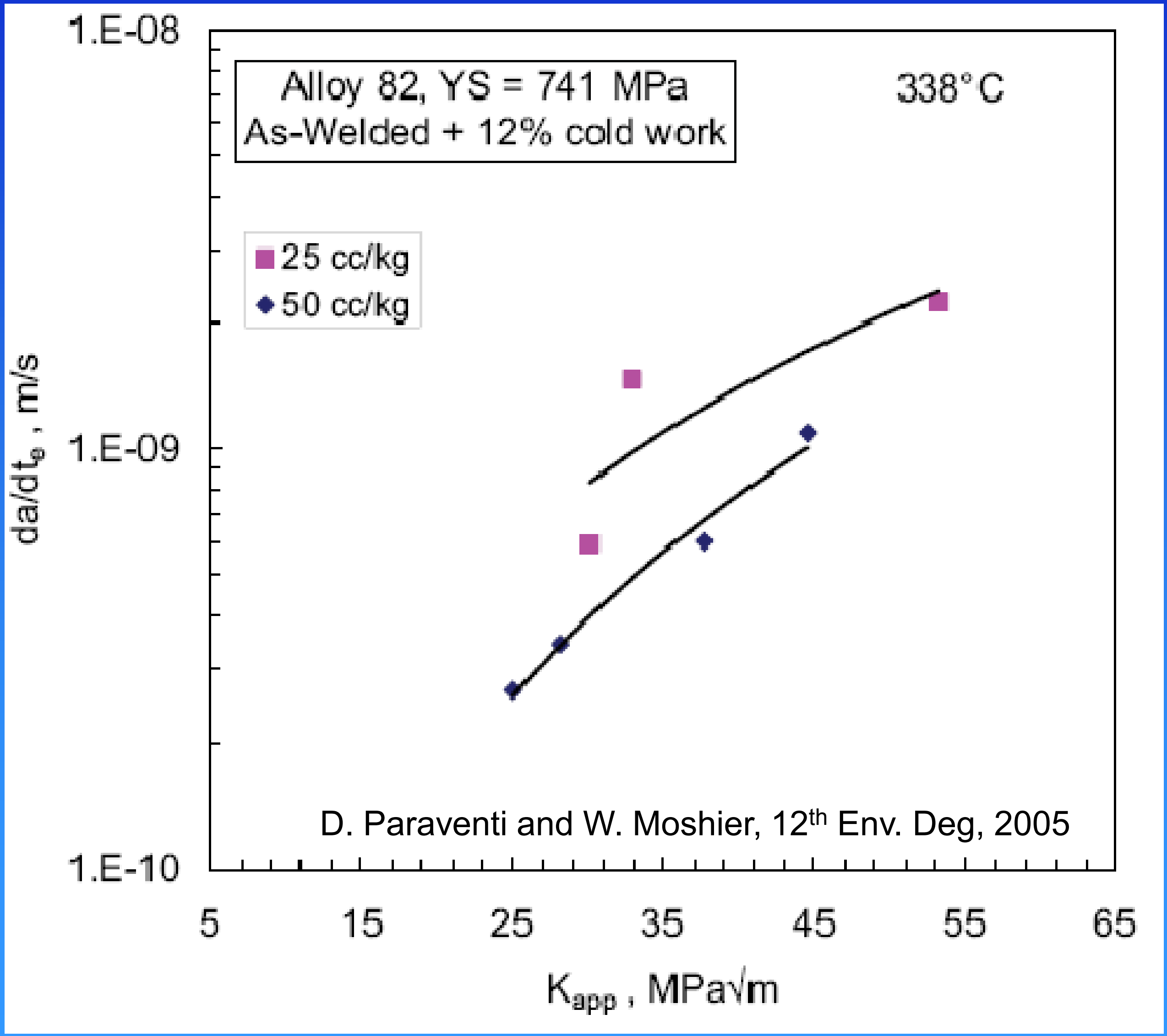
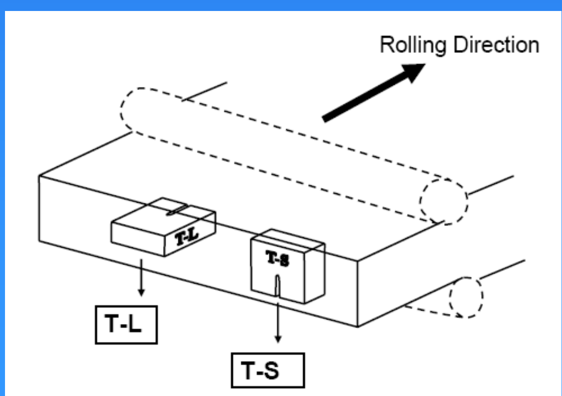
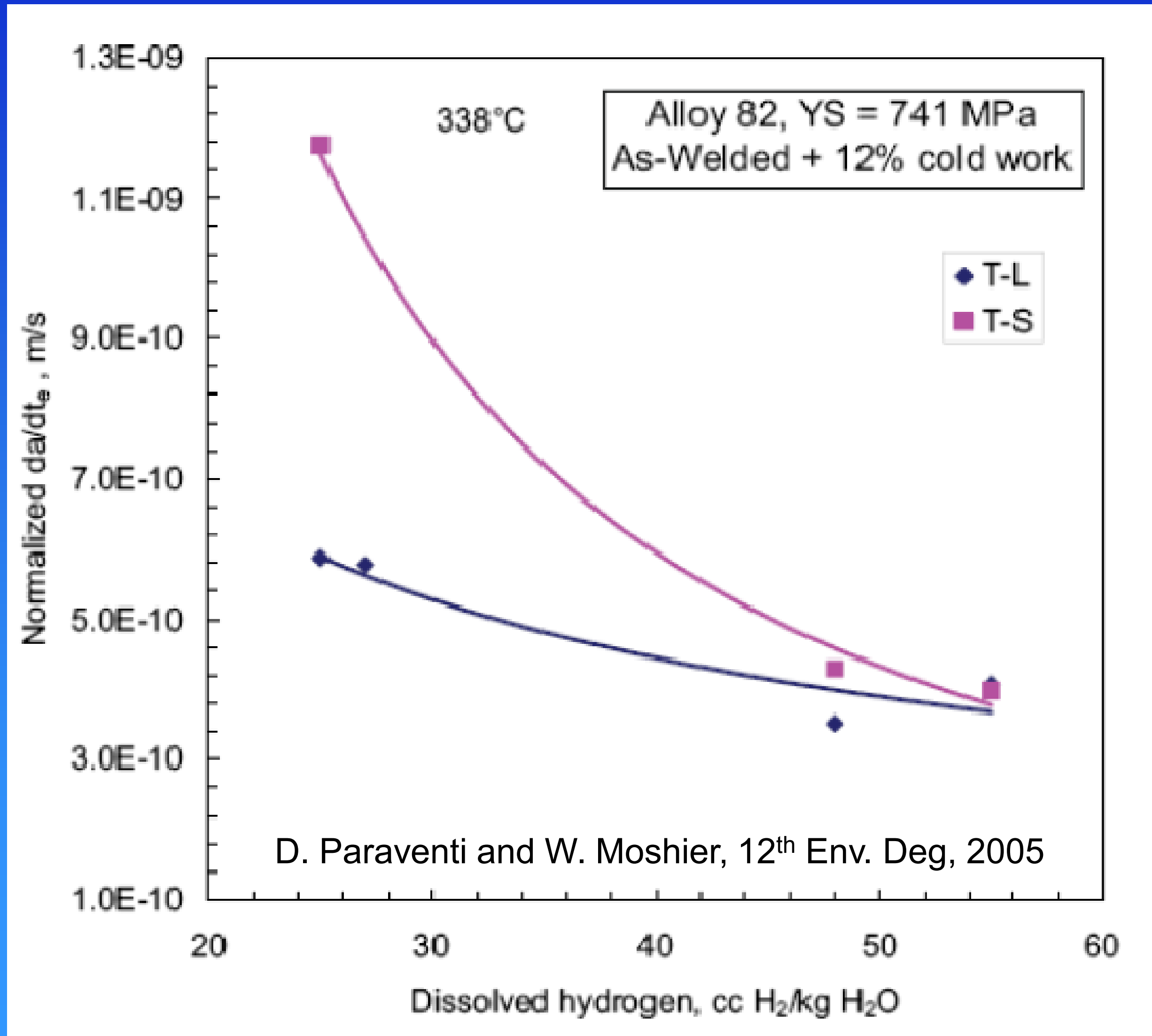
Effect of H_2 on PWSCC of Alloy 82



Structural Integrity Associates

Effect of H_2 on PWSCC of Alloy 82



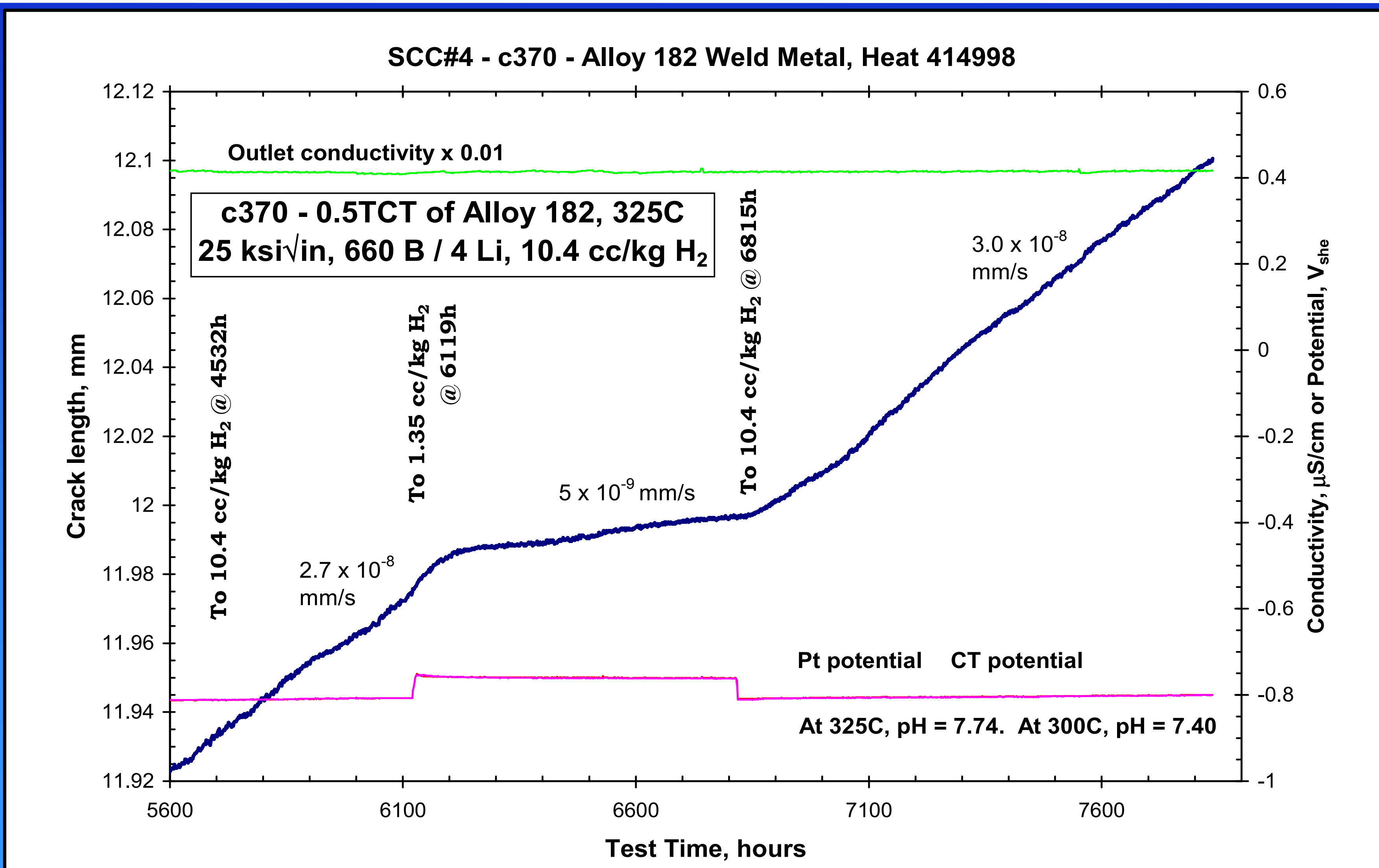


Reduced H_2 to Mitigate PWSCC

- To reduce crack growth rates to a level comparable to that of 50 cc/kg (4.5 ppm), H_2 would have to be reduced to ~2.5 cc/kg (223 ppb) H_2 at 325°C (617°F), which does not provide an adequate operating margin
- Current data indicate that >1-5 cc/kg (>90-450 ppb) H_2 is required to suppress radiolysis and avoid oxidizing conditions
- Japan Atomic Power Company (JAPC) has developed a multi- year plan to investigate operation as low as 5 cc/kg (450 ppb) H_2
- Possible Issues:
  - Effect on corrosion product transport and deposition
  - Effect on crack growth rates

P. Andresen, MRP/PWROG Briefing to NRC RES, 5/30/07

Effect of H_2 on Alloy 182
Crack Growth Rate at 325ºC – Low H_2

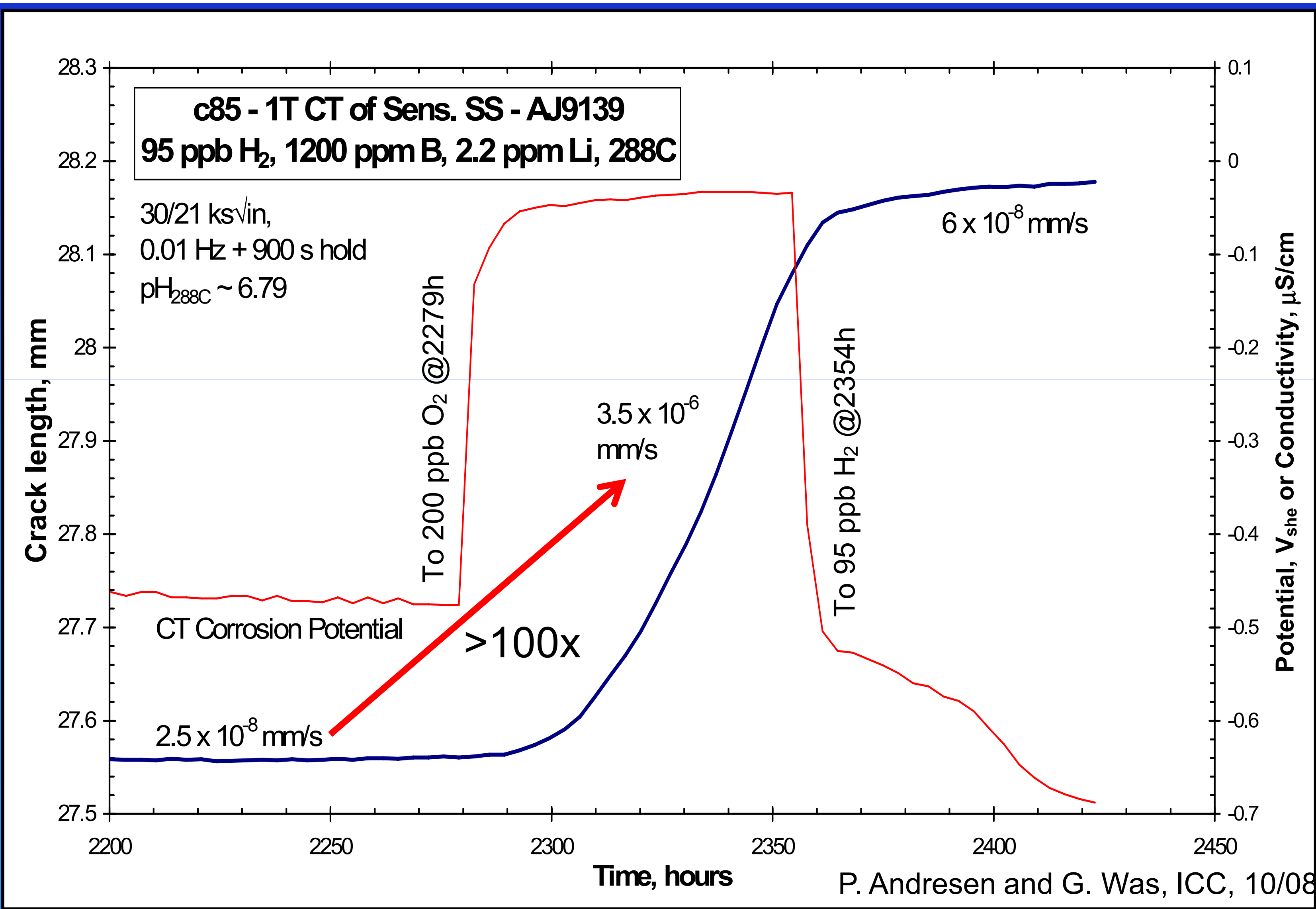


P. Andresen, Corr., Vol. 64, No. 9, 2008

Effect of H_2 on PWSCC

- H_2 does have a strong effect on PWSCC initiation and growth
  - Electrochemically avoiding Ni/NiO transition region in oxide stability is clearly beneficial
- Optimized control of H_2 appears to be a very promising PWSCC mitigation technique
- No effect of DH on stainless steel CGR?

Effect of O_2 on SCC of Furnace Sensitized Type 304



P. Andresen and G. Was, ICC, 10/08

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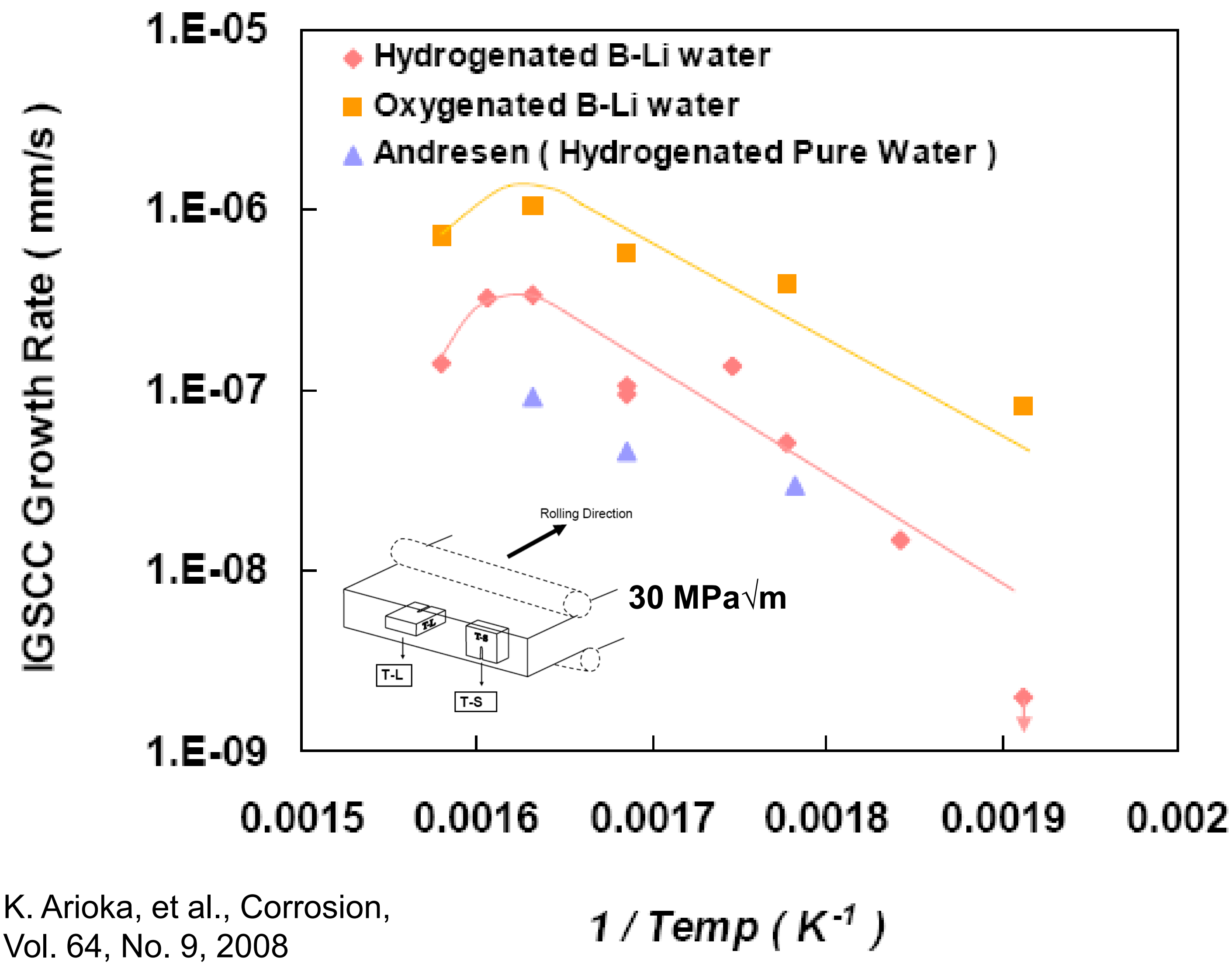
CGR vs. T of Non-sensitized 20% CW Type 316 SS in DH and DO PWR Water

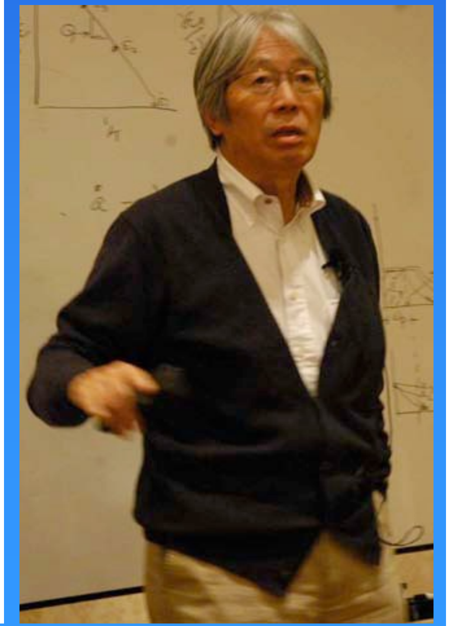


K. Arioka, et al., Corrosion, Vol. 64, No. 9, 2008

500 ppm B, 2 ppm Li, 30cc H_2/kg H_2O, T-S

or

500 ppm B, 2 ppm Li, 8 ppm O_2, T-S

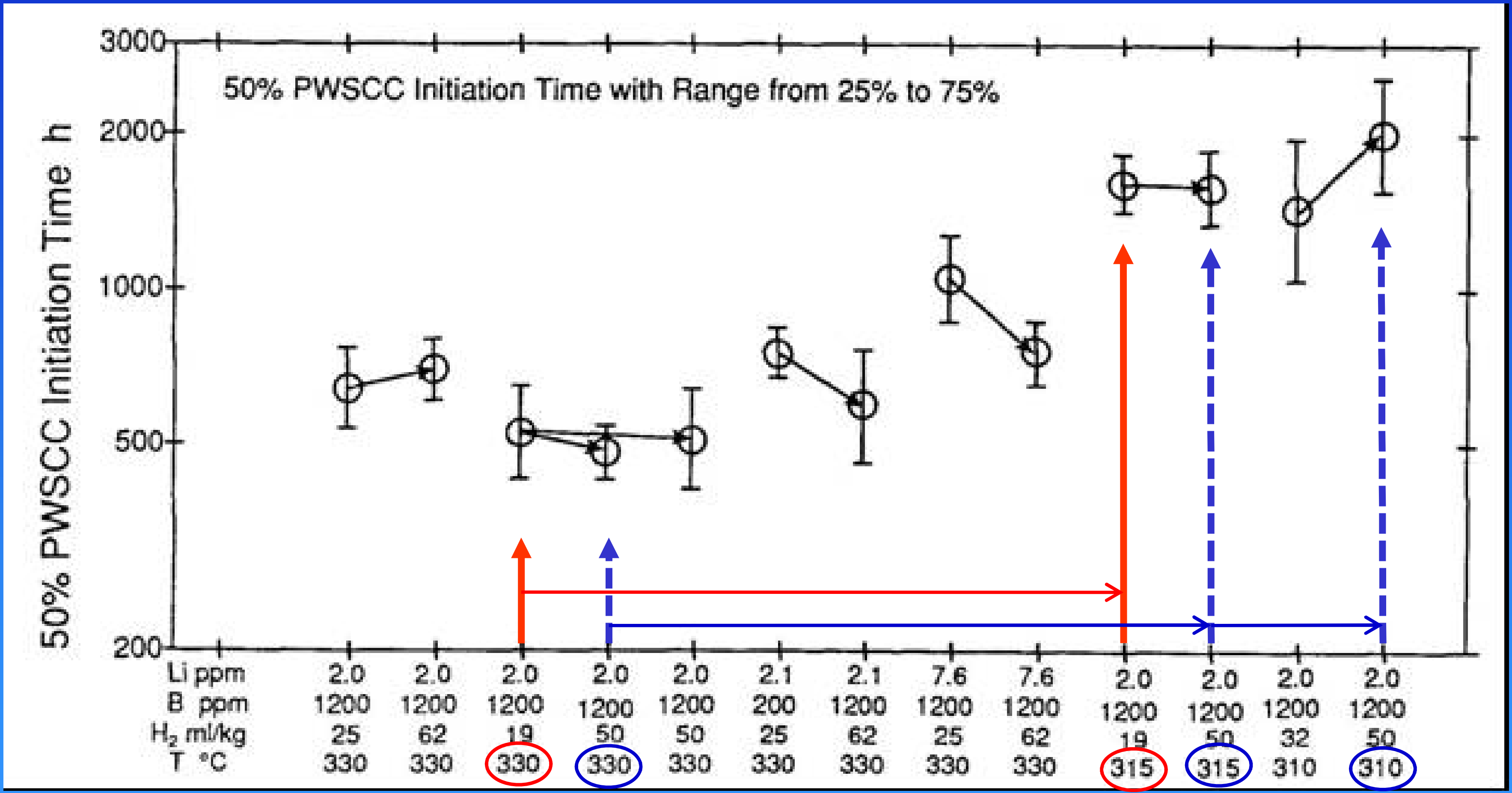


Effect of O_2 on PWSCC

- Oxygen produces CGRs that are ~10X higher than measured in relatively concentrated B and Li water chemistries
- Oxidants should be avoided in PWR primary water
  - Common practice of adding of H_2O_2 during PWR shutdown (typically at <130°C [266°F]) to react with the dissolved H_2 should be re-evaluated to determine the extent to which cracking is accelerated

P. Andresen and G. Was, ICC, 10/08

Effect of Temperature on PWSCC Initiation of Alloy 600 RUBs



R. Jacko, et al., 5th Env. Deg., 1991

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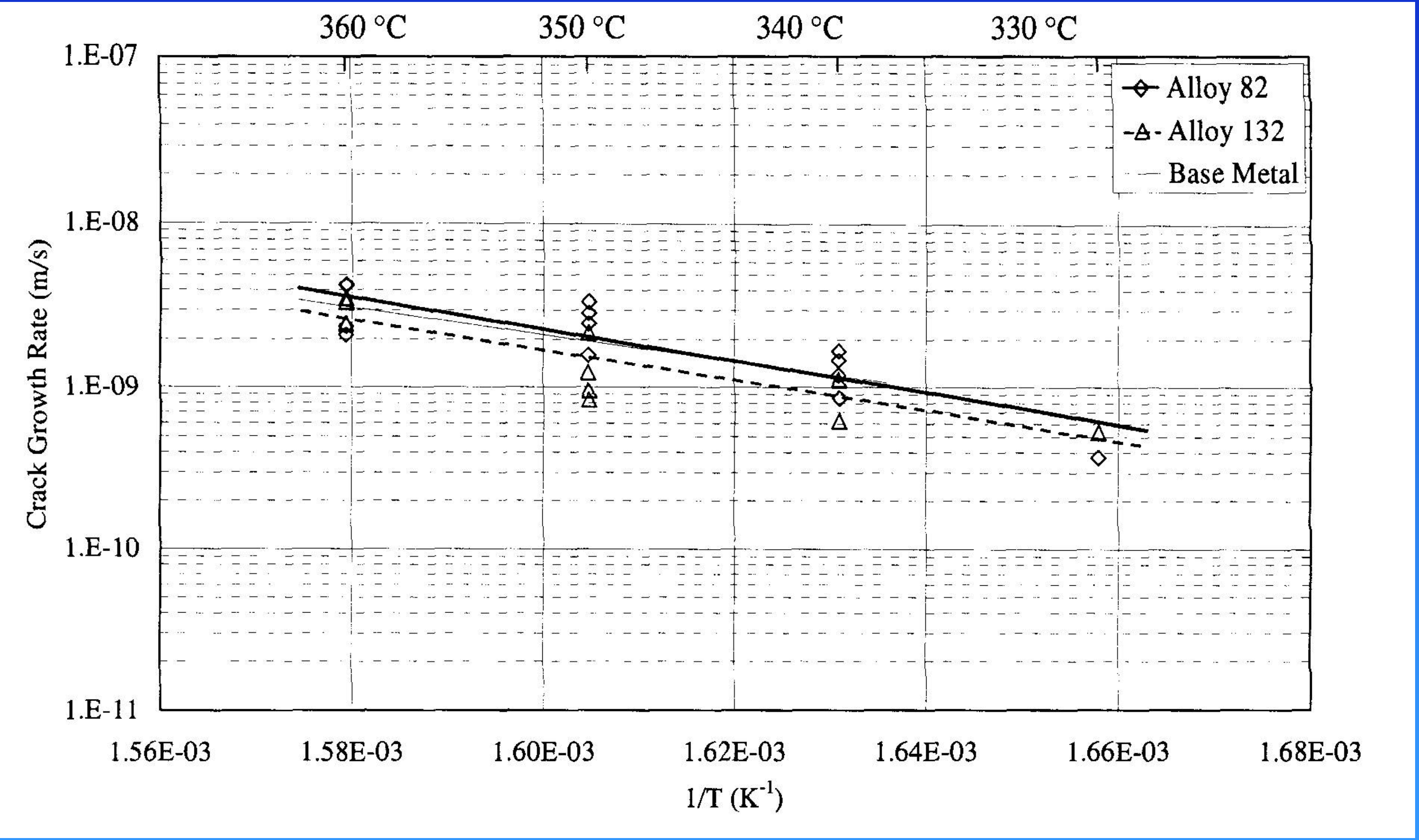
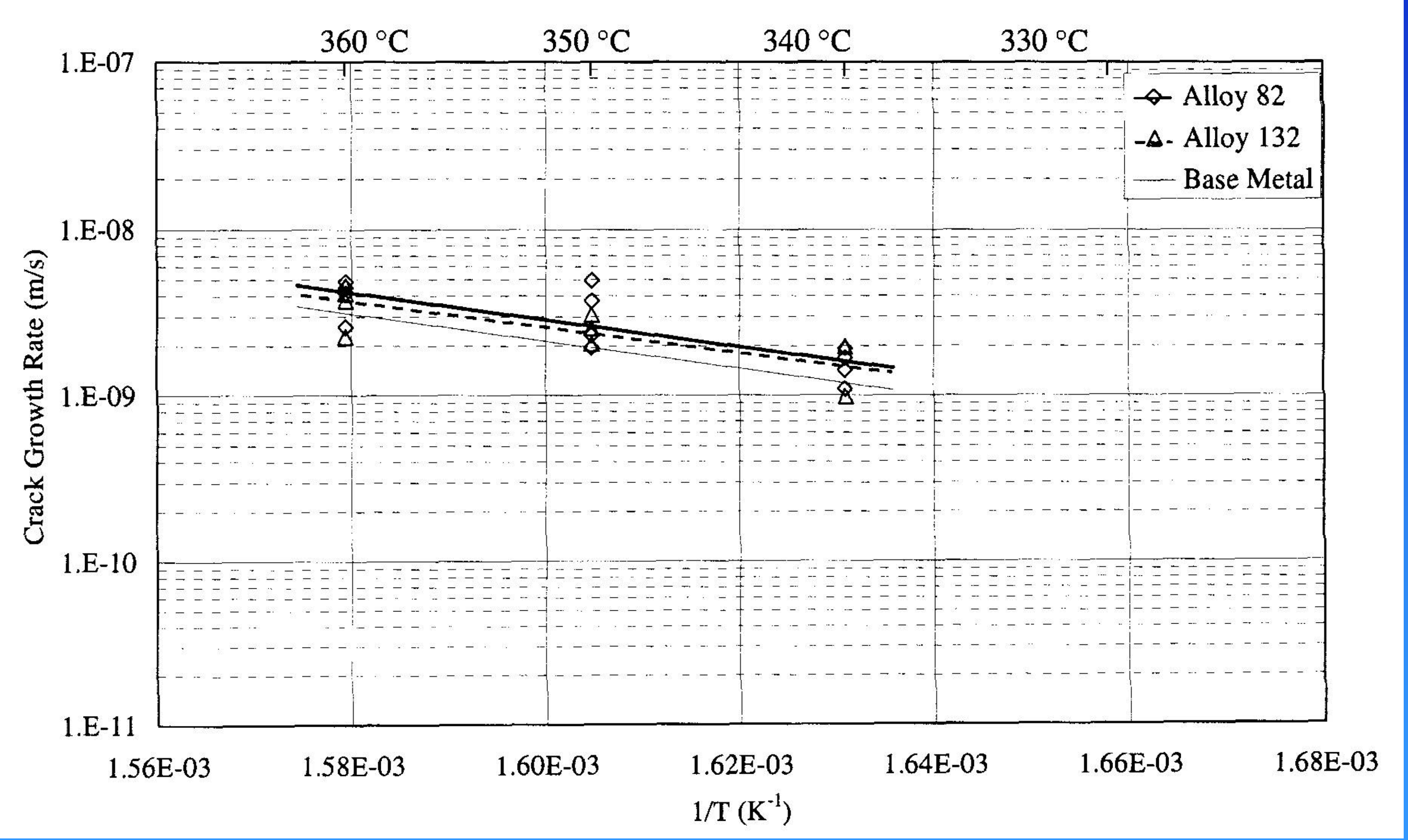
Effect of Temperature on PWSCC CERT "CGR" of Alloys 82 and 132



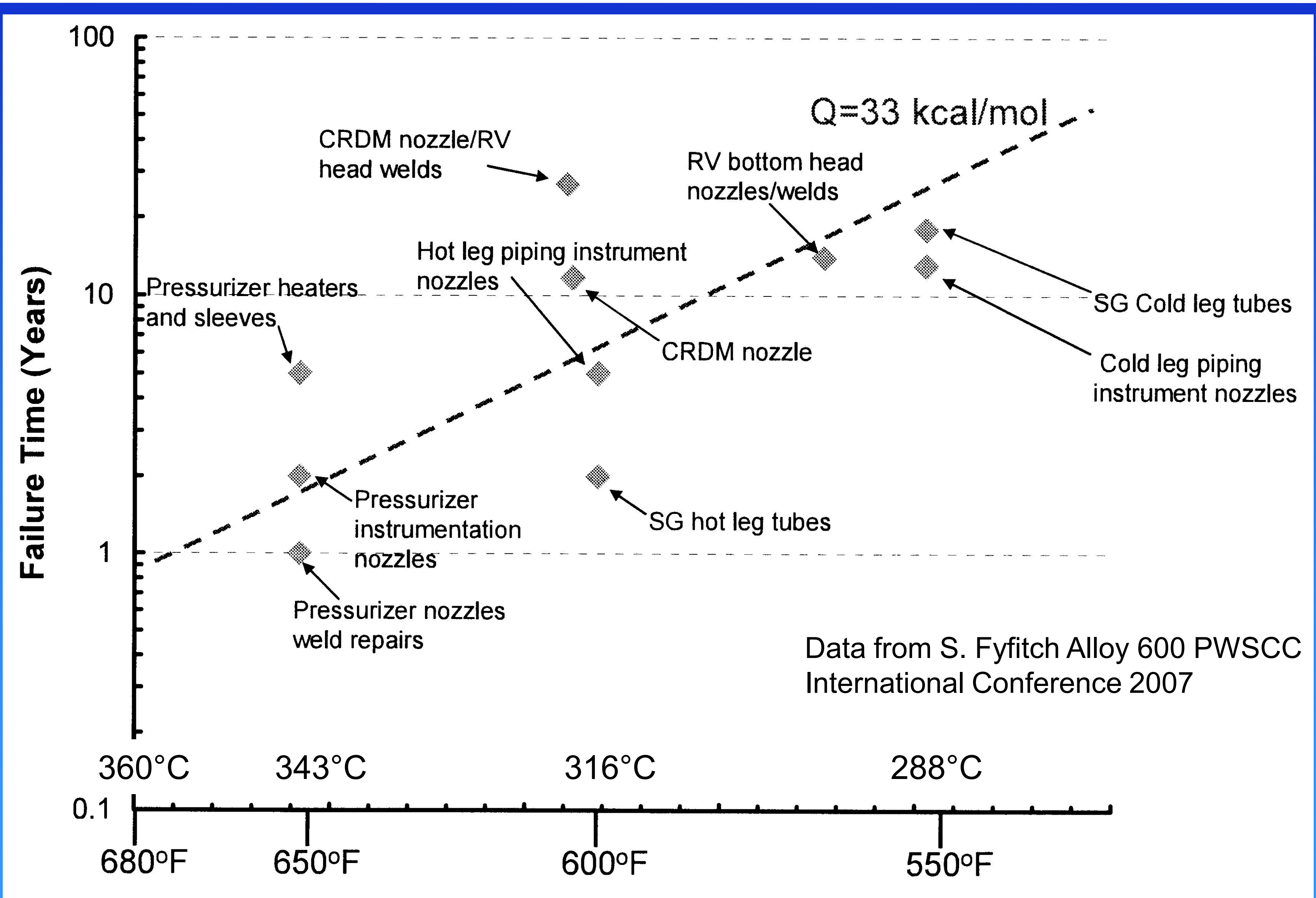
Y. Nishikawa, et al., paper 04670, Corrosion 2004

Effect of T on PWSCC CERT "CGR" of Alloys 82 and 132 HAZs



Y. Nishikawa, et al., paper 04670, Corrosion 2004

Effect of Temperature on PWR Component PWSCC



Effect of Temperature on PWSCC Summary

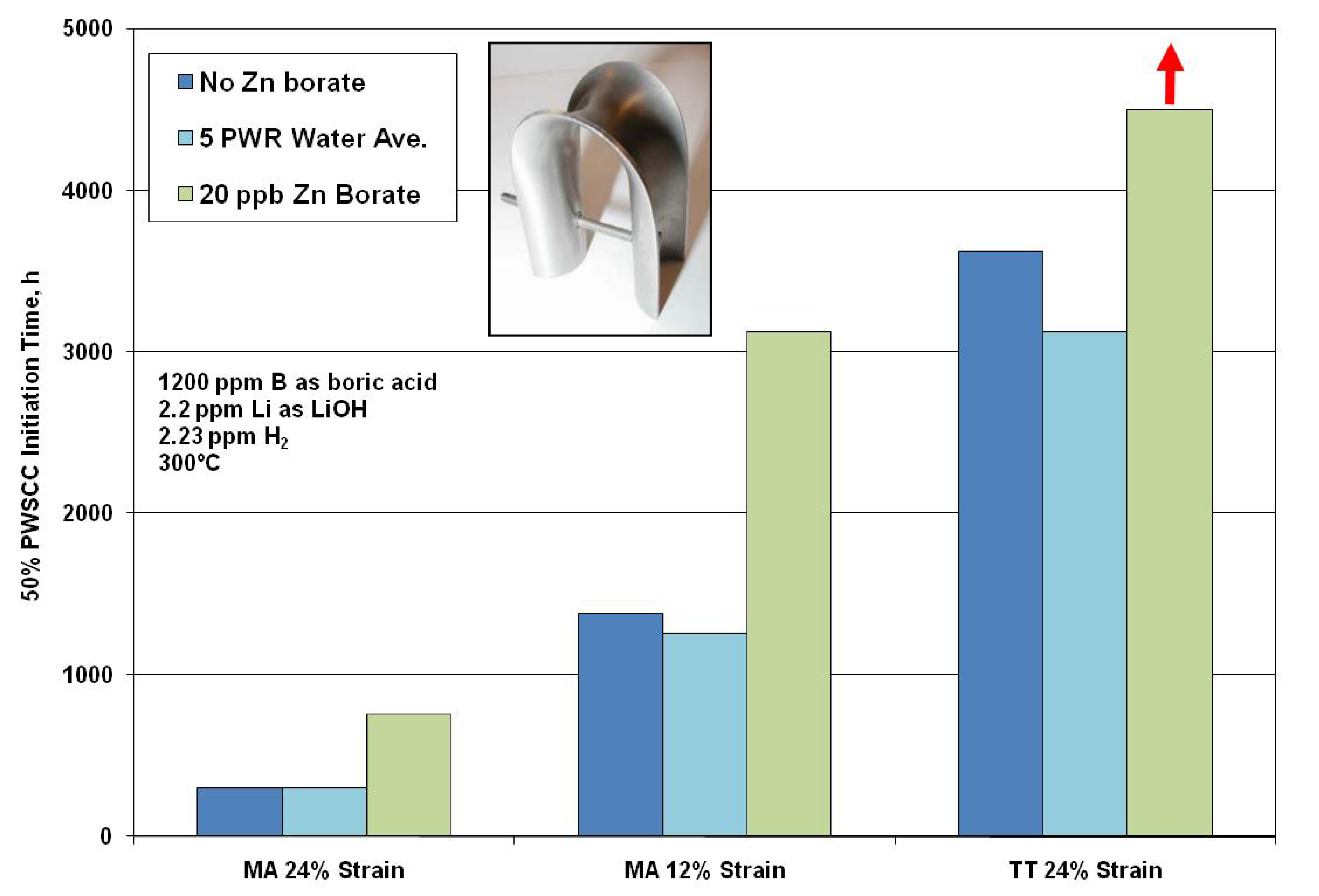
- Both PWSCC initiation and propagation mechanism are thermally activated and will increase with increasing temperature for Ni-base alloys
- Therefore, decreasing the T of the PWR coolant would be beneficial for mitigating PWSCC of Ni-base alloys
- There appears to be a maximum in CGR for 20% CW non-sensitized Type 316 SS at ~350ºC (662ºF)
  - Same maximum CGR behavior as occurs in BWRs in high purity NWC, but at ~250ºC (482ºF)

Ni Alloy PWSCC CGR Temperature Adjustment

$$V_R = \exp\frac{-Q}{R}\left\{\frac{1}{T1}-\frac{1}{T2}\right\}$$

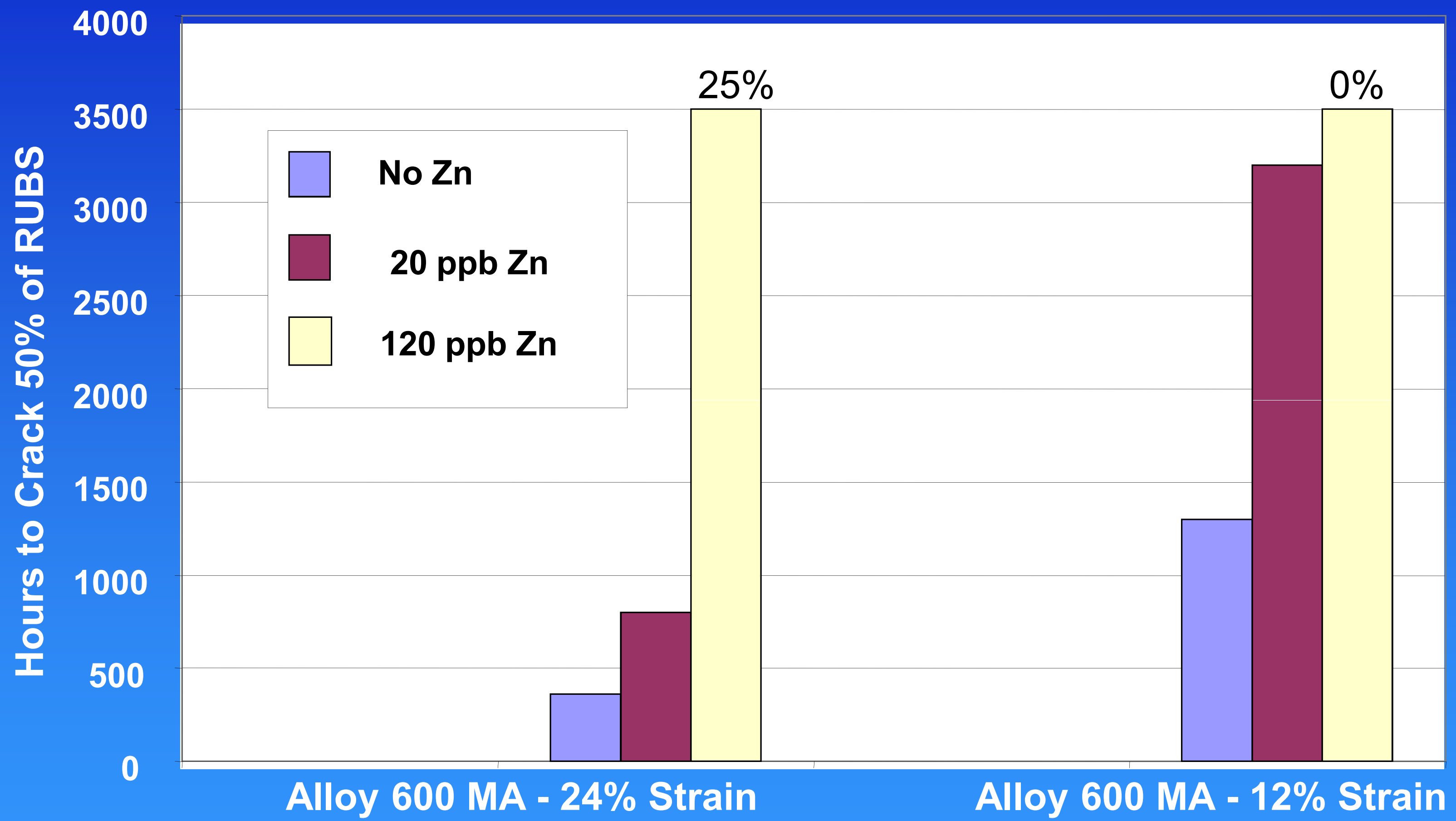
V_R = the ratio of the CGR at one temperature (T2) vs. another temperature (T1)
Q = activation energy for PWSCC growth (31,050 kcal/mole)
R = gas constant (0.00198722 kcal/mole-K)
T = absolute temperature ºK (ºC + 273.16)

Alloy 600 RUBs Mean PWSCC Initiation Times w/wo 20 ppb Zn



Based on J. Esposito, et al., 5th Env. Deg., 1991

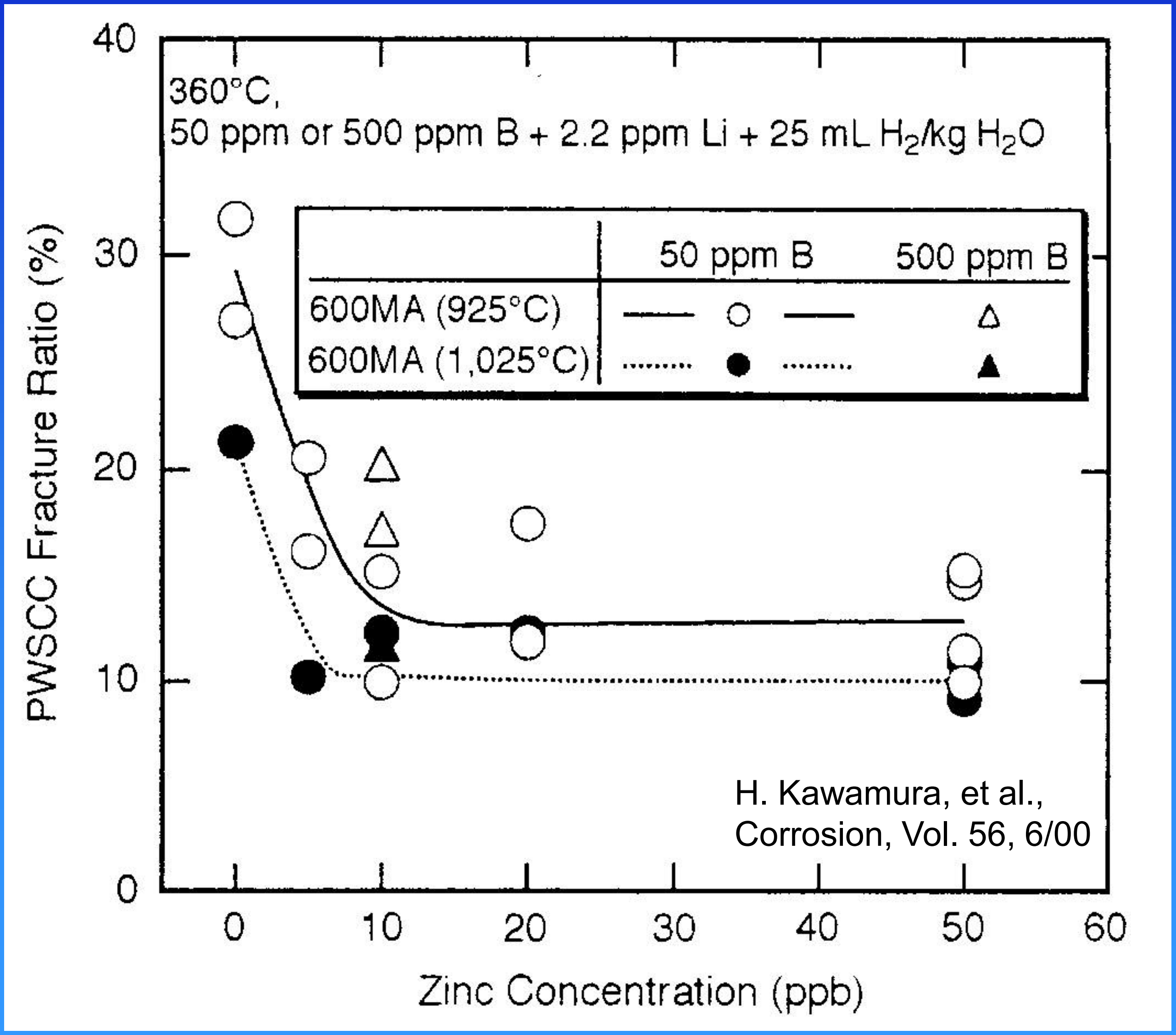
Effect of Zinc on PWSCC Initiation Time in Simulated PWR Coolant



Zinc extends the time required to initiate PWSCC by a factor >11

W. Conner, BNFL, 2002

Effect of Zn on PWSCC Fracture Surface Ratio of MA Alloy 600 at 360°C



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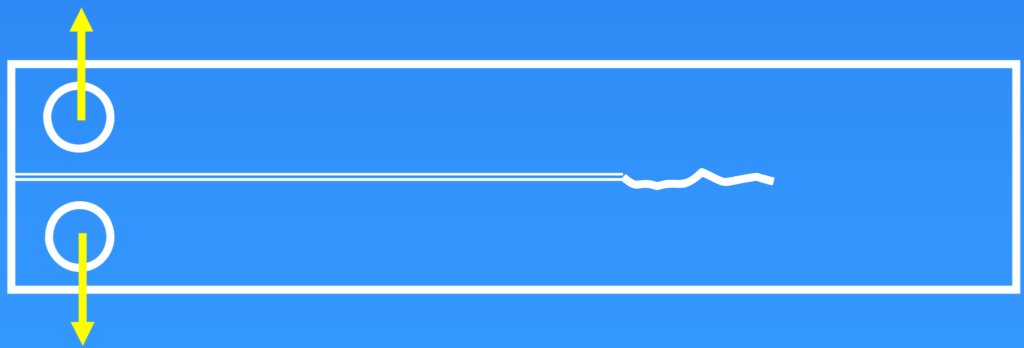
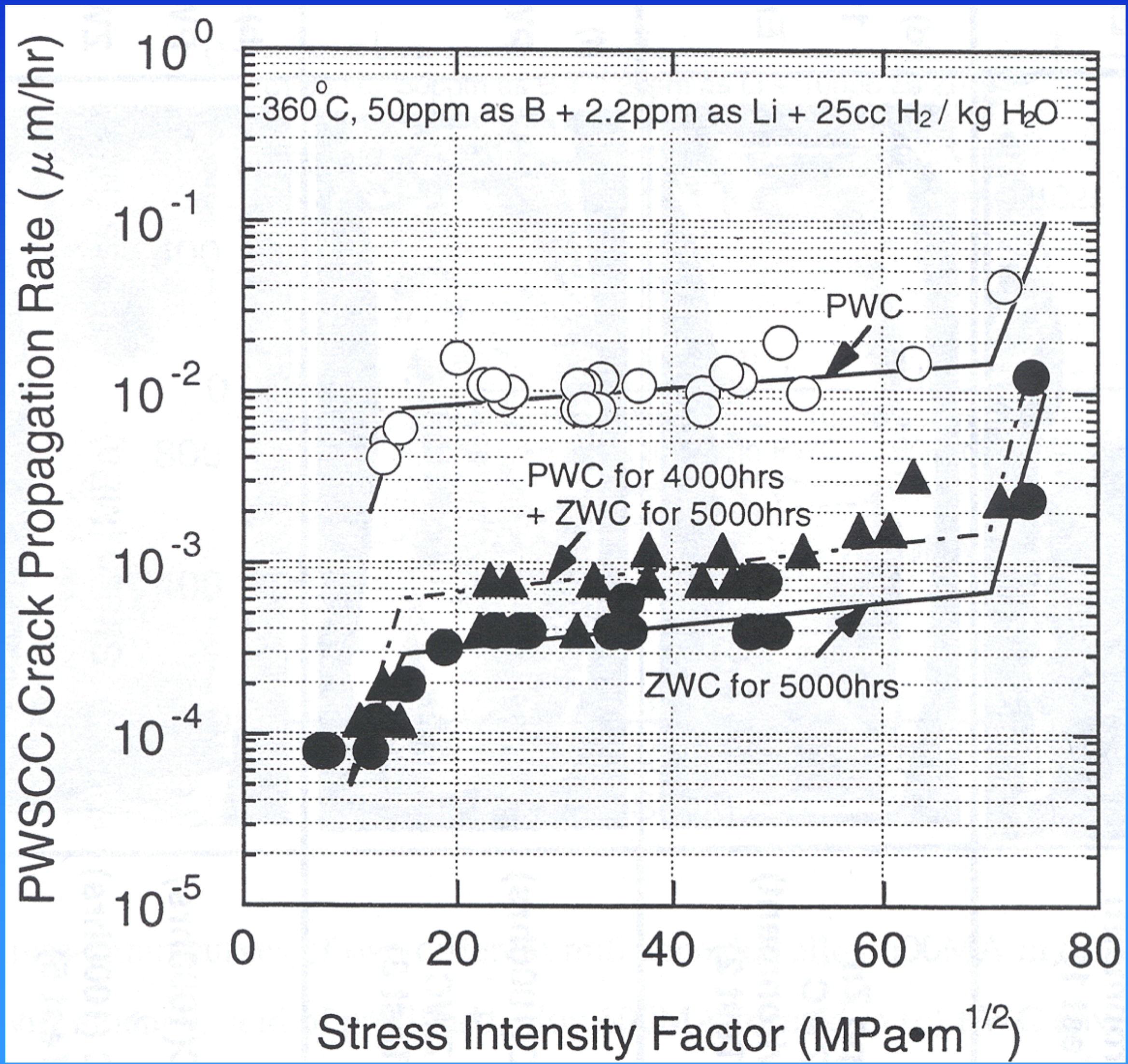
PWSCC Crack Growth Studies

- MA Alloy 600 DCBs
- Three test conditions, all with 50 ppm B, 2.2 ppm Li and 25 cc/kg (2.2 ppm) H_2
  - PWC: 0 h pre-filming in PWR environment, 0 h in ZWC, i.e., control test
  - PWC + ZWC: 4,000 h pre-filming in PWR environment + 5,000 h in ZWC (10 ppb Zn as borate)
  - ZWC: 5,000 h in ZWC (10 ppb Zn)



H. Kawamura, paper 141, Corrosion 98

Effect of K on Crack Velocity in Zn and Zn-free PWR Environments



H. Kawamura, paper 141, Corrosion 98

Effects of Zn on SCC Growth Rate

Test	Li, ppm	B, ppm	pH_{300C}	Zn, ppb	Test Time, hr
1	2.2	600	7.2	0 → 30	5000
2	2.2	600	7.2	0 → 10 → 30 → 0	6500
3	0.3	1200	6.9	0 → 30 → 0	5000

500 hrs for SCC transitioning + 1500 hrs per test segment

Zn acetate - $Zn(O_2CCH_3)_2$

Each test uses two 1T-CT specimens; 325ºC (617ºF), 30 cc/kg H_2

Spike Zn for several weeks to saturate system and crack

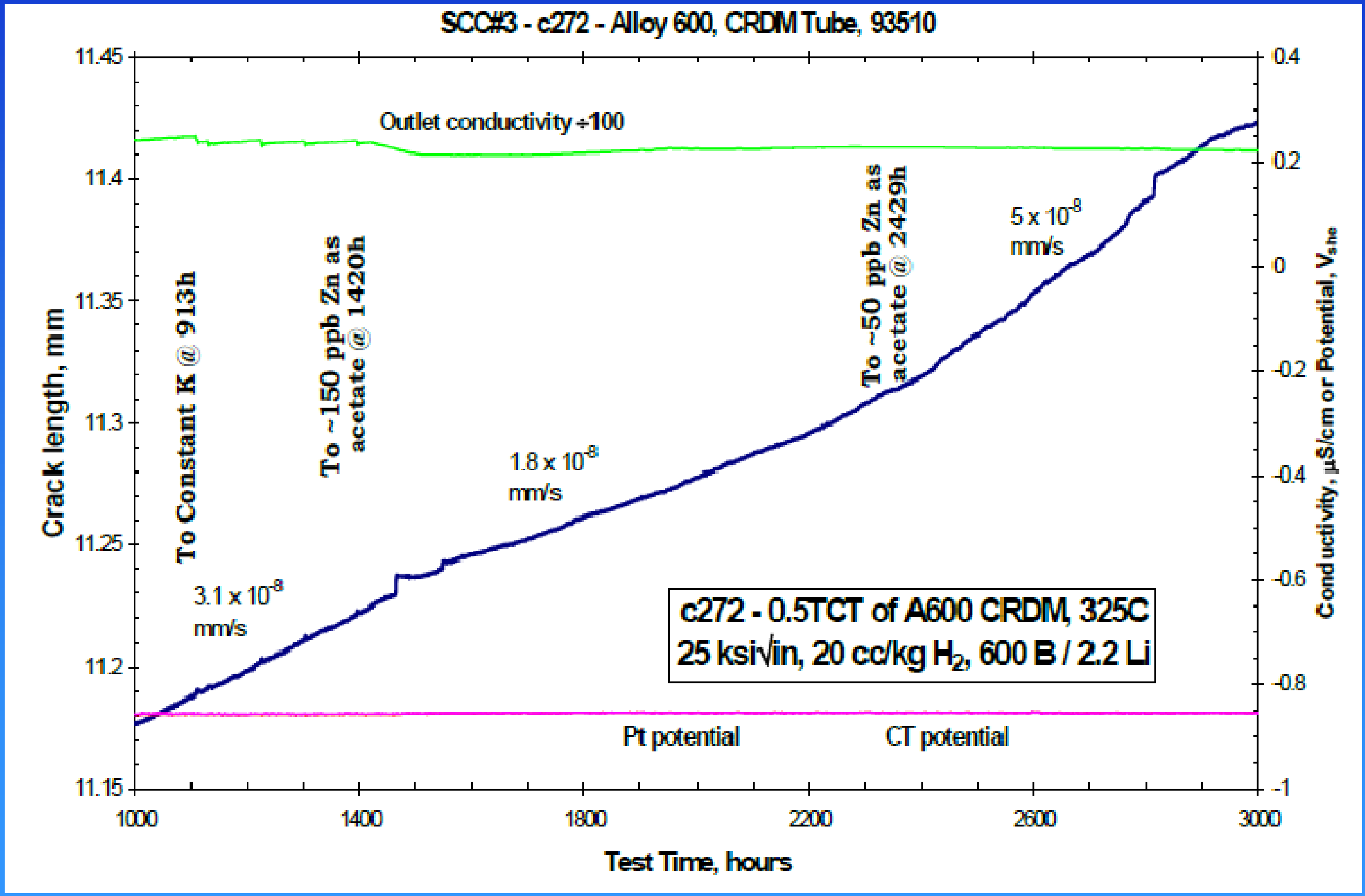
Testing focused on Ni-metal stability = high H_2

Testing now underway on Alloy 182 weld metal

P. Andresen, MRP/PWROG Briefing to NRC RES, 5/30/07

30 ppb Zn Test 1 A600 Specimen c272

Spiked to 150 ppb Zn injected for six weeks

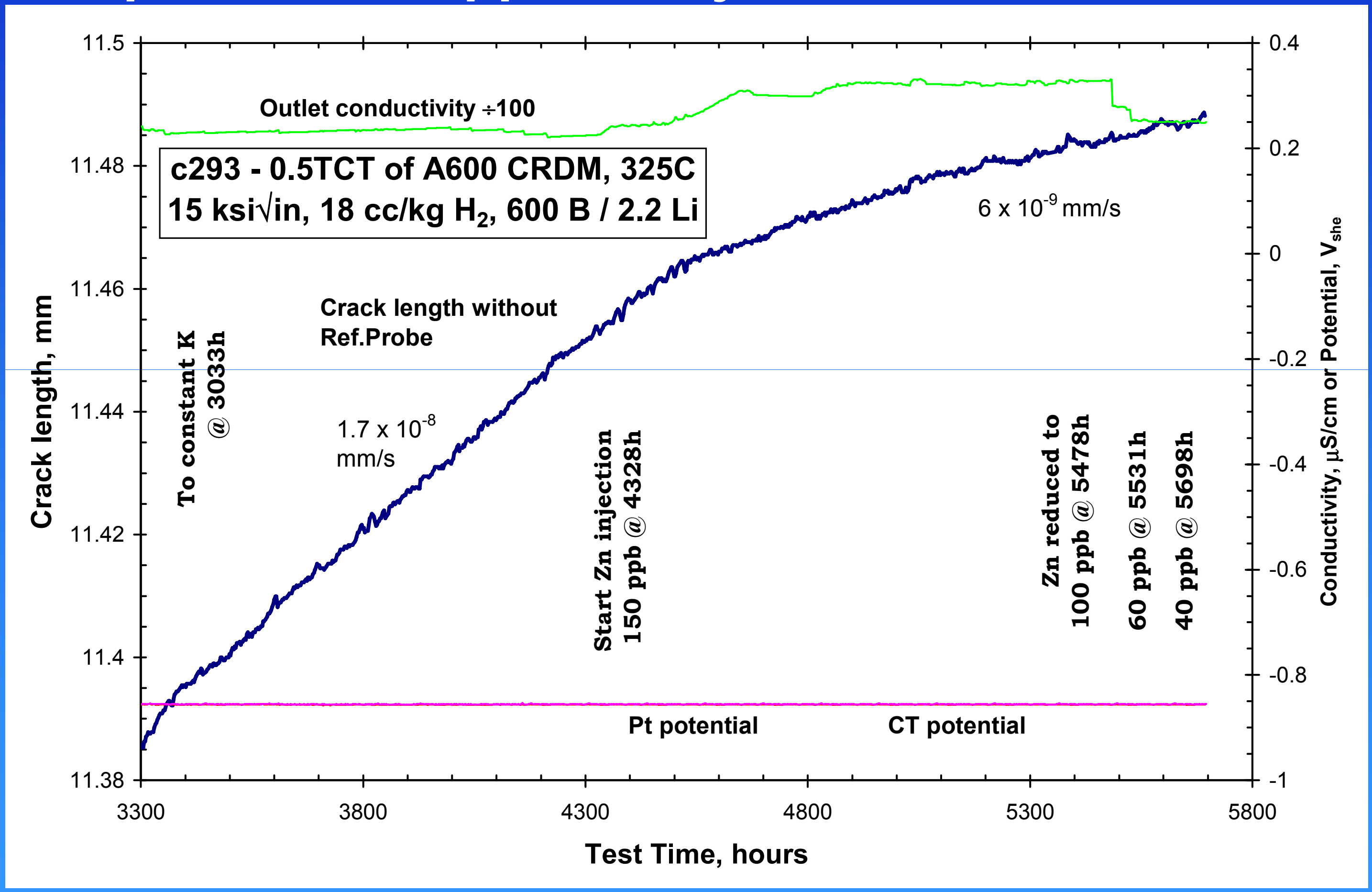


P. Andresen, MRP/PWROG Briefing to NRC, 7/08

Specimens run at 325ºC, 600 B/2.2 Li, 20 cc/kg H_2

30 ppb Zn Test 2 A600 Specimen c293

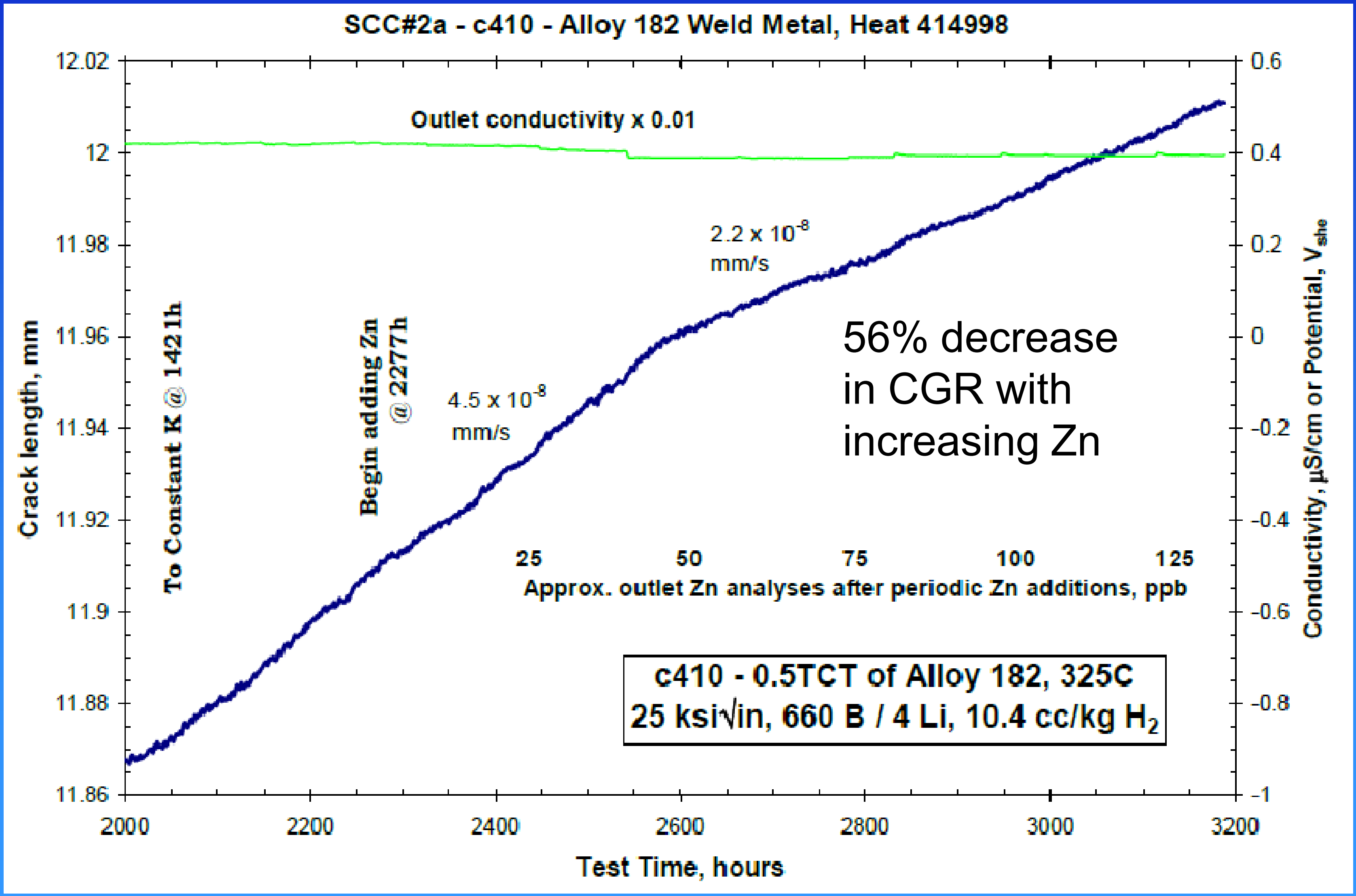
Spiked to 150 ppb Zn injected for six weeks



Specimens run at 325ºC, 600 B/2.2 Li, 18 cc/kg H_2
Used 16.5 MPa√m for lower CGRs

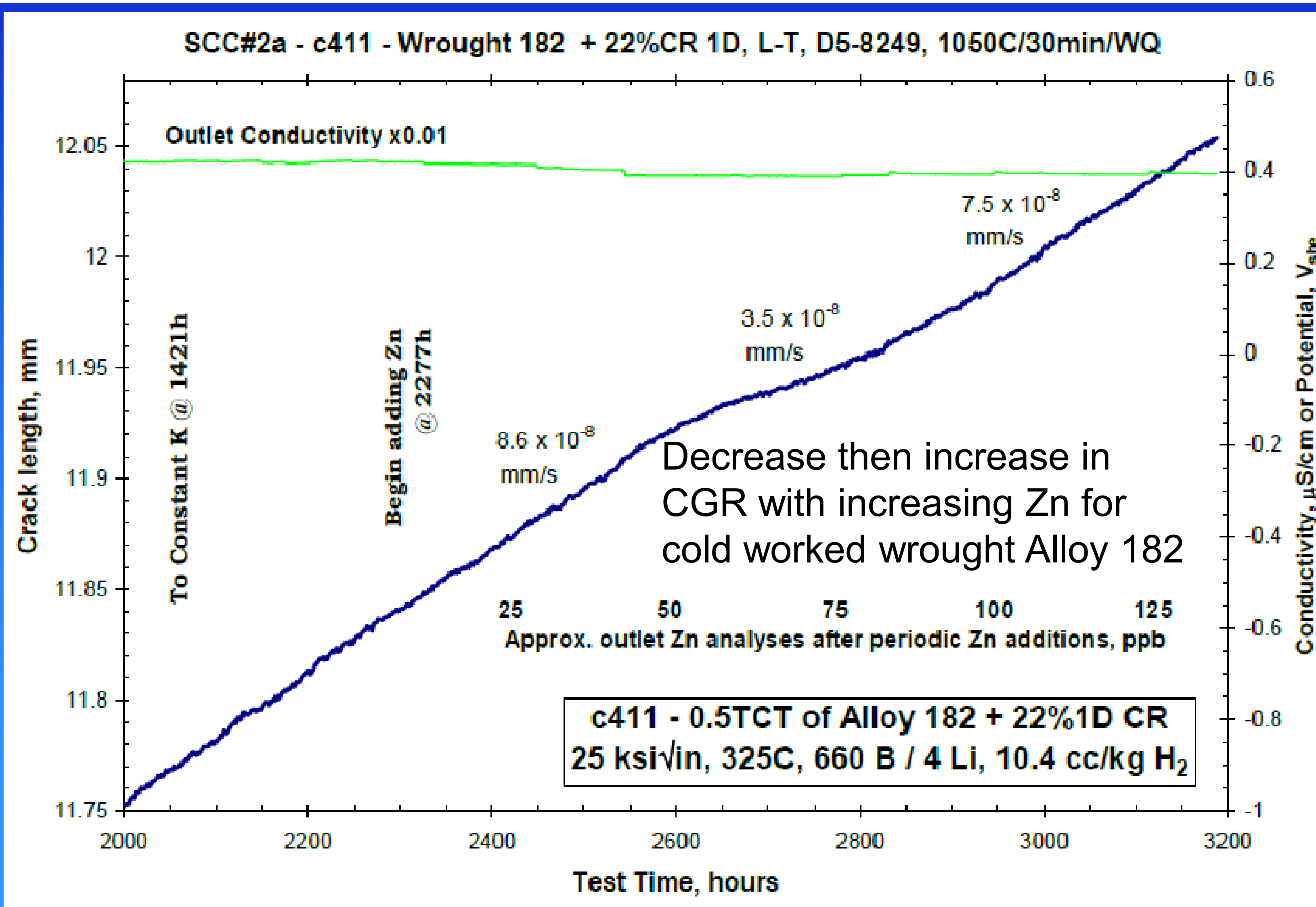
P. Andresen, MRP/PWROG Briefing to NRC RES, 5/30/07

Effect of Zn on Alloy 182 Weld Metal Crack Growth Rate



P. Andresen, MRP/PWROG Briefing to NRC, 7/08

Effect of Zn on Cold Worked Wrought Alloy 182 Crack Growth Rate



P. Andresen, MRP/PWROG Briefing to NRC, 7/08

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Conclusions on GE Zn PWSCC Tests

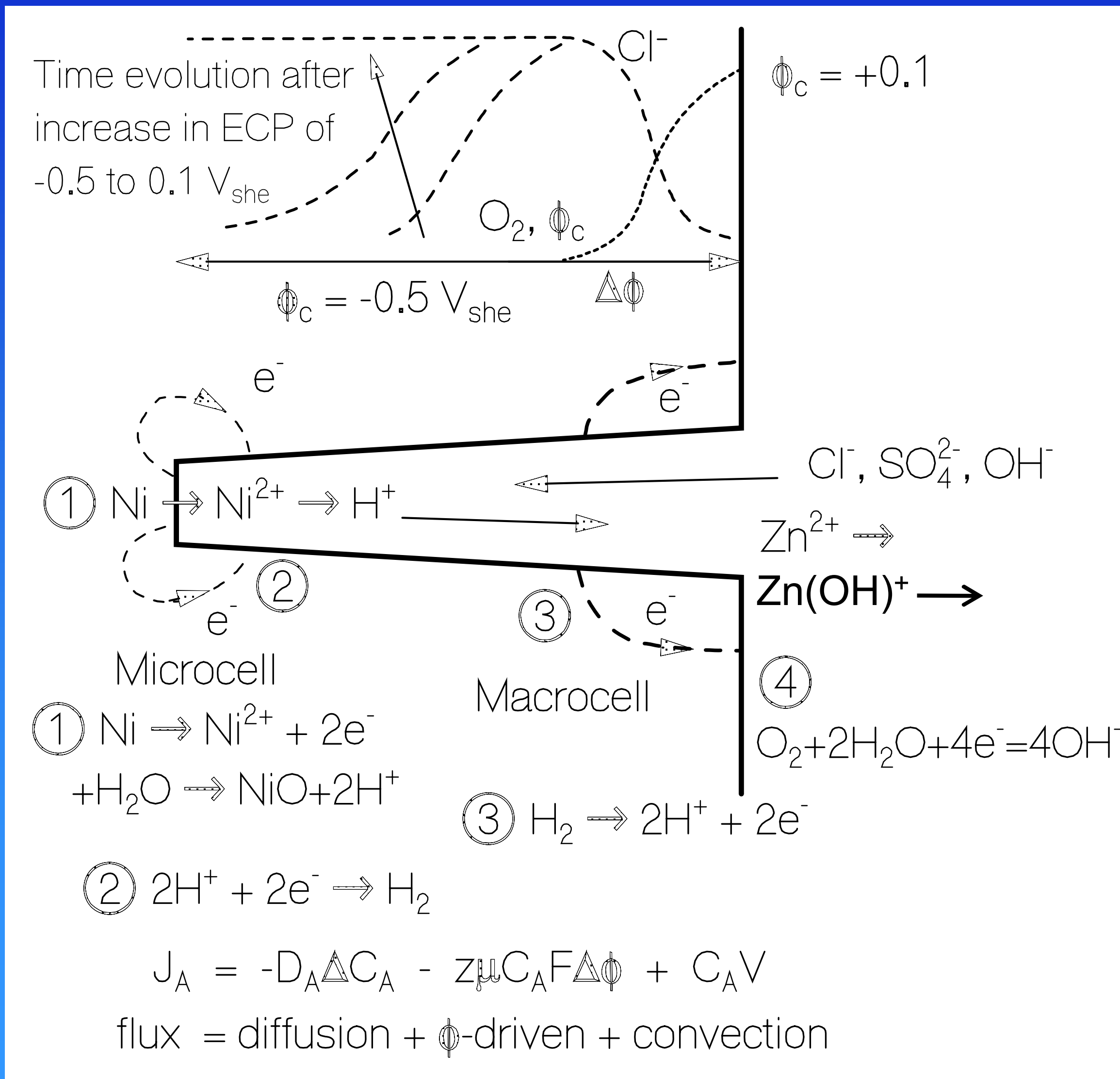
- Inconsistent and (at best) limited effect of Zn on Alloy 600 and Alloy 182 weld metal suggests that it is not a reliable way to mitigate SCC growth in Ni alloys
- Initial data showed a larger benefit at low K (e.g., 16.5 MPa√mn), but subsequent tests did not show any benefit
  - Longer term (>3000 hours) of Zn exposure did not produce a larger cumulative benefit over time
- Since the oxides that form near the crack tip in Ni alloys are NiO and Zn is only known to incorporate and affect the properties of spinel oxides (e.g., $NiCr_2O_4$), into which Zn substitutes in the place of Ni^+, no CGR benefit may be achieved

Zn PWR Thermodynamic Studies

- Alloy 600
  - Stable oxide film is $NiCr_2O_4$ (nichromite) and NiO
  - Addition of Zn changes oxide to $ZnCr_2O_4$ (zinc chromite)
  - Solubility of $ZnCr_2O_4$ is 100X lower than $NiCr_2O_4$
- Stainless steel
  - Stable oxide film is $FeCr_2O_4$ (iron chromite)
  - Addition of Zn changes oxide to $ZnCr_2O_4$
  - Solubility of $ZnCr_2O_4$ is 3 times lower than $FeCr_2O_4$

K. Miyajima and H. Hirano, paper 01143, Corrosion 2001

Zn Penetration into Crack Tip



Limited benefit of Zn in NWC BWRs related to high ECP, which drives Zn^{2+} away from crack

But at low ECP, Zn diffuses slowly and is initially “consumed” by incorporation into crack oxides

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History and Status of PWR Zn Injection

- 1986 - BWRs (Hope Creek) started adding Zn for radiation field control
- 1994 - Farley 2 was the 1st US PWR to inject Zn
- December 2006 - 39 PWRs injecting Zn, including 18 international units
- Of the 21 US PWRs, 5 are injecting for PWSCC mitigation (≥15 ppb Zn), remainder for radiation field control, using lower Zn injection levels
- Additional 10 PWRs have indicated plans to implement Zn within the next two years

P. Andresen, MRP/PWROG Briefing to NRC RES, 5/30/07

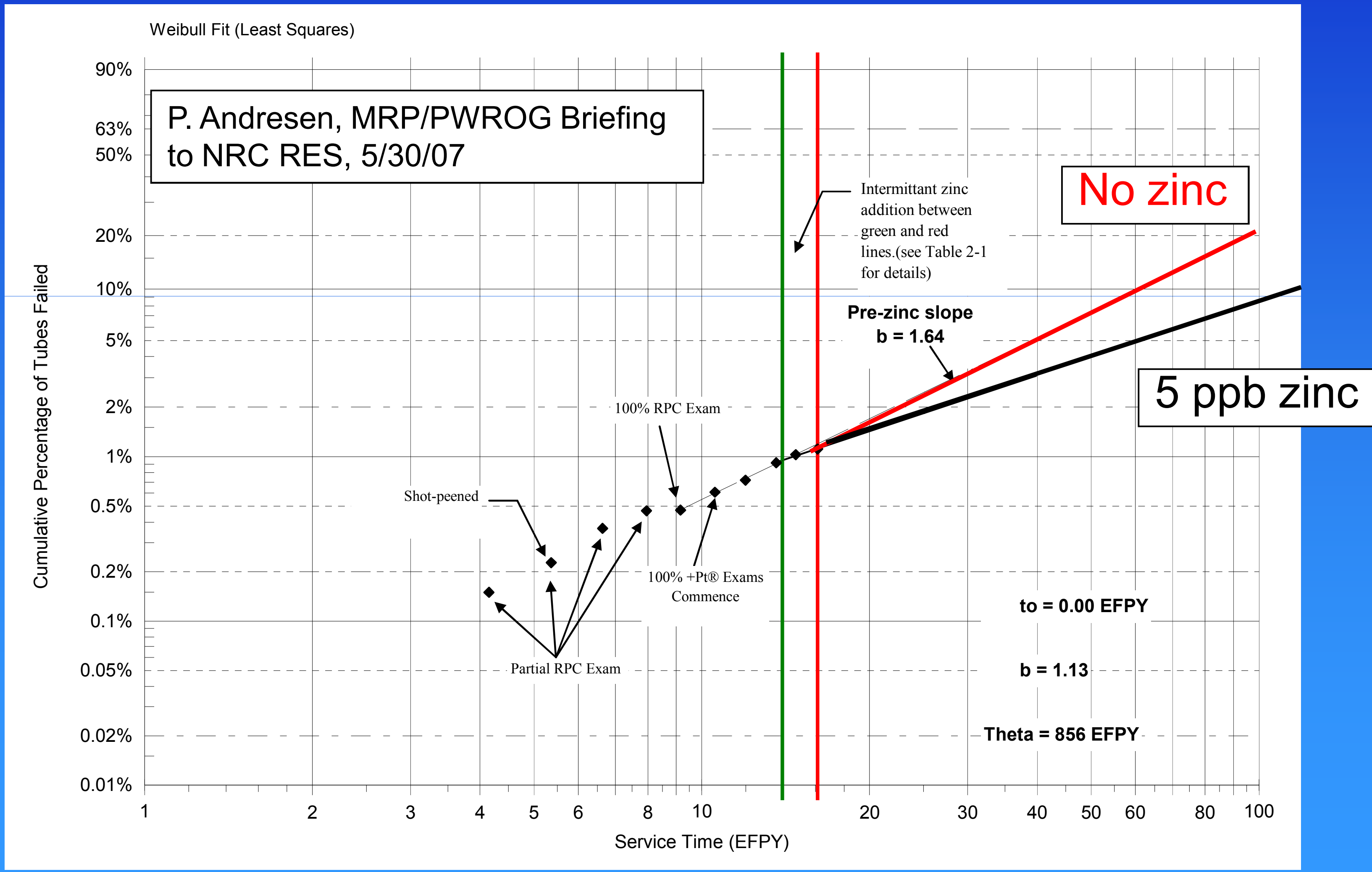
Field SG Data Evaluation: Zn PWSCC Mitigation

- Five units injecting Zn primarily for PWSCC mitigation (15-40 ppb)
  - Farley 1 and 2, Diablo Canyon 1 and 2, and Beaver Valley 1
- Steam Generator data analyzed for PWSCC indications:
  - Numbers of cumulative PWSCC indications
    - Decrease in PWSCC observations (2 to 10X reduction)
- DCPD CGR data
  - Growth rate measurements (20 to 60% reduction)
- Comparisons performed of the results for periods of operation with and without Zn

P. Andresen, MRP/PWROG Briefing to NRC RES, 5/30/07

Example of Smallest Zn SG Benefit Observed

Sequoyah 2 (5 ppb zinc): 31% decrease in Weibull Slope
(It would take 1.9 times as long to go from 1% to 10% tubes affected)



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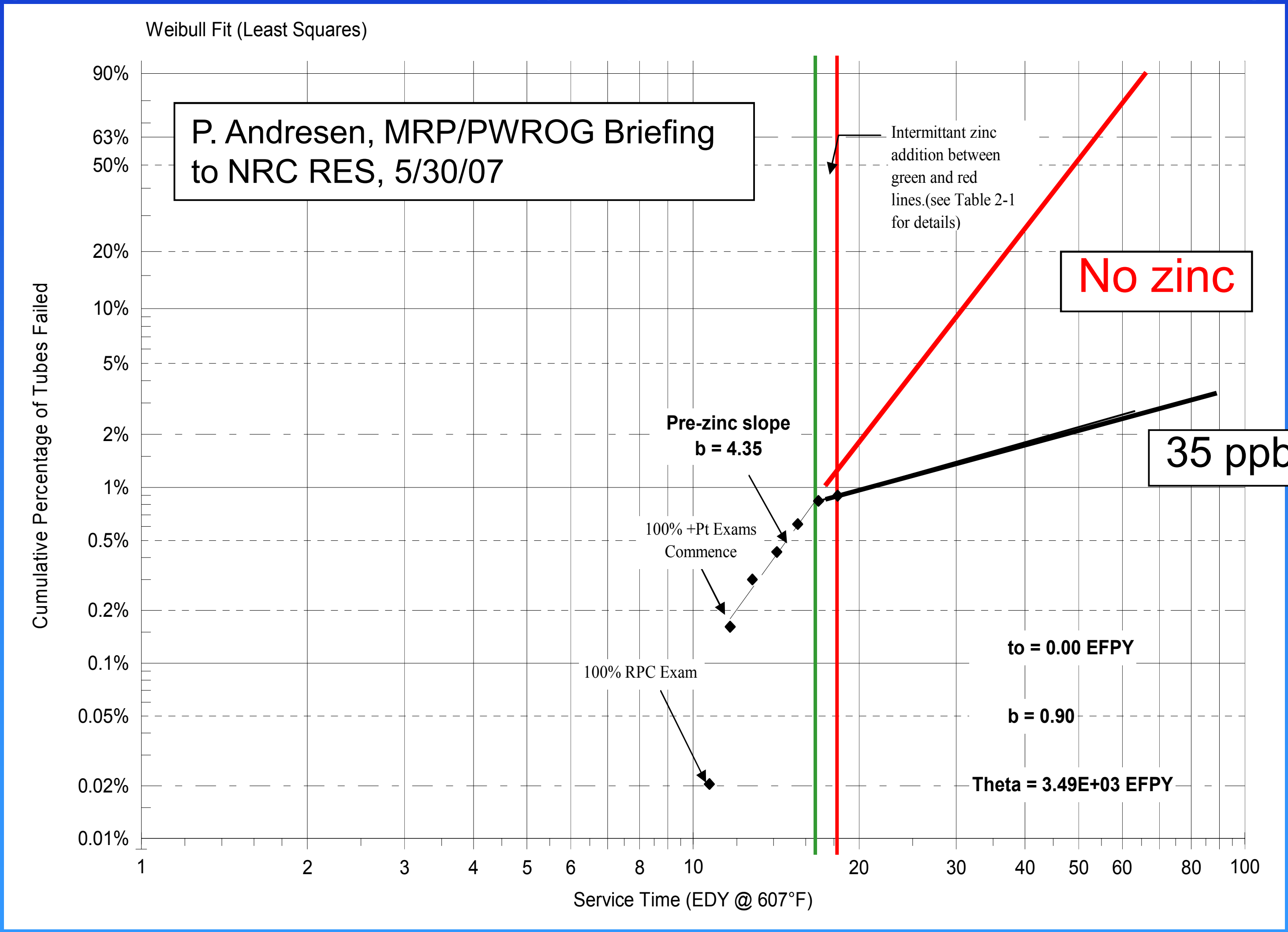
Example of Largest Zn SG Benefit Observed

Beaver Valley 1 (35 ppb zinc): 79% decrease in Weibull Slope
(It would take 9.6 times as long to go from 0.8% to 10% tubes affected)



Farley 2 Pilot Plant for Zn Addition

- Laboratory and test reactor experiments indicated reduced general corrosion and PWSCC mitigation benefits of zinc addition
- EPRI sponsored demonstration plant
- Zinc injection began June 12, 1994
- RCS zinc concentration
  - 30 ppb Cycles 10, 12–14
  - 15 ppb Cycles 15–17 (post SG replacement)

Farley 2 CRDM Penetration Material

- **B&W tubular products Alloy 600 heat M3935**
- **Less than optimum annealing heat treatment**
- **Heat M3935 used in top head penetrations of five RPV heads:**
  - ♦ **Farley 2**
  - ♦ **Davis-Besse**
  - ♦ **Oconee 3**
  - ♦ **Beaver Valley**
  - ♦ **ANO 1**

M. Stinson, SNOC, 8/05

Alloy 600 Heat M3935 Industry Experience

PWR	# of nozzles M3935	% in industry M3935	Number UT inspected	Number that required repair	% of M3935 in RV head with defect
Oconee 3	68	49	68	14	20
Davis-Besse	5	4	5	4	80
ANO 1	1	<1	1	1	100
Beaver Valley	4	3	4	4	100
Farley 2	**61**	**44**	**61**	**0**	**0**
Total	139		139	23	
%			100	17	

Farley 2: Only RPV head with heat M3935 that has not experienced cracking
Farley 2: Only PWR that operated with heat M3935 and significant Zn chemistry

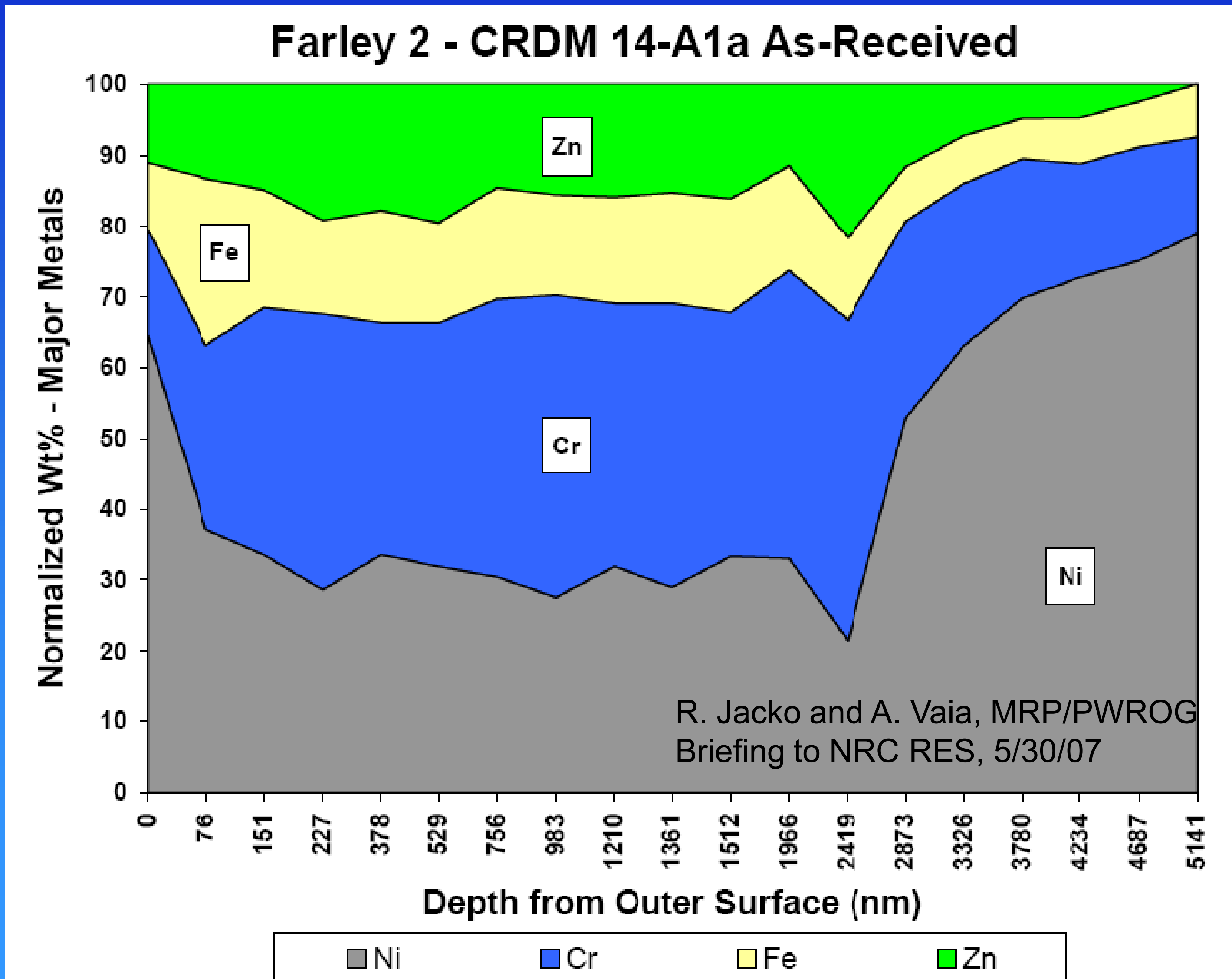
M. Stinson, SNOC, 8/05

PWROG Farley Zinc Program

- **61 of 69 Farley 2 RV head penetrations were manufactured from Alloy 600 Heat M3935**
- **Heat M3935 have shown PWSCC in *all other plants without Zn injection***
- **Replacement of the RV head at Farley 2 in 2005 outage provided a unique opportunity to obtain Alloy 600 CRDM material that operated for an extended period with Zn additions**
- **PWROG goal: Acceptance of Zn as a chemical mitigation method to support inspection relief**
- **5 year program with 5 distinct phases**

R. Jacko and A. Vaia, MRP/PWROG Briefing to NRC RES, 5/30/07

Zn Incorporation into Farley Alloy 600



- After ~1800 ppb-mo of Zn exposure, Zn has fully penetrated the oxide film
- Auger and EDS analysis indicates Zn is ~10 wt% of the metals in the oxide film

Zn Mitigation of PWSCC Initiation and Growth

- The inhibitive effect of zinc on PWSCC initiation is well documented
  - ♦ Decrease in SG degradation rate (indications) by 2 to 10X
  - ♦ Farley 2 head experience is excellent
- However:
  - ♦ Reduced crack growth benefit of Zn shown for A600 SG tubes does not necessarily transfer to thick-wall RCS components and to A82/182 welds

P. Andresen, MRP/PWROG Briefing to NRC RES, 5/30/07

Effects of Zn on PWSCC Summary

- Field and test data shows Zn inhibits PWSCC initiation in Alloys 600/82/182
- Some initial tests indicate Zn can reduce CGR of undetected (shallow-low K) cracks in thick A600 components, confirmatory tests underway
- A600 tests to date have not shown Zn can reduce CGR of deep cracks in high stress areas (high K cracks)
  - It appears that crack-tip in a fast-growing crack out runs Zn that deposit on crack flanks rather than on the tip
- SCC tests require thousand hours; results are slow

P. Andresen, MRP/PWROG Briefing to NRC RES, 5/30/07

Effects of Water Chemistry on PWSCC Summary

- Effects of relevant variations in PWR primary water chemistry (B, Li and pH_T) have little effect on the CGR in Alloy 600, and thus provide little opportunity for mitigation of PWSCC
- Peak in CGR vs. H_2 fugacity is observed, but opportunity for mitigation is limited to perhaps 2X in Alloy 600 and perhaps 5X in Alloys 182, 82 and X-750
- PWSCC mitigation by adding Zn requires further study, although 2 of 4 tests shows a decrease in growth rate of >3X, which should be additive to the benefit of adjusting H_2

P. Andresen, et al, Env. Deg., 2007

PWR Zn Fuel Materials Compatibility

- Zn is not expected to negatively affect fuel cladding integrity
  - Early autoclave and in-reactor tests showed no impact
  - Cladding corrosion measurements have shown Zn to have little or no impact on performance
- Vendors have determined that Zn does not interact with or exacerbate the degradation of leaking rod failure locations caused by other mechanisms
- Zn had no negative effect on other fuel component materials during early autoclave testing
- Vendors are expanding the fuel surveillance database as higher duty plants inject Zn

Summary of PWR PWSCC Parameters