EPRI/MRP Boric Acid Corrosion (BAC) Testing Program: *Immersion Test Results*

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NRC / ANL / MRP Meeting
Argonne National Laboratory (ANL)
Argonne, Illinois
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Presentation Outline

- Background
- Immersion Test Setup
  - Closed pressure vessels
  - Coupon designs
  - Electrode development
- Immersion Corrosion Rate Results
  - Test matrix
  - Free coupons in oxygenated solutions
  - Free coupons in deoxygenated solutions
  - Crevice and galvanic coupons
- Comparison with ANL Results for Molten H-B-O Mixtures

- *Afternoon Discussions:* Review of Planned MRP BAC Testing Addressing Molten H-B-O Environments

Background
Purpose of Immersion Tests

- Description:
  Immersion tests in concentrated boric acid solutions and molten boric acid at a range of temperatures and pressures. Test specimens included bare metal specimens, creviced specimens, and galvanically coupled specimens
- Areas Addressed:
  - Corrosion rates and location for low alloy steel in a concentrated boric acid solution or molten boric acid (H-B-O) environment
  - Galvanic corrosion behavior in these environments
  - Crevice corrosion behavior in these environments
  - Effect of moisture content on the corrosivity of molten boric acid

Background
Overall MRP BAC Test Program

Task 1 - Heated Crevice test device to address stagnant and low flow chemistry definition and their influence on corrosion rates.

Task 2 – Test in a flowing loop to address moderate and high flow condition with ability to monitor real time corrosion rates and ECP under laminar and impact flow.

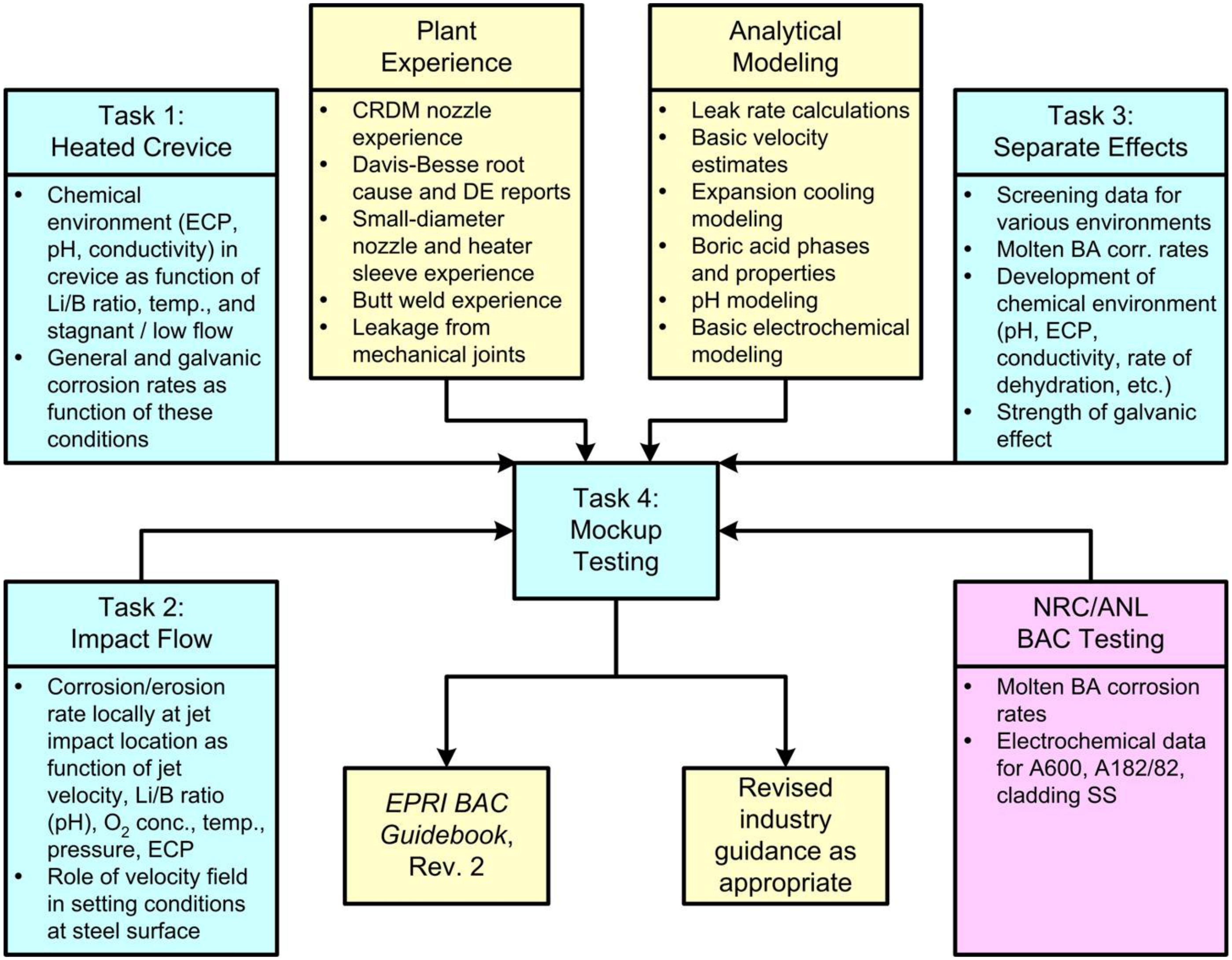
Task 3 – Separate effects tests to obtain data on corrosion rates for conditions not previously tested such as galvanic coupling and corrosion in contact with molten boric acid.

Task 4 – Full scale mockup testing to determine corrosion rates under prototypical CRDM nozzle leakage conditions including full-size nozzles, interference fits, simulated crack geometries, range of leak rates from 0.0001 to 0.3 gpm, and controlled thermal conditions.

Background
Program Organizations

- Program Management
  - MRP (Craig Harrington—TXU Energy, Les Spain—Dominion)
  - EPRI (Allan McIlree, Al Ahluwalia, John Hickling)
- Task 1: Heated Crevice
  - Rockwell Scientific (Jesse Lumsden)
- Task 2: Impact Flow Loop
  - University of New Brunswick (Derek Lister, Willy Cook)
- Task 3: Separate Effects Testing
  - Dominion Engineering, Inc. (Chuck Marks, Glenn White)
  - Pennsylvania State University (Digby Macdonald)
- Task 4: Full-Scale Mockup Testing
  - Southwest Research Institute (Richard Page)

Background
Overall MRP BAC Testing Program



Plant Experience
- CRDM nozzle experience
- Davis-Besse root cause and DE reports
- Small-diameter nozzle and heater sleeve experience
- Butt weld experience
- Leakage from mechanical joints

Analytical Modeling
- Leak rate calculations
- Basic velocity estimates
- Expansion cooling modeling
- Boric acid phases and properties
- pH modeling
- Basic electrochemical modeling

Task 1: Heated Crevice
- Chemical environment (ECP, pH, conductivity) in crevice as function of Li/B ratio, temp., and stagnant / low flow
- General and galvanic corrosion rates as function of these conditions

Task 3: Separate Effects
- Screening data for various environments
- Molten BA corr. rates
- Development of chemical environment (pH, ECP, conductivity, rate of dehydration, etc.)
- Strength of galvanic effect

Task 4: Mockup Testing

Task 2: Impact Flow
- Corrosion/erosion rate locally at jet impact location as function of jet velocity, Li/B ratio (pH), O_2 conc., temp., pressure, ECP
- Role of velocity field in setting conditions at steel surface

NRC/ANL BAC Testing
- Molten BA corrosion rates
- Electrochemical data for A600, A182/82, cladding SS

EPRI BAC Guidebook, Rev. 2

Revised industry guidance as appropriate

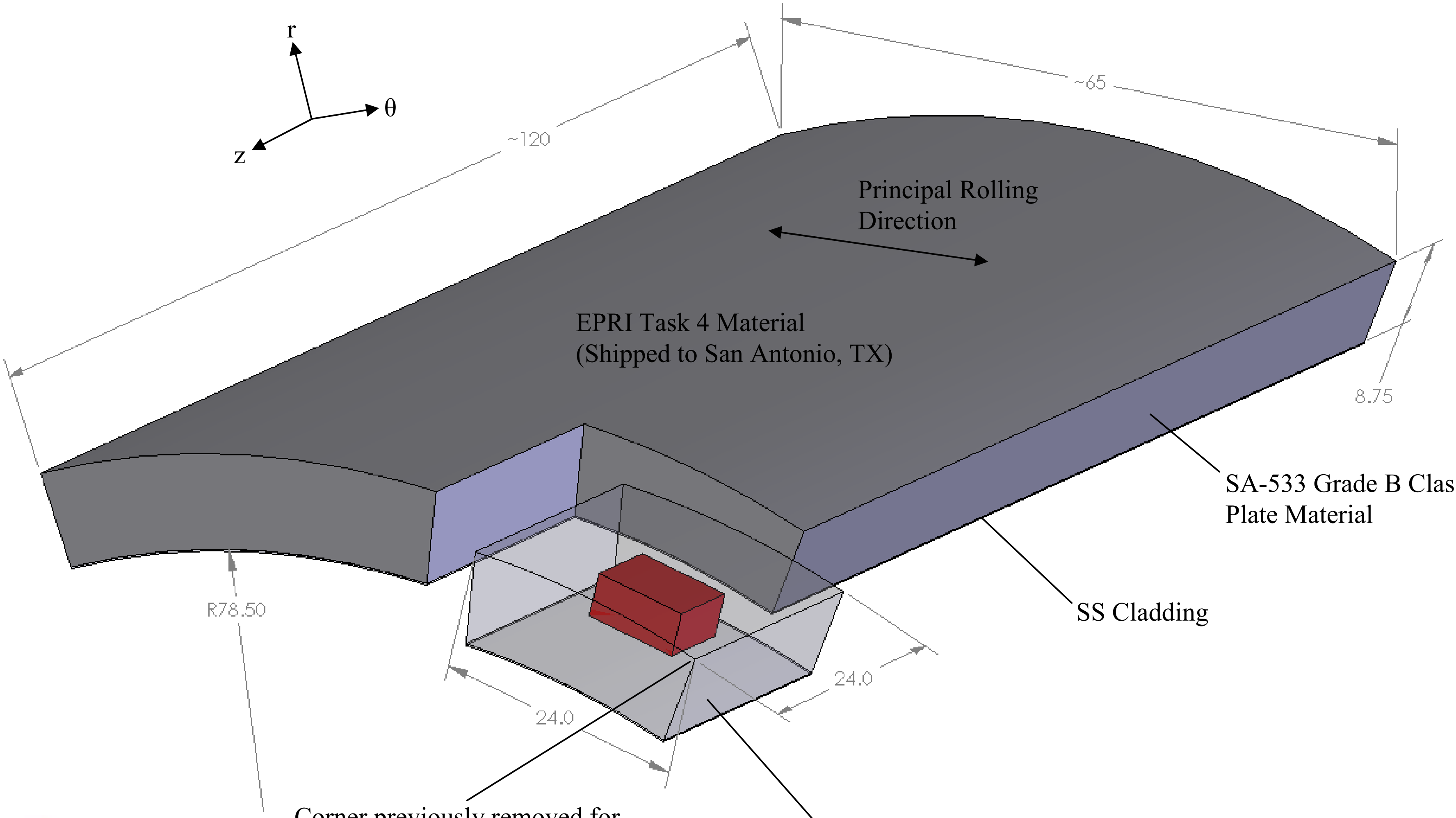
Background
MRP Program Schedule

- Program Kickoff Meeting
  - October 29–30, 2003, Reston, Virginia
  - Participation of MRP, EPRI, Program Test Labs, NRC Research, and ANL
- Tasks 1, 2, and 3
  - Initiated in fall of 2003
  - Testing continuing into 2005
- Task 4 Mockup Testing
  - Planned for 2005 and 2006
- Revision 2 to BAC Guidebook
  - Planned for late 2006 / early 2007

Background
Reactor Vessel Steel Material Source

- Original RPV heads were fabricated from low alloy steel reactor vessel plate material
  - SA 302 Grade B
  - SA 533 Grade B Class 1
- A common material source for BAC testing is desirable to minimize influence of any processing / microstructural effects although such effects are expected to be small
- A 20,000 lb section of reactor vessel shell from a canceled plant was procured
  - Cut from center cylindrical portion of vessel
  - Representative material processing and microstructure
  - Cr content (0.04%) at low end of range typical for PWR vessels

Background
Reactor Vessel Steel Material Source



Principal Rolling Direction

EPRI Task 4 Material
(Shipped to San Antonio, TX)

SA-533 Grade B Class 1
Plate Material

SS Cladding

Corner previously removed for
composition testing prior to
procurement of large plate

EPRI Tasks 1, 2, and 3 Material
(Shipped to Forest Hill, MD)

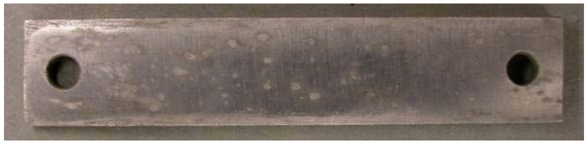
Background
Weld Detection in Reactor Vessel Test Material

- Ammonium Persulfate Indicator
- Two Channels Tested

No Welds in the Removed Corner

Positive Control

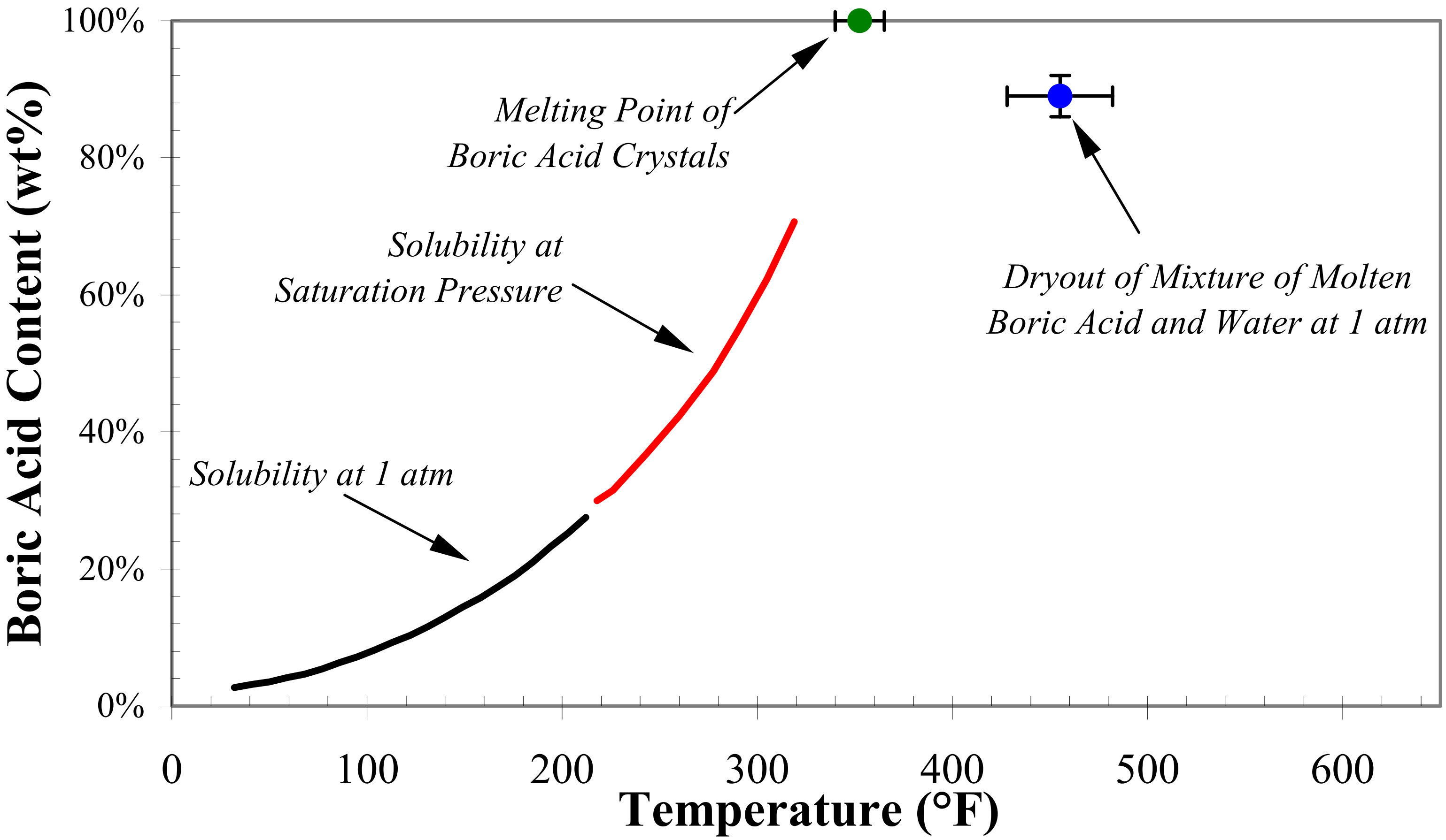
Negative Control



Test Material

Background

Boric Acid Properties—Solubility and MP



Melting Point of Boric Acid Crystals

Solubility at Saturation Pressure

Solubility at 1 atm

Dryout of Mixture of Molten Boric Acid and Water at 1 atm

Background
Boric Acid Properties—Phases

- *Boric acid solutions and dry crystals*
  - During evaporative concentration, boric acid solutions precipitate boric acid crystals
  - The end results depend upon the rate of concentration and drying
    - If drying is fast, boric acid powder will result
    - If drying is slow, a single irregularly shaped mass is likely
- *Molten boric acid*
  - When heated above 170–185°C (340–365°F), solid boric acid melts to form a highly viscous liquid that will fuse into a single mass and flow under the influence of gravity
  - Molten boric acid can contain 8–14% water by weight and is known to be corrosive
- *Solid boric oxide*
  - Above 150°C (302°F) boric acid is subject to a dehydration reaction to form boric oxide
  - The resultant crystalline mass is an anhydrous, white, opaque, stony solid
- *Molten boric oxide*
  - Above 325°C (617°F) boric oxide begins to soften and at about 450°C (842°F) becomes a highly viscous liquid

Background
Boric Acid Properties—Phases

5 Phases:

Ortho Boric Acid: H_3BO_3
Meta Boric Acid I: HBO_2
Meta Boric Acid II: HBO_2
Meta Boric Acid III: HBO_2
Boric Oxide: B_2O_3

H_3BO_3 Metastable until B_2O_3

Source: Kemp, *The Chemistry of Borates*

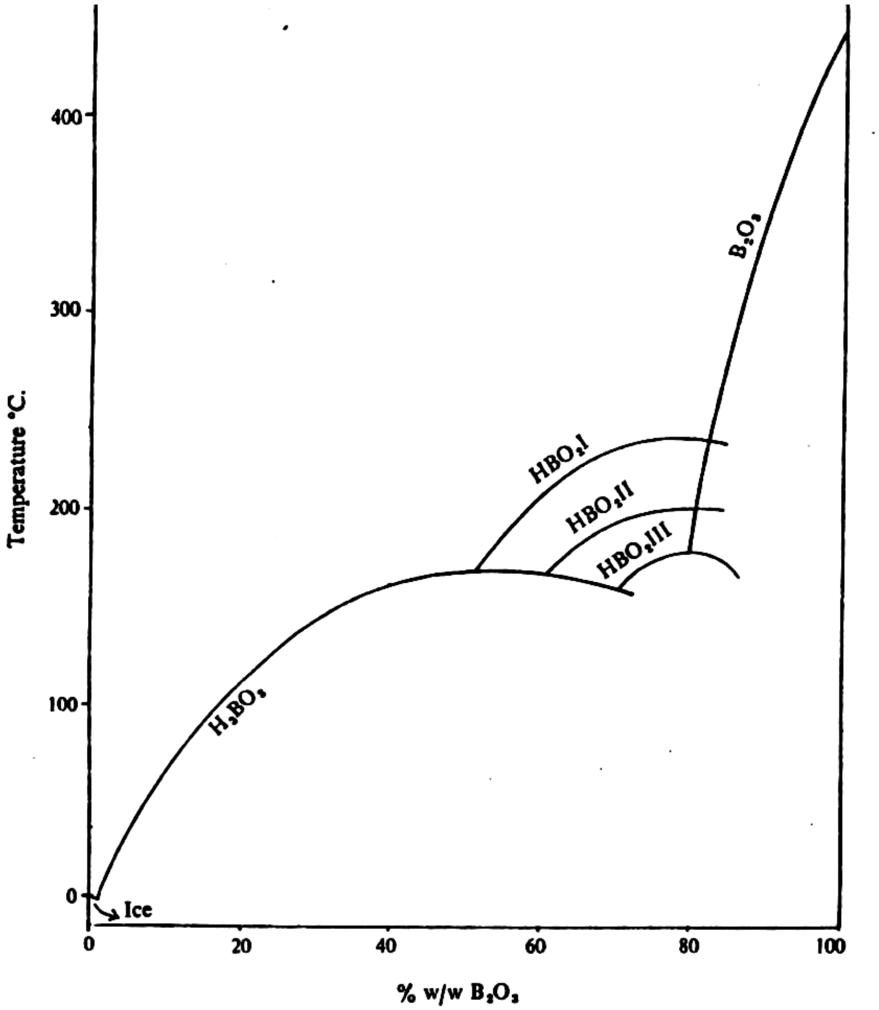
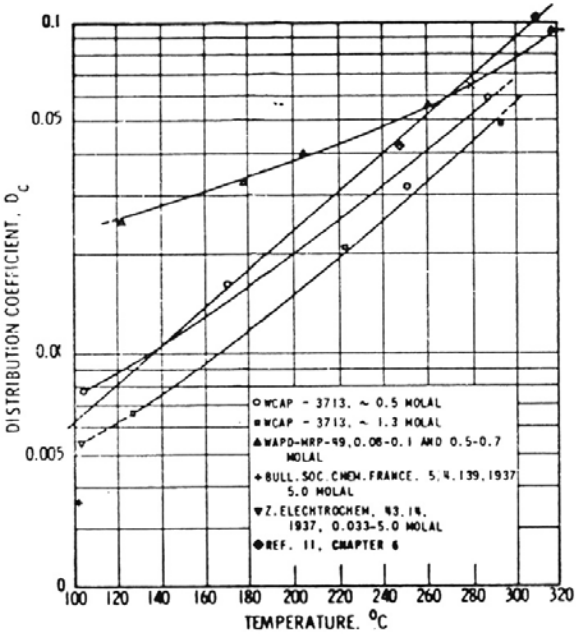


Figure 1
Phase diagram for the system $B_2O_3 - H_2O$(19).

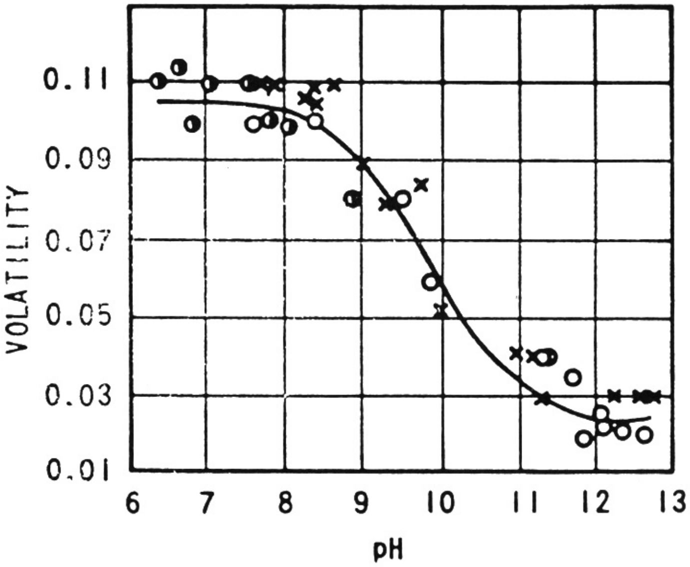
Background
Boric Acid Properties—Patent Literature

- Crystallization of B_2O_3 from H_3BO_3 Melts
  - Can take 1 to 30 days for initiation of B_2O_3 precipitation
  - Speed of transformation varies with temperature and purity
    - Transformation fastest between 220 and 250°C
    - Transformation faster with lower purity H_3BO_3
  - Process accelerated by “seeds” of B_2O_3
- Softening of B_2O_3 at about 325°C

Background
Boric Acid Properties—Boric Acid Volatility



Volatility of Boric Acid from
its Aqueous Solution*

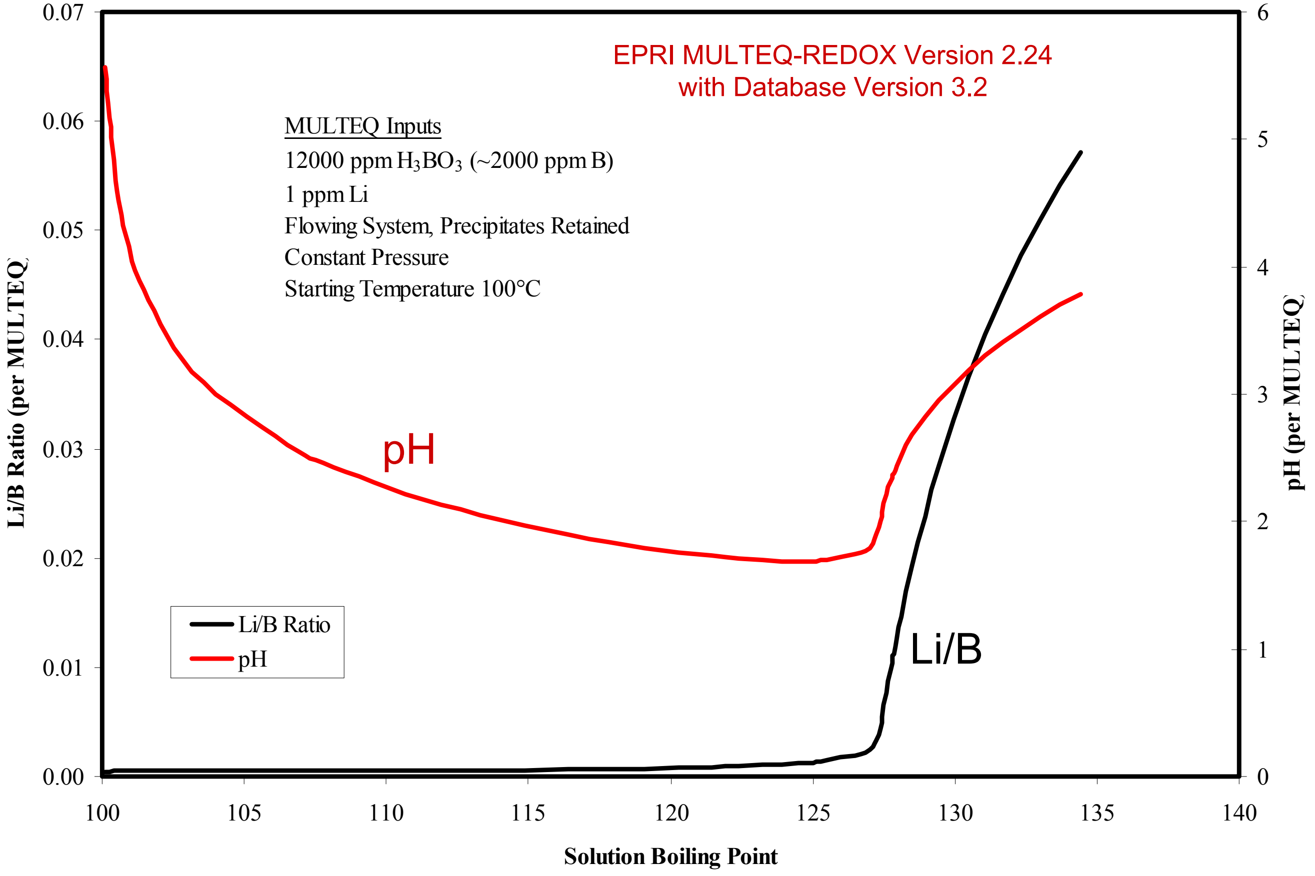


Effect of Low Temperature pH on the
Volatility of Boric Acid at 1500 psia*

- Increased boric acid volatility at higher temperatures limits ability to concentrate, increasing Li/B ratio

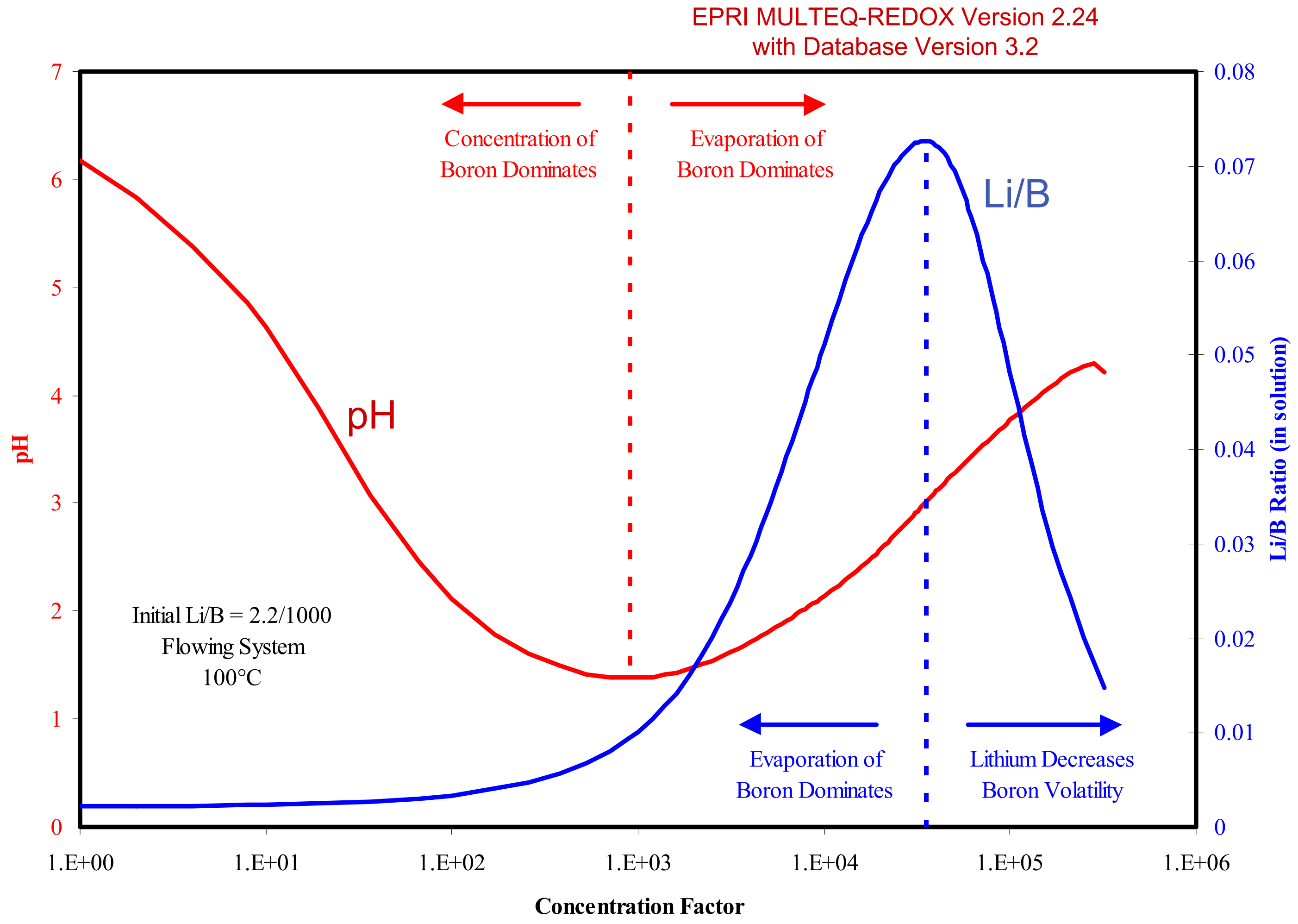
*Source: *Boric Acid Application Guidelines for Intergranular Corrosion Inhibition*, EPRI, Palo Alto, CA: 1987. NP-5558.

Background
MULTEQ Equilibrium Model of Li/B Ratio & pH



Cautionary Note: The literature indicates that $H_3BO_3/BO_2/H_2O$ systems have long equilibrium times, and MULTEQ does not predict the formation of expected precipitates.

Background
MULTEQ pH in a Flowing System at 100°C



Immersion Test Setup
Closed Vessel

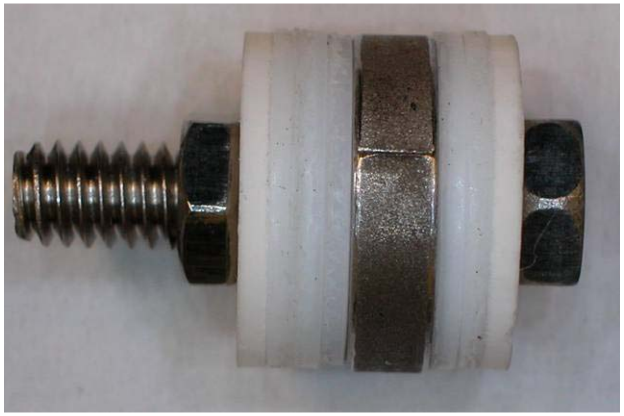
Glass Coupon Holder

Closed 300 ml Stainless Steel (T316) Vessel

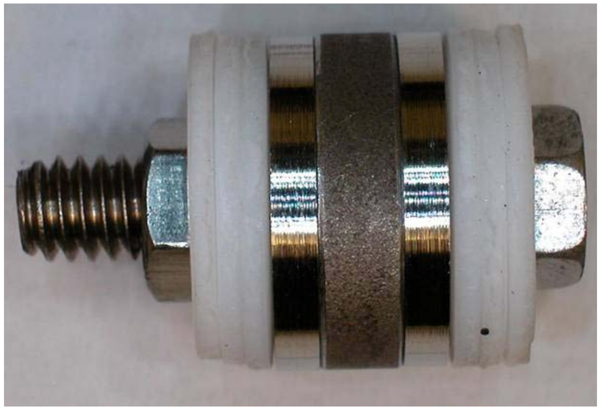
Immersion Test Setup
Test Coupons

Free Specimen

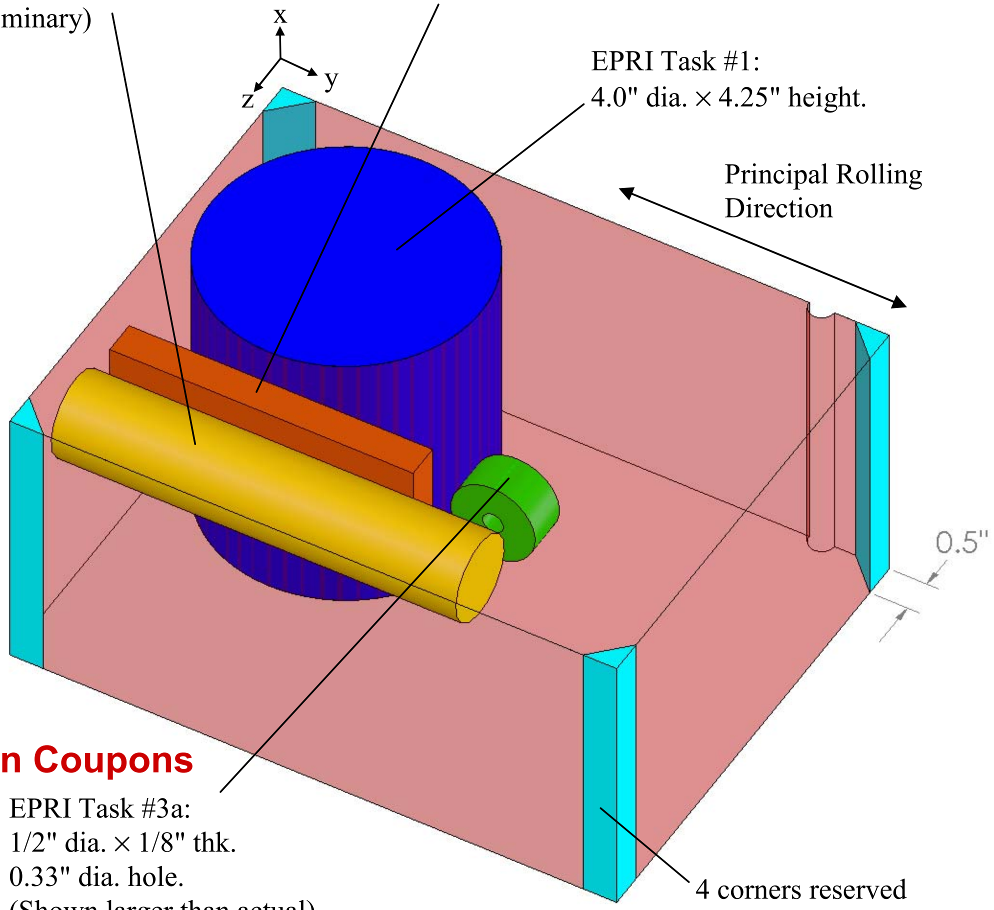
Creviced Specimen



Galvanically Coupled Specimen



Immersion Test Setup
Coupon Orientation versus Original Plate



EPRI Task #3c:
1/4" dia. × 6" length.
(Shown larger than actual)
(Preliminary)

EPRI Task #2:
4.5" × 1.0625" × 0.55"

EPRI Task #1:
4.0" dia. × 4.25" height.

Principal Rolling Direction

Immersion Coupons

EPRI Task #3a:
1/2" dia. × 1/8" thk.
0.33" dia. hole.
(Shown larger than actual)

4 corners reserved for metallography

Immersion Test Setup
Test Parameters and Measured Results

Test Parameters

- Boric Acid Concentration
- Lithium Concentration
  - $[H_3BO_3]$ & [Li] give pH_T
- Oxygen Concentration
- Temperature

Measured Results

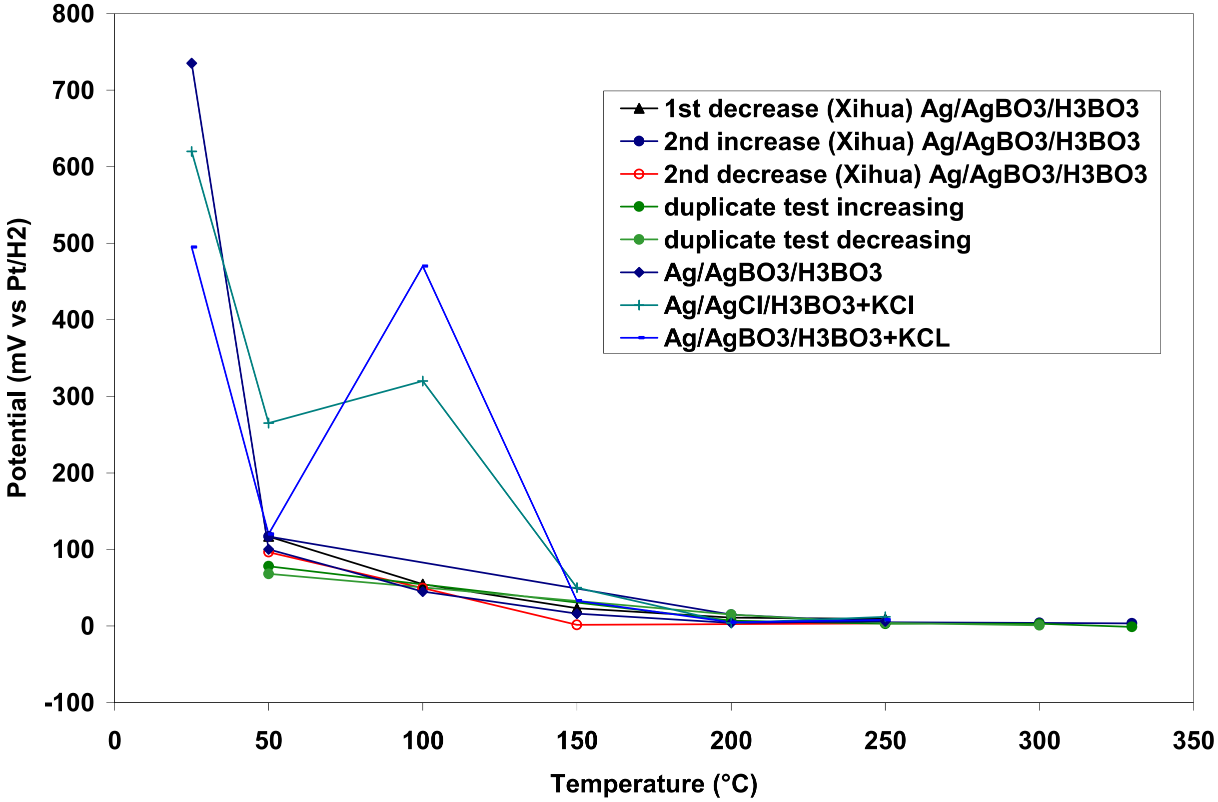
- Average Corrosion Rate
  - Microscopy (optical & SEM/EDS)
  - Weight Loss
  - Dissolved Iron
- Corrosion Product ID
  - XRD
  - SEM/EDS

Immersion Test Setup
Electrode Development

- Specialized electrodes have been developed for concentrated boric acid and molten H-B-O environments at elevated temperature and pressure
- Work performed by Pennsylvania State University (Digby Macdonald)
- Candidate ECP and pH electrodes were prepared and electrochemical potential measured as function of temperature

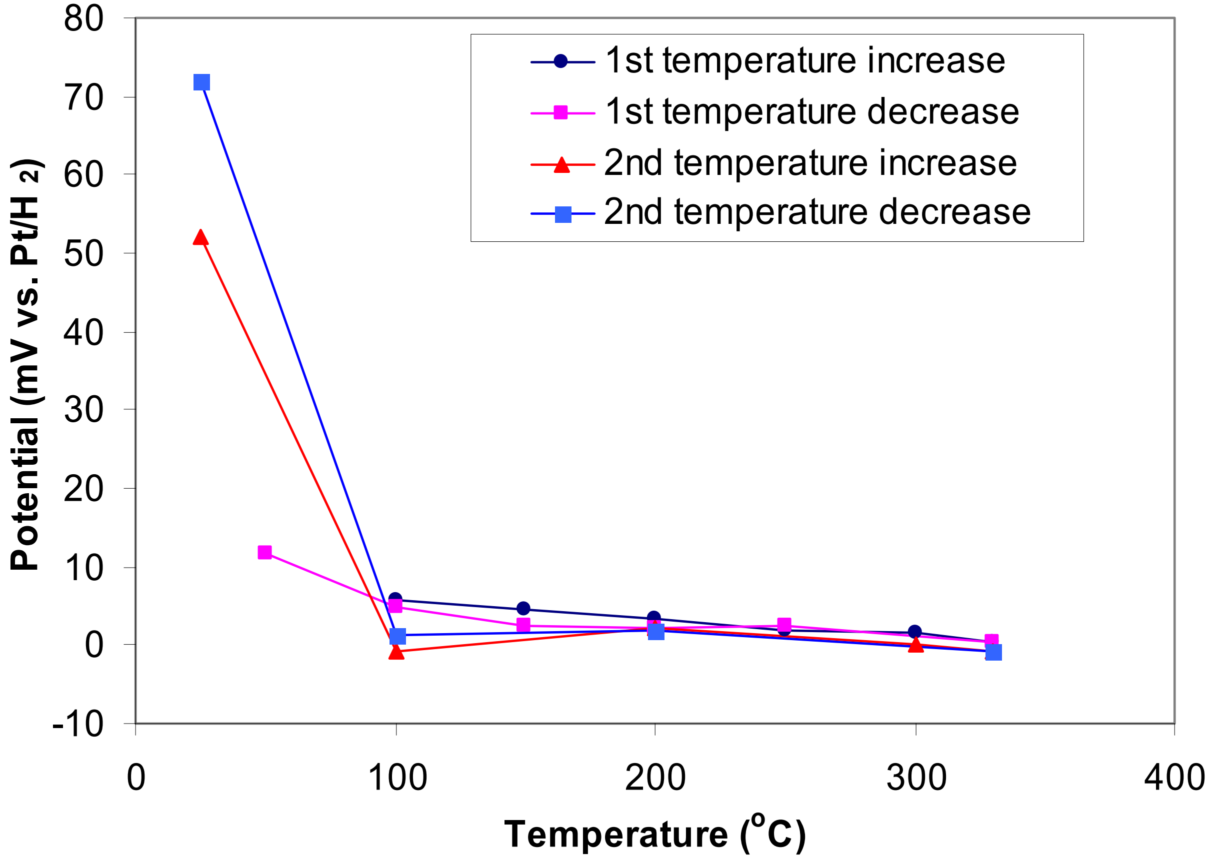
Electrode	Electrolyte	Temperature Range (°C)
Ag/Ag_3BO_3	H_3BO_3	25 ~ 330
Ag/Ag_3BO_3	H_3BO_3+KCl	25 ~ 250
Ag/AgCl	H_3BO_3+KCl	25 ~ 250
W/WO_3	H_3BO_3+NaOH	50 ~ 330

Immersion Test Setup
Reference Electrode Potential Measurements



Potentials of the Silver-Silver Borate and Silver-Silver Chloride reference electrode as a function of temperature

Immersion Test Setup
Reference Electrode Potential Measurements



Performance of the W/WO_3 (H_3BO_3, NaOH) reference electrode as function of temperature

Immersion Test Setup
Electrode Development

- Silver-Silver Borate and Tungsten-Tungsten Oxide reference electrodes selected for DEI electrochemical tests
- Tungsten-Tungsten Oxide electrode selected for sensing electrode to measure pH for conditions tested in immersion tests and for DEI chemical concentration tests
- Work in Progress
  - Qualification of reference electrodes
    - Quantify electrode performance by calibrating to the Standard Hydrogen Electrode scale
  - Qualification of pH Sensor
    - Demonstrate insensitivity to redox conditions (H_2)
    - Relate measured potential to “pH” using molten $B(OH)_3$ + trifluoromethane sulfonic acid buffer

Immersion Test Results
Initial Test Matrix (Oxygenated Conditions)

Test #	Temperature °C	[H_3BO_3]		[$LiOH-H_2O$]	
		g/kg_{water}	basis	g/kg_{water}	basis
1	100	11.4	2000 ppm B	0	Li/B = 0
2	100	1000	50:50 slurry	0	Li/B = 0
3	100	9000	10% water	0	Li/B = 0
4	100	11.4	2000 ppm B	0.024	Li/B = 0.002
5	100	1000	50:50 slurry	2.13	Li/B = 0.002
6	100	9000	10% water	19.54	Li/B = 0.002
7	100	11.4	2000 ppm B	0.607	Li/B = 0.05
8	100	1000	50:50 slurry	56.22	Li/B = 0.05
9	100	9000	10% water	919.5	Li/B = 0.05
10	200	11.4	2000 ppm B	0	Li/B = 0
11	200	1000	50:50 slurry	0	Li/B = 0
12	200	9000	10% water	0	Li/B = 0
13	200	11.4	2000 ppm B	0.024	Li/B = 0.002
14	200	1000	50:50 slurry	2.13	Li/B = 0.002
15	200	9000	10% water	19.54	Li/B = 0.002
16	200	11.4	2000 ppm B	0.607	Li/B = 0.05
17	200	1000	50:50 slurry	56.22	Li/B = 0.05
18	200	9000	10% water	919.5	Li/B = 0.05
19	315	11.4	2000 ppm B	0	Li/B = 0
20	315	1000	50:50 slurry	0	Li/B = 0
21	315	9000	10% water	0	Li/B = 0
22	315	11.4	2000 ppm B	0.024	Li/B = 0.002
23	315	1000	50:50 slurry	2.13	Li/B = 0.002
24	315	9000	10% water	19.54	Li/B = 0.002
25	315	11.4	2000 ppm B	0.607	Li/B = 0.05
26	315	1000	50:50 slurry	56.22	Li/B = 0.05
27	315	9000	10% water	919.5	Li/B = 0.05

- Base Test Length = 7 days
- Some tests showing relatively low or high corrosion rates repeated with a different test length between 2 and 10 days

Immersion Test Results

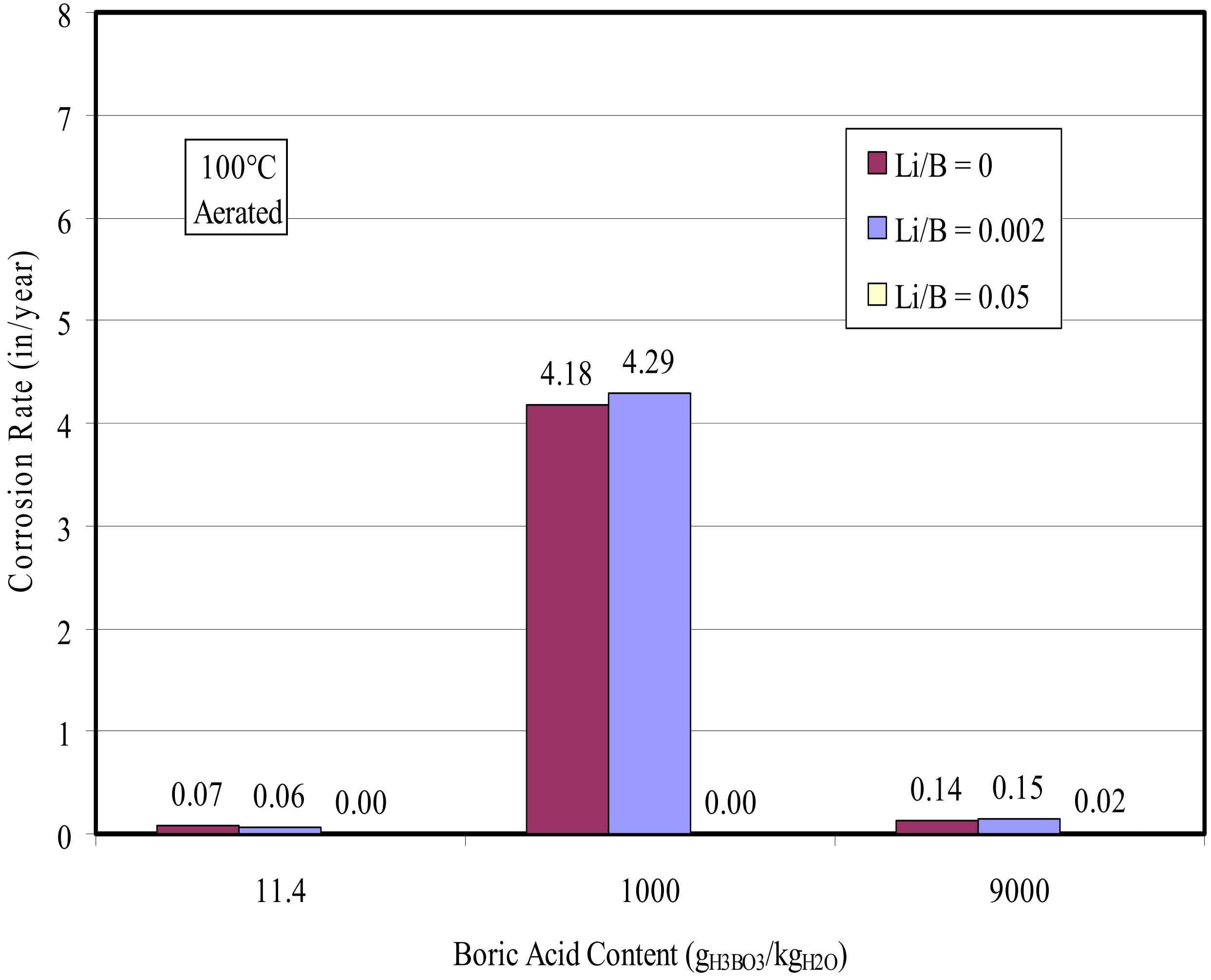
Examples of Coupon Condition after 7 days

Initial
Condition

Mild Corrosion
(Test #6)

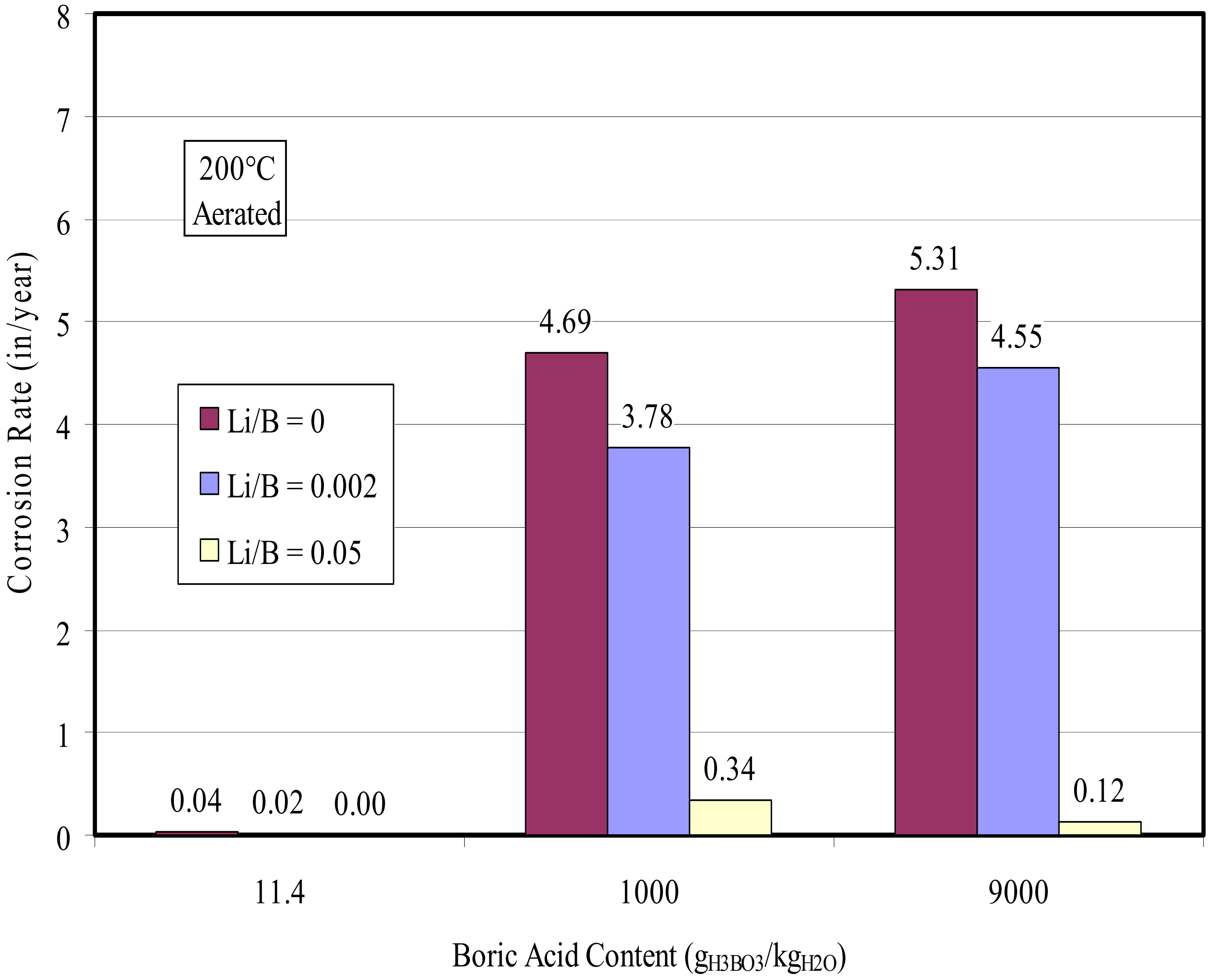
Complete Corrosion
(Test #11)

Immersion Test Results
Oxygenated General (Free) Corrosion—100°C

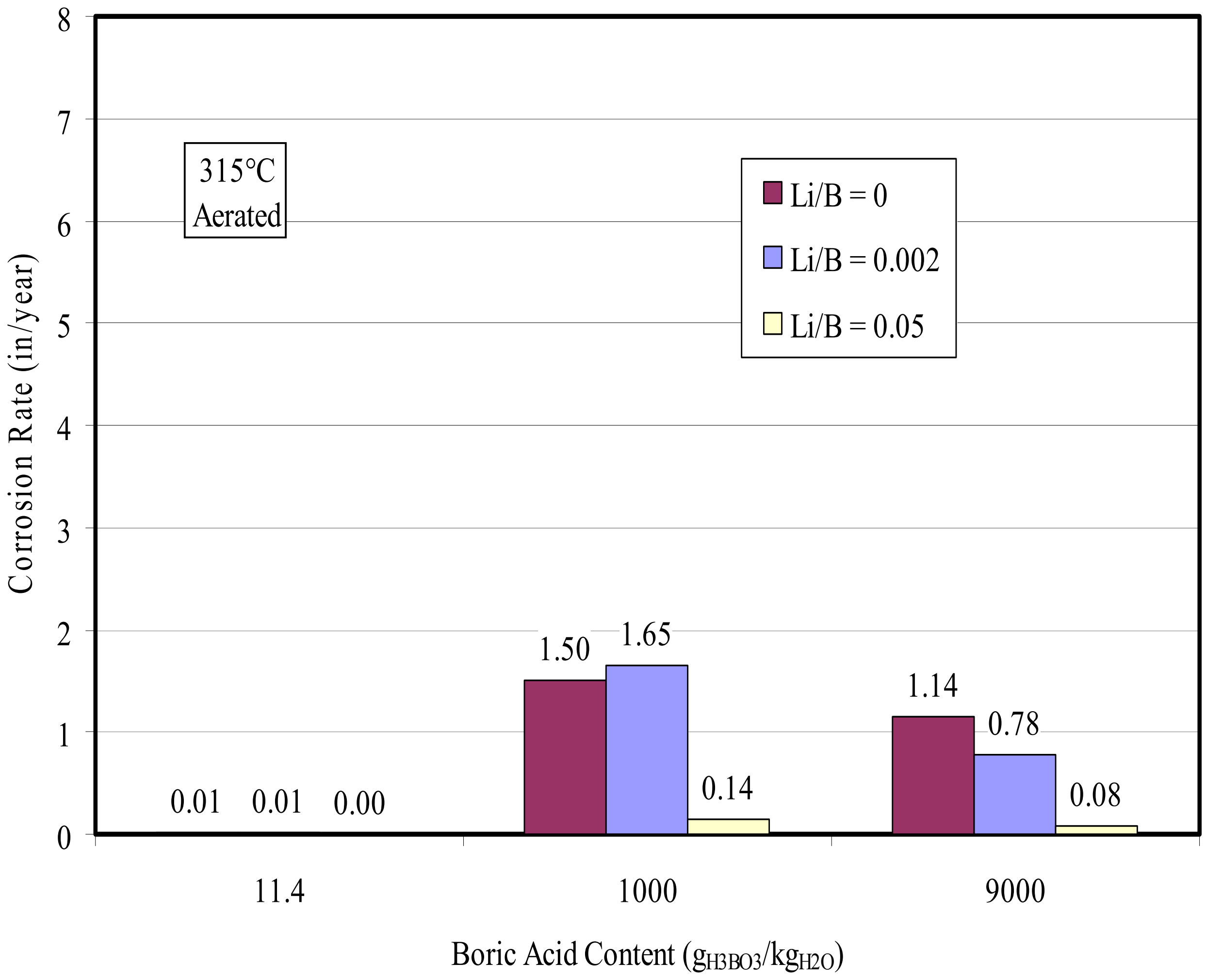


Immersion Test Results

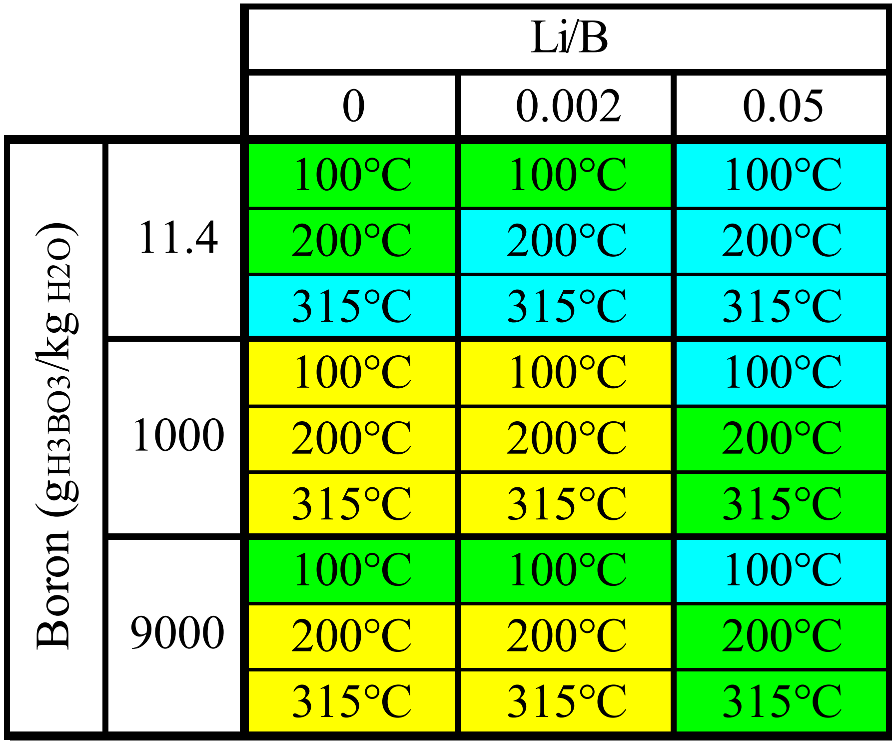
Oxygenated General (Free) Corrosion—200°C



Immersion Test Results
Oxygenated General (Free) Corrosion—315°C



Immersion Test Results
Conclusions Regarding General Corrosion



		Li/B		
		0	0.002	0.05
Boron ($g_{H_3BO_3}$/kg $_{H_2O}$)	11.4	🟩 100°C	🟩 100°C	🟦 100°C
		🟩 200°C	🟦 200°C	🟦 200°C
		🟦 315°C	🟦 315°C	🟦 315°C
	1000	🟨 100°C	🟨 100°C	🟦 100°C
		🟨 200°C	🟨 200°C	🟩 200°C
		🟨 315°C	🟨 315°C	🟩 315°C
	9000	🟩 100°C	🟩 100°C	🟦 100°C
		🟨 200°C	🟨 200°C	🟩 200°C
		🟨 315°C	🟨 315°C	🟩 315°C

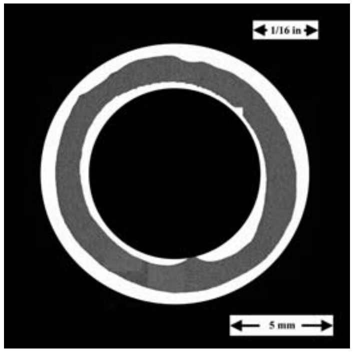
- Corrosion significantly slowed by the presence of lithium, with effect most apparent at high temperatures
- Corrosion highest at intermediate boric acid concentration (50%, versus 1% or 90%)
- Corrosion highest at intermediate temperature

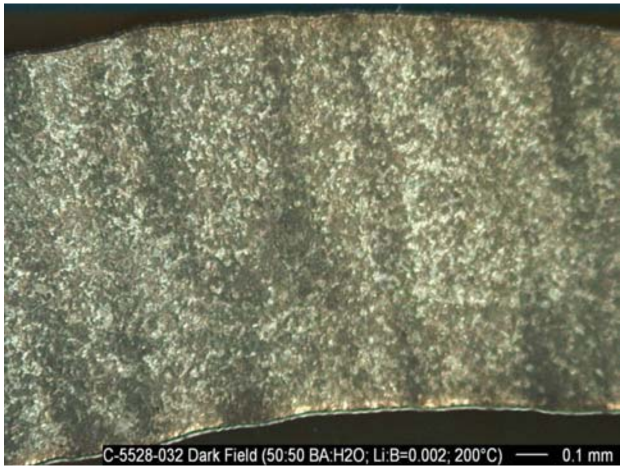
🟦 0 to 0.05 in/year
🟩 0.05 to 1 in/year
🟨 >1 in/year

Temperature effects likely related to conversion of boric acid to boric oxide, temperature dependence of volatility and dissociation constant of boric acid, and change in water vapor pressure

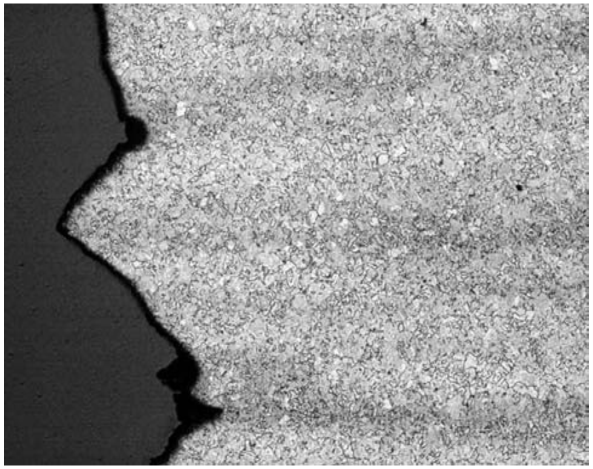
Immersion Test Results
Micrographs for Test 14

- Conditions:
  - Free coupon
  - Oxygenated
  - 200°C
  - 50:50 slurry of boric acid
  - Li/B = 0.002
- Corr. rate = 3.8 in/yr
- Coupon after test with best estimate of positions of initial surfaces:





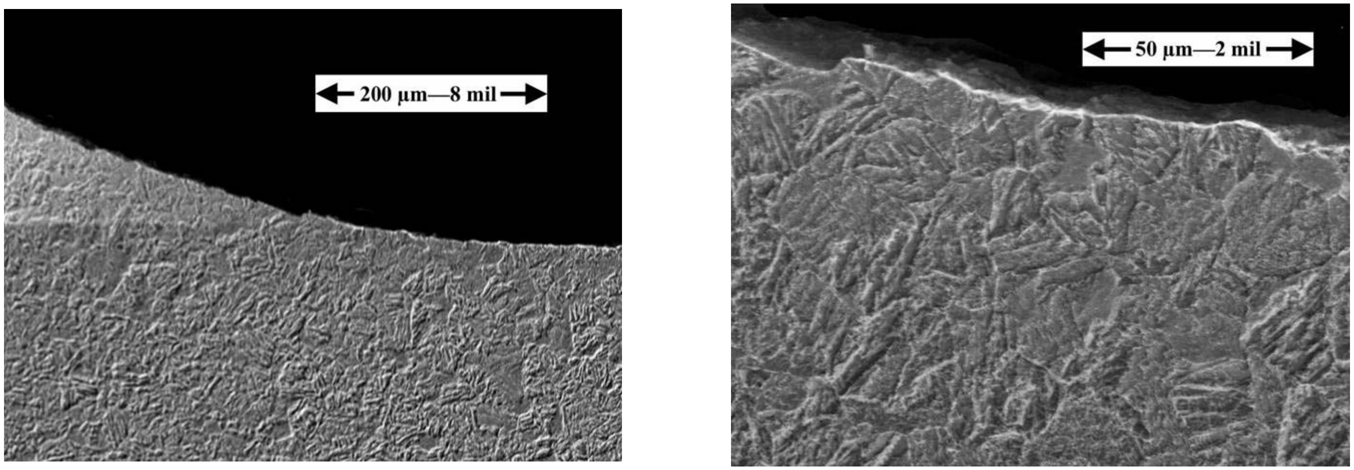
Test 14: Optical Photomicrograph for Cross Section Cut Parallel to Flat Outer Surfaces
(10% nital etchant)



Davis-Besse Cavity Low Alloy Steel Sample Showing Slightly Higher Local Corrosion Rate along Striations for Some Locations*

**Examination of the Reactor Vessel (RV) Head Degradation at Davis-Besse*, Final Report, BWXT Services, Inc., Lynchburg, VA: 2003. 1140-025-02-24.

Immersion Test Results
Micrographs for Test 14



Test 14: SEM Micrographs for Cross Section Cut Parallel to Flat Outer Surfaces
(10% nital etchant)

Micrograph for Typical Davis-Besse Low Alloy Steel*

**Examination of the Reactor Vessel (RV) Head Degradation at Davis-Besse,* Final Report, BWXT Services, Inc., Lynchburg, VA: 2003. 1140-025-02-24.

Immersion Test Results
Micrographs for Test 14—Conclusions

- The Test 14 coupon does not indicate any microstructural corrosion features, and there does not appear to be any correlation between the local corrosion rate and microstructural banding (striations)
- Two possible explanations for the apparent difference in the role of striations versus Davis-Besse cavity samples:
  - Since the striations are due to segregation of carbides, the bulk metal is expected to be depleted in Cr in the striation regions. The Davis-Besse material (Cr = 0.19% according to plate producer records) would have a greater level of Cr depletion compared to the immersion test material (Cr = 0.04% as measured).
  - The final stages of corrosion in the areas of the Davis-Besse cavity that showed this effect may have been less active (lower corrosion rate) than the corrosion for Test 14.
- Although the Davis-Besse samples may indicate some slight local effect of striations, microstructural differences are highly unlikely to result in any effects of engineering significance for general BAC

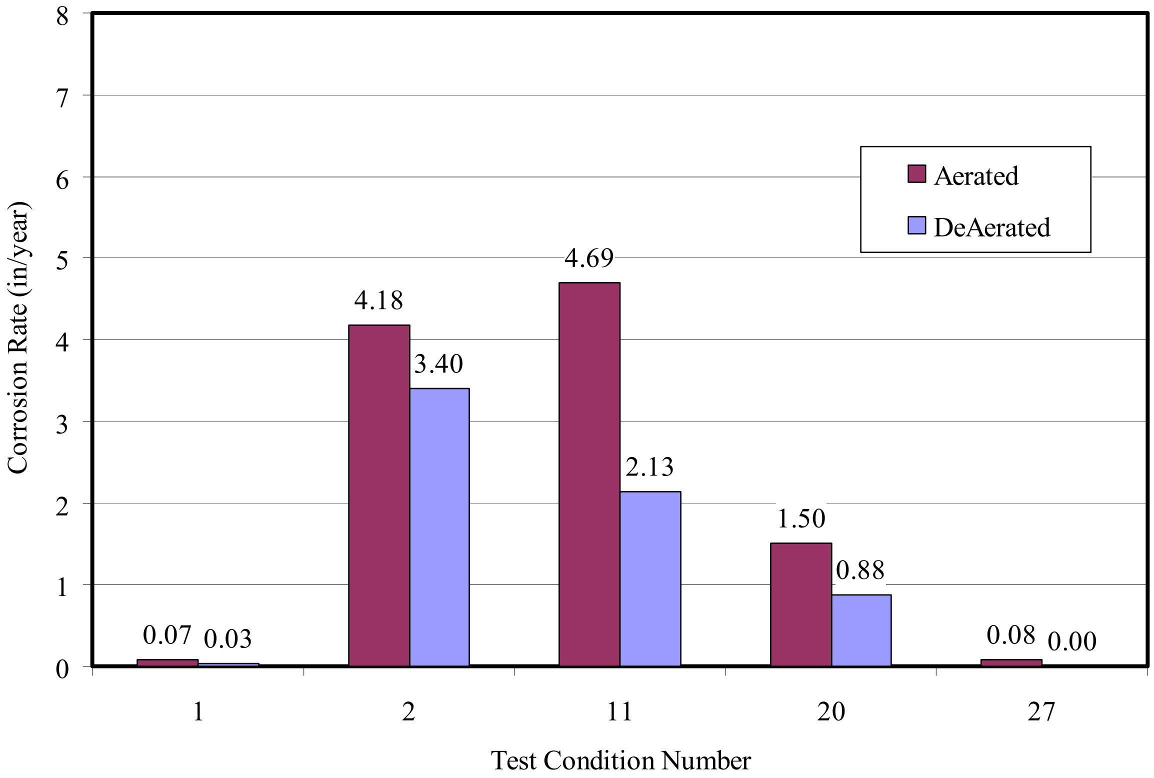
Immersion Test Results

Test Results for Deoxygenated Conditions

Nitrogen Cover Gas

Boron (g_{H3BO3}/kg_{H2O})		Li/B		
		0	0.002	0.05
	11.4	100°C	100°C	100°C
		200°C	200°C	200°C
		315°C	315°C	315°C
	1000	100°C	100°C	100°C
		200°C	200°C	200°C
		315°C	315°C	315°C
	9000	100°C	100°C	100°C
		200°C	200°C	200°C
		315°C	315°C	315°C

Test #	T (°C)	g_{H3BO3}/kg_{H2O}	Li/B
1	100	11.4	0
2	100	1000	0
11	200	1000	0
20	315	1000	0
27	315	9000	0.05

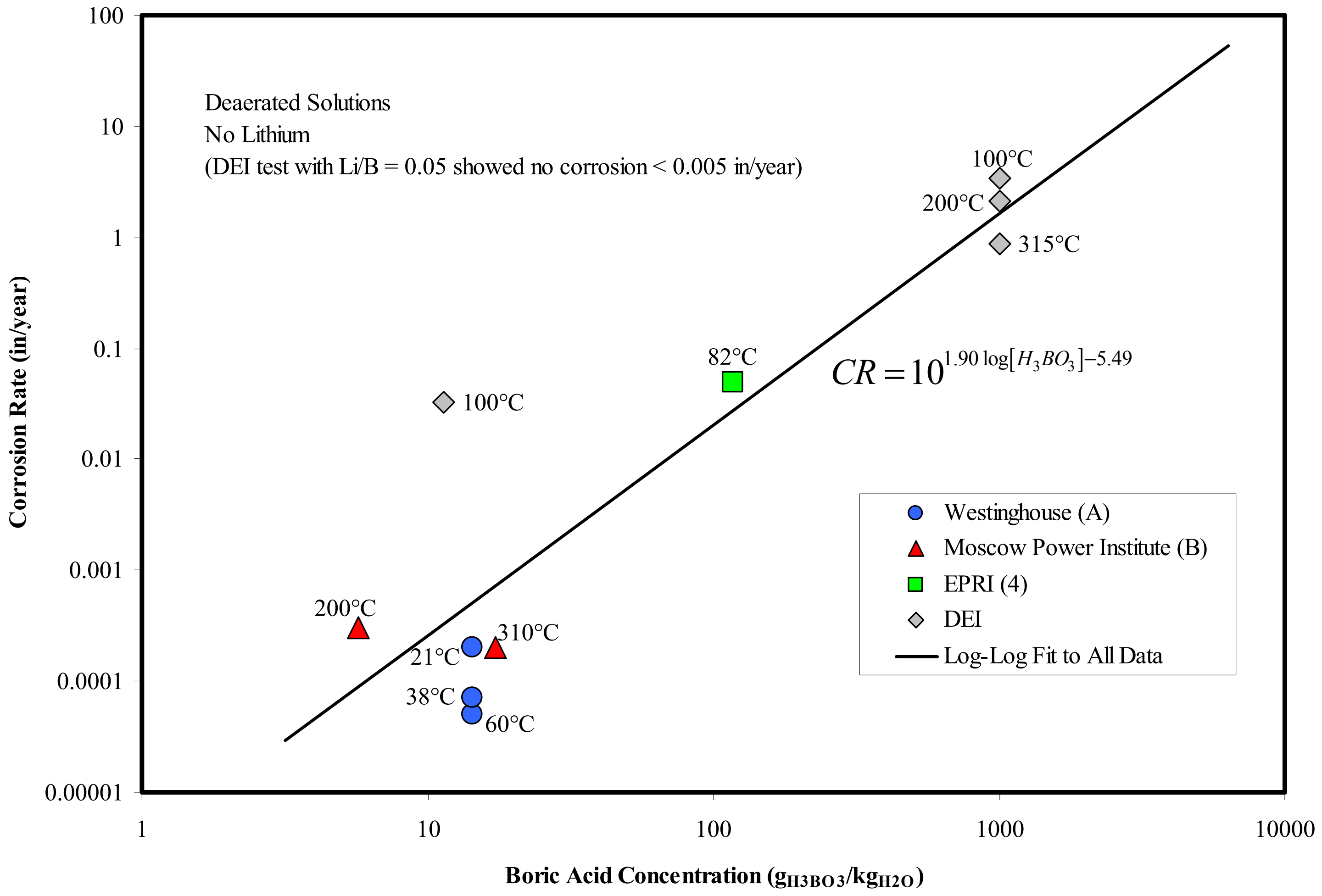


Immersion Test Results
Test Results for Deoxygenated Conditions

- Corrosion products observed to oxidize after exposure to air
  - **Indicates deoxygenated conditions were achieved and maintained**
- After test vessels were cooled to room temperature, contents were under slight pressure
  - **Consistent with a hydrogen generating corrosion mechanism**
  - **Contrasts with oxygenated vessels, which were under slight vacuum**

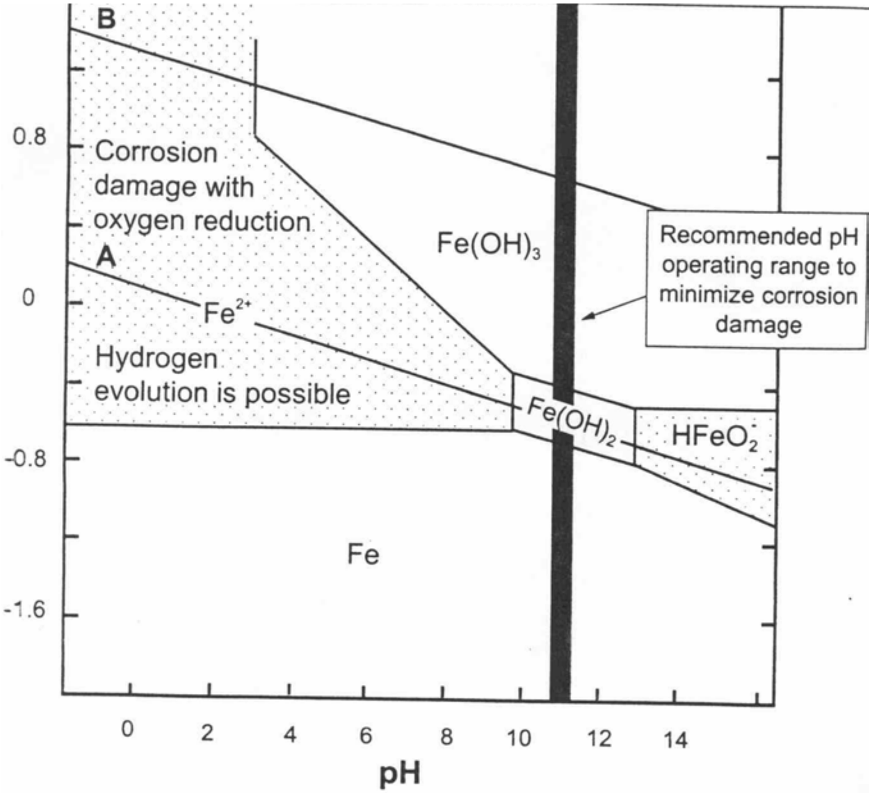
Immersion Test Results

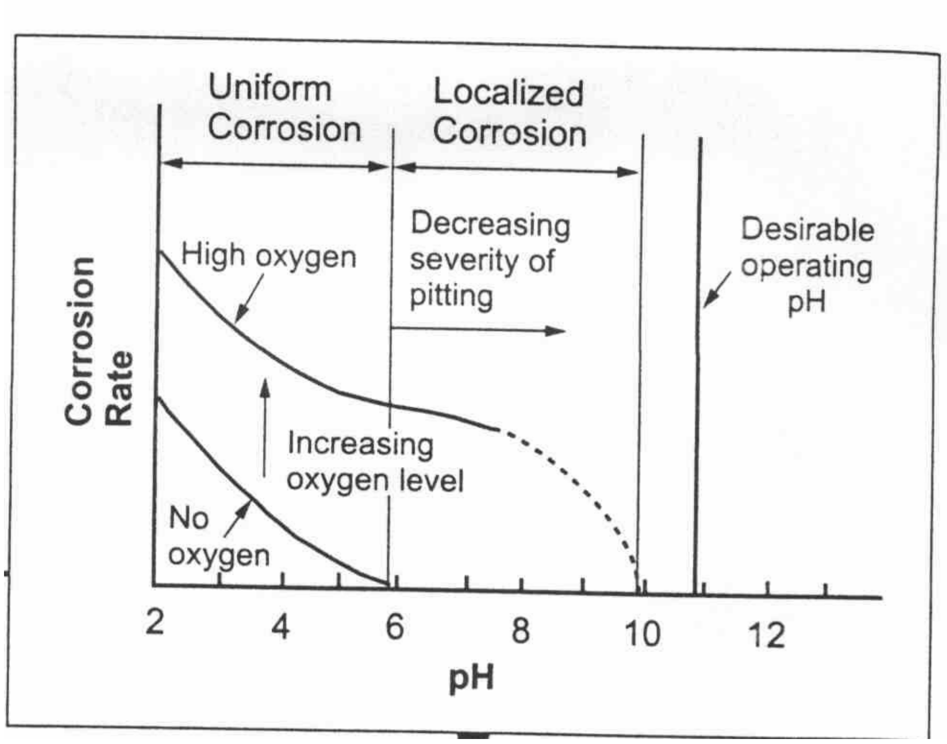
Deoxygenated Corrosion—Comparison to Literature



Immersion Test Results
Deoxygenated Corrosion Conclusions

- *Iron in Water at 25°C and 1 atm*

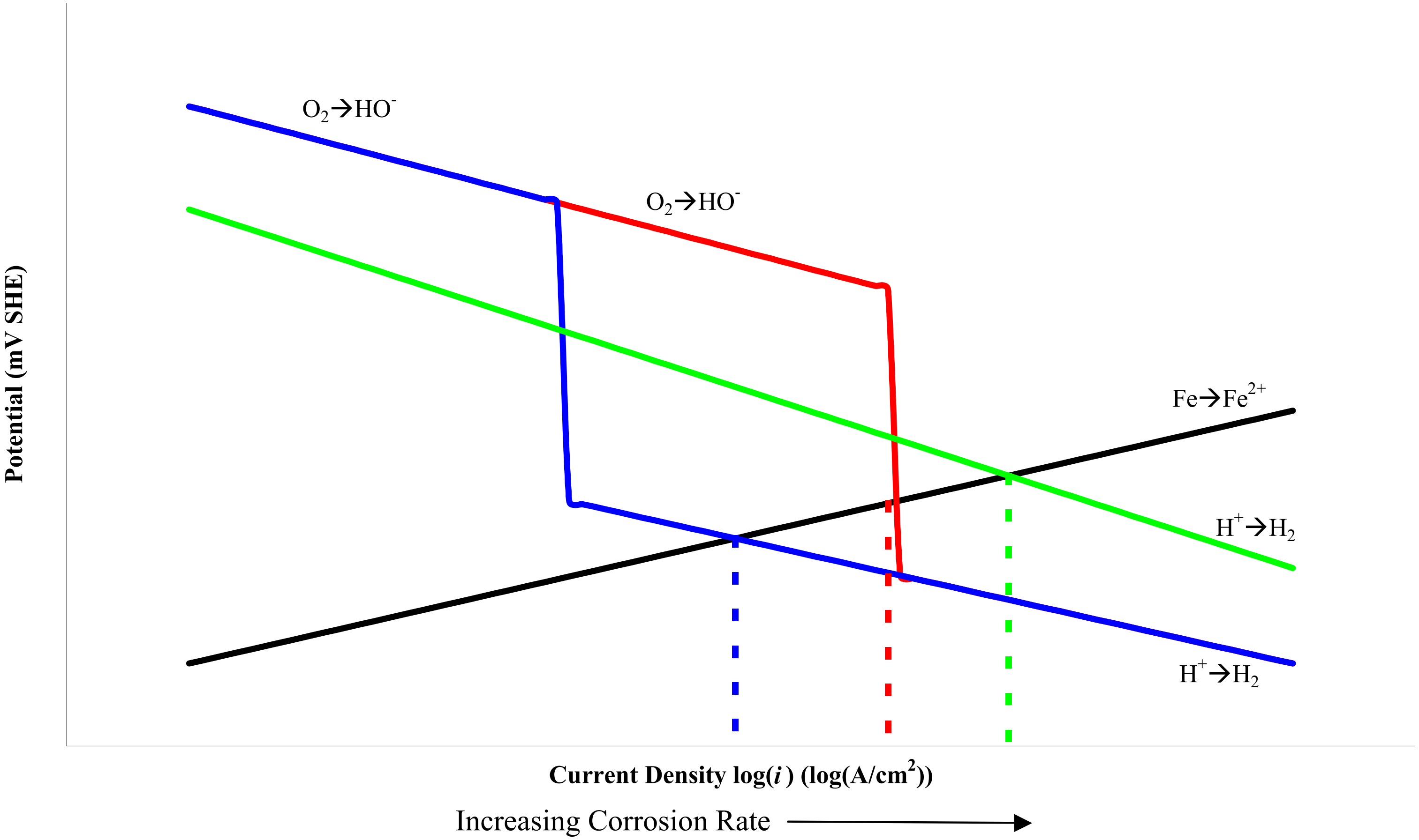




Source: P. R. Roberge, *Handbook of Corrosion Engineering*, McGraw-Hill, New York, 1999.

Immersion Test Results
Deoxygenated Corrosion Conclusions

- *Galvanic Corrosion Electrochemistry for a Non-Passivating Metal*



Immersion Test Results
Deoxygenated Corrosion Conclusions

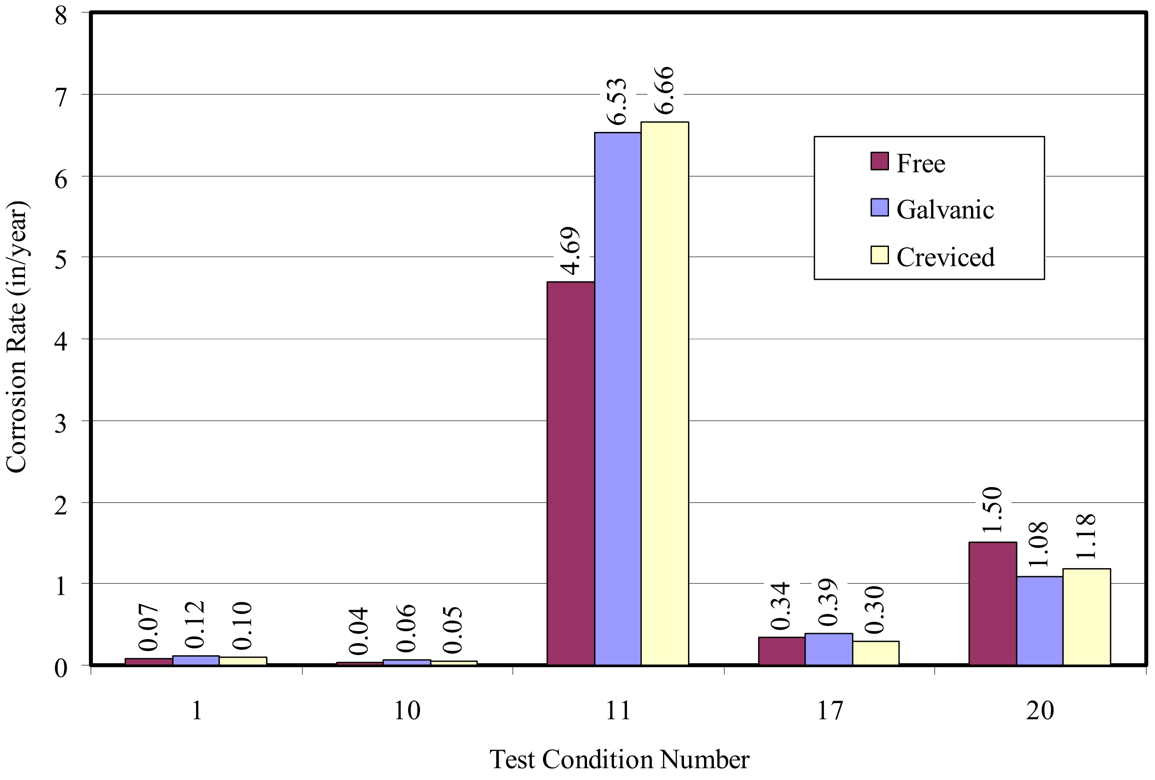
- Corrosion rates in deaerated environments are less than those in comparable aerated environments, but of the same order of magnitude
- Rates in aggressive environments are still relatively high
  - **1000 g_{H3BO3}/kg_{H2O} on the order of 2–4 in/year**
- Rates measured are comparable to literature values
  - **BAC Guidebook has limited data on very high boric acid concentrations**
  - **BAC Guidebook has no data on effect of lithium**
  - **New data not inconsistent with existing data**

Immersion Test Results
Galvanic and Crevice Corrosion Results

Oxygen Cover Gas

		Li/B		
		0	0.002	0.05
Boron (g H_3BO_3/kg H_2O)	11.4	100°C	100°C	100°C
		200°C	200°C	200°C
		315°C	315°C	315°C
	1000	100°C	100°C	100°C
		200°C	200°C	200°C
		315°C	315°C	315°C
	9000	100°C	100°C	100°C
		200°C	200°C	200°C
		315°C	315°C	315°C

Test #	T (°C)	g_{H3BO3}/kg_{H2O}	Li/B
1	100	11.4	0
10	200	11.4	0
11	200	1000	0
17	200	1000	0.05
20	315	1000	0



Immersion Test Results
Galvanic Coupon Corrosion Results

Condition #11 Free

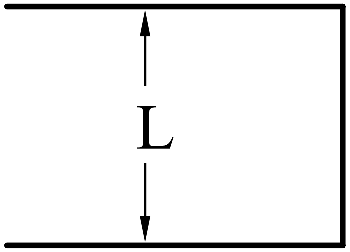
Condition #11 Galvanic

Immersion Test Results
Galvanic and Crevice Corrosion Results

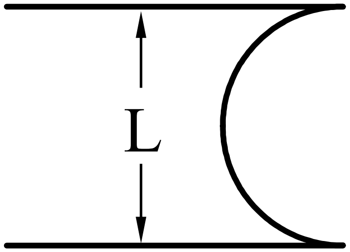
Condition
#11
Free

Condition
#11
Crevice

Condition
#11
Galvanic



$A=\pi DL$

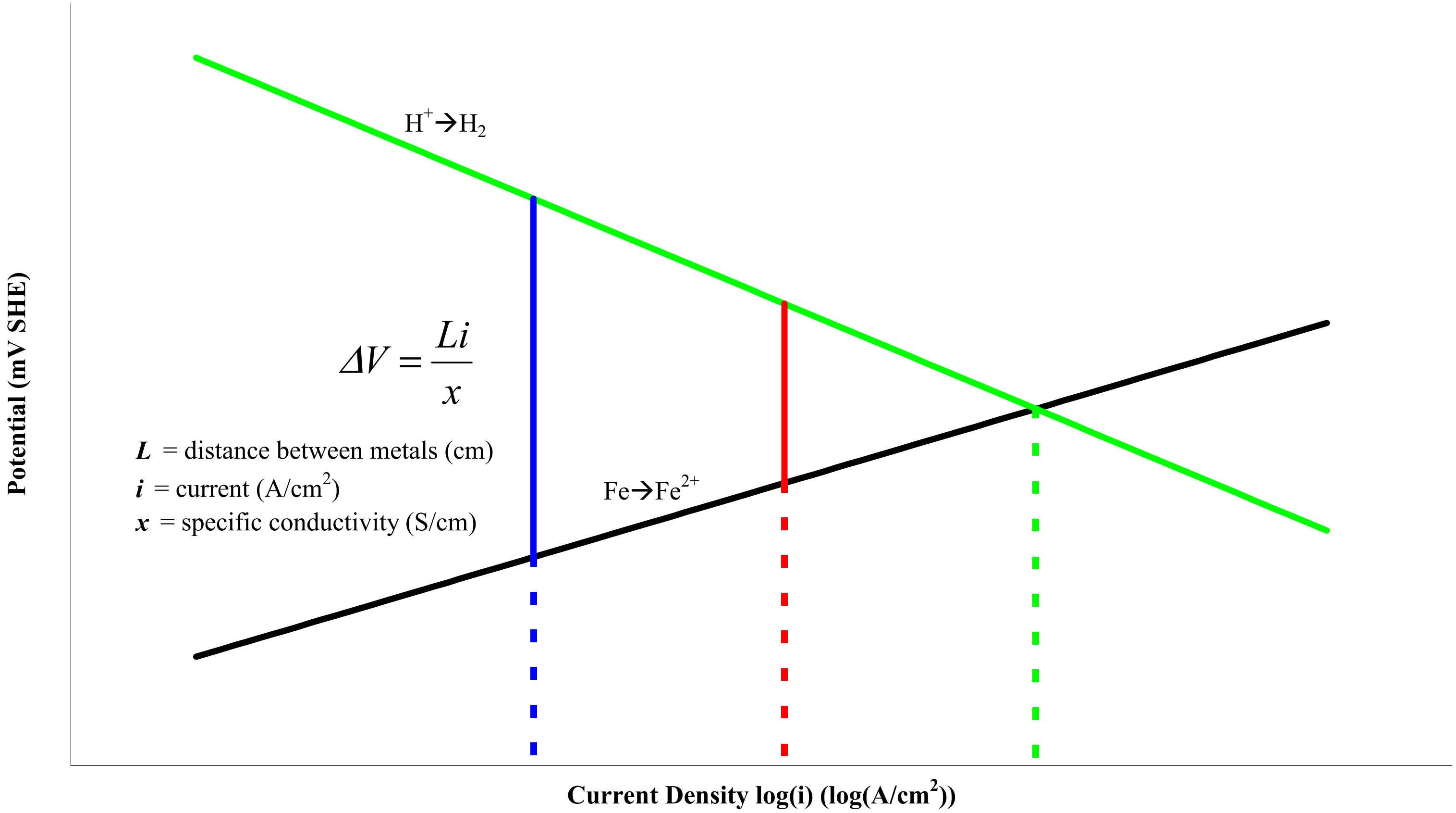


$A=\pi D(\pi L/2)$

Shape could cause factor of $\pi/2$ difference in calculated corrosion rate

Immersion Test Results
Galvanic and Crevice Corrosion Conclusions

- *IR Drop Effect acts to limit corrosion rate because of solution resistance between separated anodic and cathodic sites*



$$\Delta V = \frac{Li}{x}$$

L = distance between metals (cm)
i = current (A/cm^2)
x = specific conductivity (S/cm)

Increasing Corrosion Rate →

Immersion Test Results
Galvanic and Crevice Corrosion Conclusions

- No significant changes in corrosion rates for creviced or galvanically coupled coupons compared to freely exposed coupons
- No visual evidence of crevice corrosion
- Possible gross morphological differences
  - May indicate mild overestimation of actual corrosion rate as the corrosion rate was calculated based on initial coupon surface area

Immersion Test Results
Overall Conclusions to Date

- Corrosion rates up to about 6 inches/yr were observed for the laboratory conditions tested
- Corrosion significantly slowed by the presence of lithium, with effect most apparent at high temperatures
- Corrosion greatest at intermediate temperatures and boric acid concentration (50%, versus 1% or 90%)
- For high boric acid concentrations, no large reduction in corrosion rate due to deaeration for laboratory conditions tested
  - pH measurements will be used to verify that this is due to low pH
  - Corrosion rates under deoxygenated conditions were about half to two-thirds of the rate under the corresponding oxygenated conditions
- No significant acceleration due to galvanic coupling or crevices

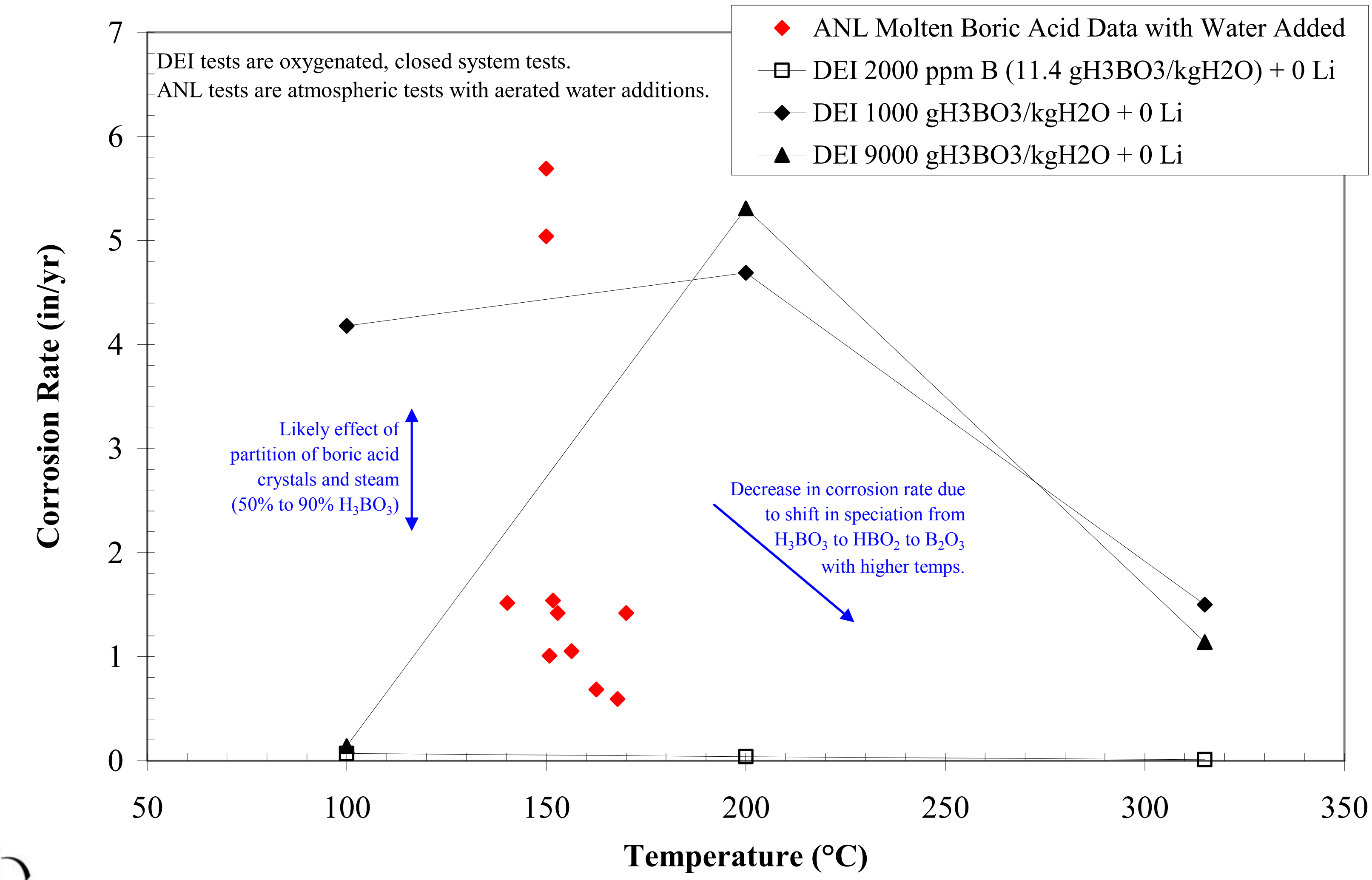
Comparison to ANL Results
Introduction

- ANL corrosion testing with molten boric acid was performed in 2003-04:
  - **No corrosion detected for Alloy 600 and Type 308 stainless steel**
  - **No corrosion detected for reactor vessel steel in dehydrated molten boric acid at 150, 260, and 300°C**
  - **High corrosion rates (0.6-6.0 in/yr) were measured for reactor vessel steel in molten boric acid with water additions at 140-170°C (40-45 hour tests)**
- Previous immersion testing has been performed under aerated concentrated boric acid solution conditions but not under the molten boric acid (H-B-O) conditions

Comparison to ANL Results
Introduction (cont'd)

- Relatively high leak rates (e.g., ~0.1 gpm) may be required to produce local cooling close to 100°C, which is necessary to support the presence of moisture in concentrated boric acid solutions at pressures at or near atmospheric pressure
- Hydrated molten boric acid (H-B-O) conditions could conceivably occur under smaller leak rates (and higher temperatures), which are less readily detectable than larger leaks
- The rate of moisture additions (from a leak) to the molten boric acid mixture must match or exceed the rate of dehydration (drying) for a hydrated molten boric acid environment to persist

Comparison to ANL Results
DEI Results with No Lithium



DEI tests are oxygenated, closed system tests.
ANL tests are atmospheric tests with aerated water additions.

Likely effect of partition of boric acid crystals and steam (50% to 90% H_3BO_3)

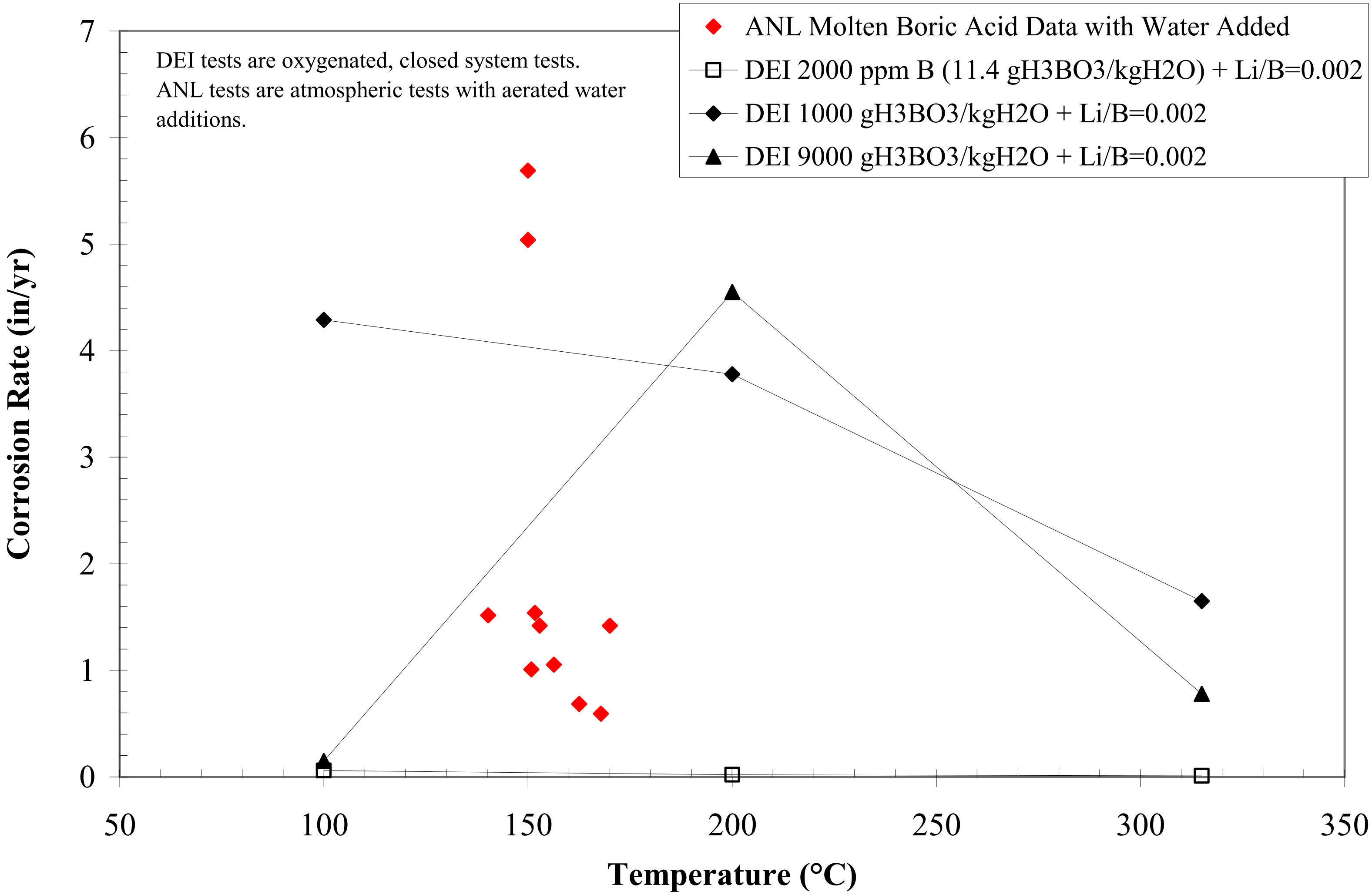
Decrease in corrosion rate due to shift in speciation from H_3BO_3 to HBO_2 to B_2O_3 with higher temps.

Comparison to ANL Results
Discussion

- The potential for high corrosion rates under wetted molten boric acid conditions was confirmed by the DEI immersion tests
- Key factors indicate that the hydrated molten boric acid environments that produced high laboratory corrosion rates may not be applicable to operating plants:
  - **Li from primary water acts to buffer the pH and reduce corr. rates**
  - **It may be very difficult under plant conditions to keep molten boric acid hydrated**
  - **Over time, viscous boron species and/or corrosion products may act as a physical barrier protective of the steel surface**
  - **For the annulus environment on the nozzle OD, the high ratio of low alloy steel surface area to solution volume may facilitate buffering of the solution pH after initial dissolution of iron into the solution, lowering the subsequent corrosion rate**
- Plant experience with leaking J-groove penetrations indicates little potential for sustained high corr. rates for relatively small leak rates

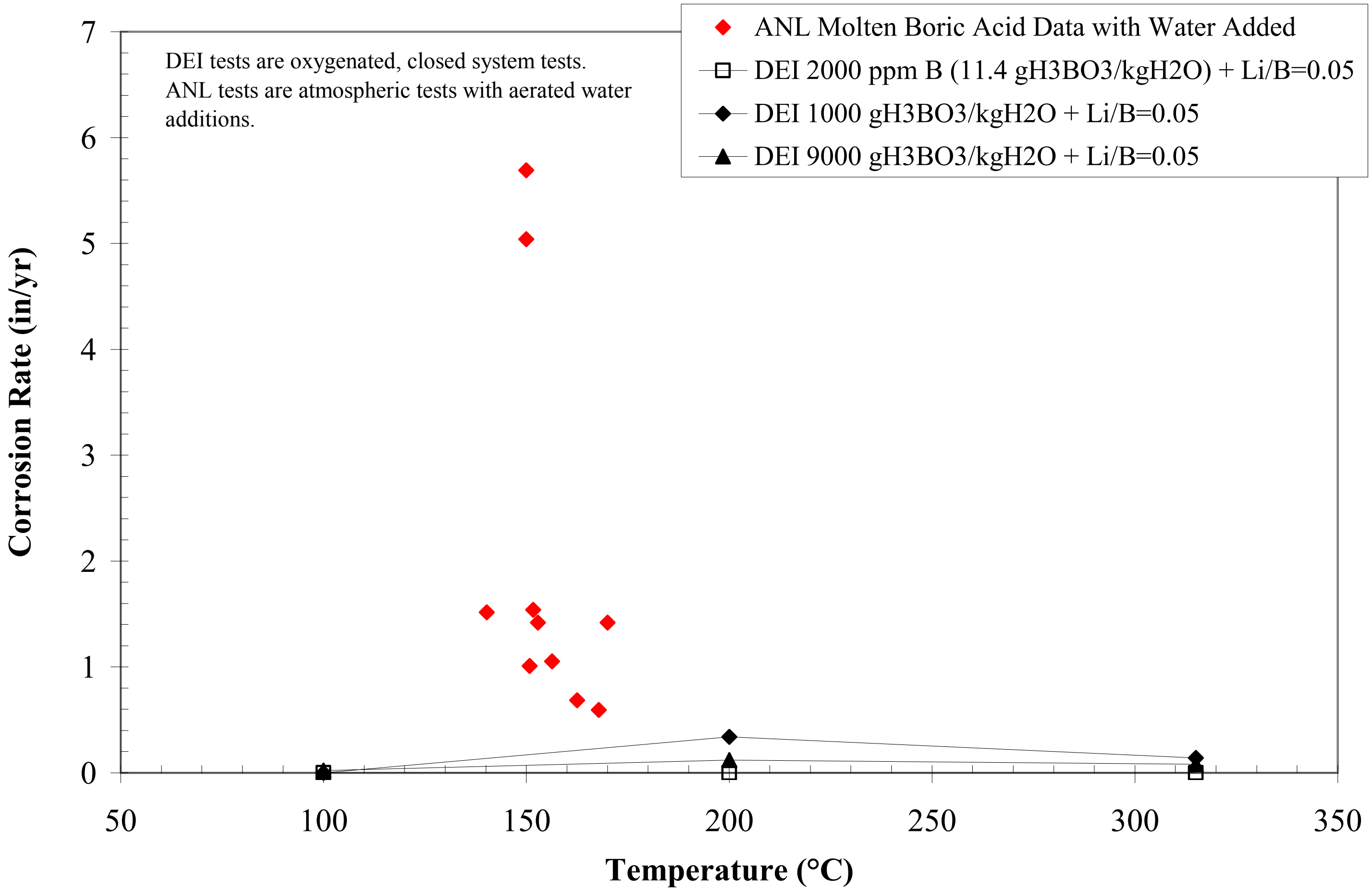
Comparison to ANL Results

DEI Results for Lithium Ratio of Li/B = 0.002



Comparison to ANL Results

DEI Results for Lithium Ratio of Li/B = 0.05



- Increased boric acid volatility at higher temperatures limits ability to concentrate, increasing Li/B ratio and lowering corrosion rate

Comparison to ANL Results
Discussion (cont'd)

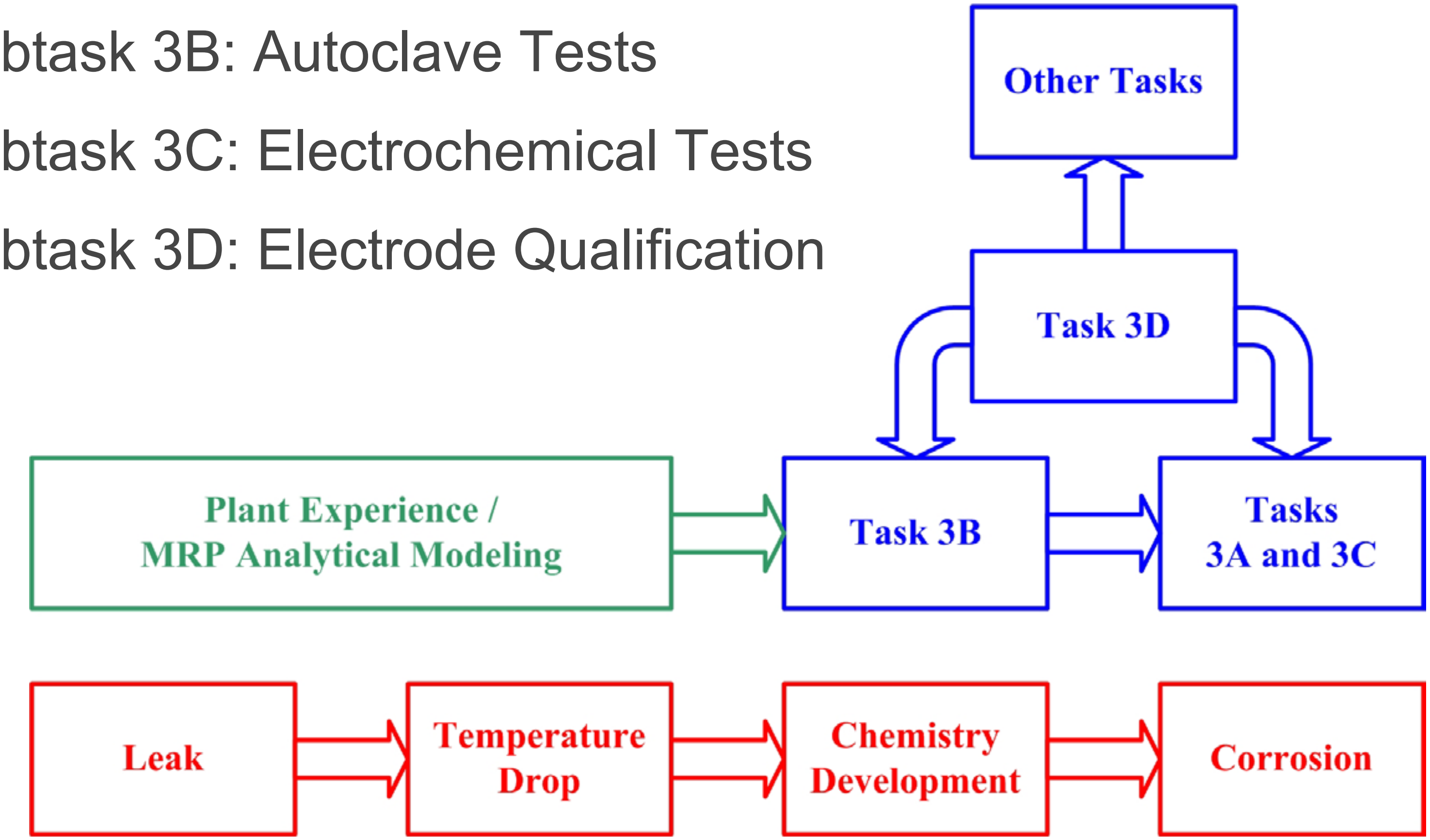
- One major purpose of other MRP BAC tests is to determine what types of molten boric acid environments can be produced under plant conditions
  - Task 3B chemical concentration tests will include, for example, pH and rate of dehydration measurements
  - Task 4 mockup tests will
    - **produce data on what types of environments can be produced under prototypical conditions as a function of leak rate**
    - **include in-testing measurements of corrosion rate to give the time dependence of the corrosion rate (including for extended durations)**
- In addition, the Task 3C electrochemical tests include molten boric acid environments to facilitate understanding of the electrochemistry of these systems

Afternoon Discussions:

Review of Planned MRP BAC Testing Addressing Molten H-B-O Environments

BAC Task 3: Separate Effects Testing
Task Structure

- Subtask 3A: Immersion Tests
- Subtask 3B: Autoclave Tests
- Subtask 3C: Electrochemical Tests
- Subtask 3D: Electrode Qualification



BAC Task 3: Separate Effects Testing

Task 3B: Autoclave Chemistry Tests

- Description:
  Autoclave tests to determine chemistry under a range of temperature, pressure, and concentration conditions in which a boric acid solution is concentrated by steaming
- Areas Addressed:
  - Basic data needed to assess various corrosion mechanisms
  - Conductivity of concentrated boric acid solutions and molten boric acid
  - Effect of large local cooling on annulus chemistry (e.g., pH)
  - Time scale for dehydration of molten boric acid
  - Time scale for development of pH, conductivity, etc.

Task 3B: Autoclave Chemistry Tests
Test Parameters and Measured Results

Test Parameters

- Source Boric Acid Concentration
- Source Lithium Concentration
- Steam Flow Rate
- Temperature

Measured Results

- pH$_T$
- Conductivity
- Electrochemical Potential
- Boric Acid Concentration
- Lithium Concentration
- Precipitate ID

Task 3B: Autoclave Chemistry Tests
Similar Data Sources

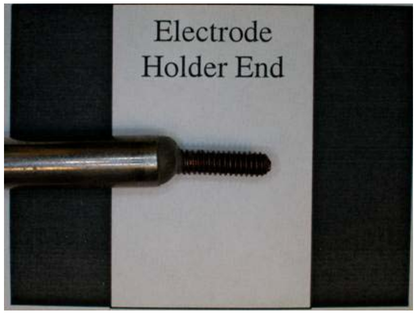
- MULTEQ
  - Not all relevant species in the database
  - May not handle extremely high concentrations correctly (molten H_3BO_3)
- Literature Data
  - Generally limited to saturation
  - Generally do not include lithium
- CEA/EDF Testing*
  - Focused primarily on concentration measurements
  - Test performed at temperature of 300°C only
  - No direct pH measurement

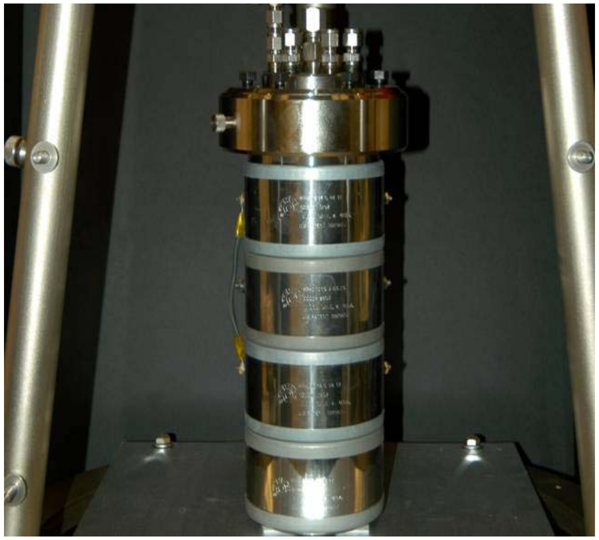
***D. You, D. Feron, and G. Turluer, "Experimental Simulation of Low Rate Primary Coolant Leaks: For the Case of Vessel Head Penetrations Affected by Through Wall Cracking," *Chimie 2002 Proceedings: International Conference Water Chemistry in Nuclear Reactors Systems: Operation Optimization and New Developments Volume 3*, Avignon, France, April 22-26, 2002, SFEN.**

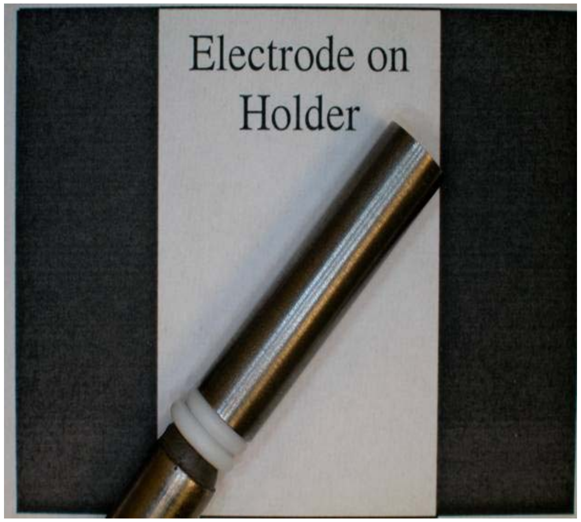
BAC Task 3: Separate Effects Testing
Task 3C: Electrochemical Tests

- Description:
  Autoclave tests to determine the corrosion rates of low alloy steel materials as a function of the electrochemical potential for the range of conditions identified in the chemistry tests
- Areas Addressed:
  - Provides theoretical basis for generalizing results
  - Anodic electrochemical polarization curves for low alloy steel in concentrated boric acid environments
  - Cathodic electrochemical polarization curves for Alloy 600 in concentrated boric acid environments

Task 3C: Electrochemical Tests
Test Equipment







Task 3C: Electrochemical Tests
Test Types and Parameters

Test Type	Sample Types	Test Parameters
Potentiodynamic Scan	Low Alloy Steel (SA 533 Gr B Cl 1)	Temperature
Linear Polarization Resistance	Alloy 600	Li/B Ratio
Potentiostatic Polarization		Boric Acid Concentration
		Scan Range
		Pre-Conditioning

Adaptations of ASTM G5/G59/G96/G102

BAC Task 4: Full Scale Mockup Tests
Program Description

Task 1 - Heated Crevice test device to address stagnant and low flow chemistry definition and their influence on corrosion rates.

Task 2 – Test in a flowing loop to address moderate and high flow condition with ability to monitor real time corrosion rates and ECP under laminar and impact flow.

Task 3 – Separate effects tests to obtain data on corrosion rates for conditions not previously tested such as galvanic coupling and corrosion in contact with molten boric acid.

Task 4 – Full scale mockup testing to determine corrosion rates under prototypical CRDM nozzle leakage conditions including full-size nozzles, interference fits, simulated crack geometries, range of leak rates from 0.0001 to 0.3 gpm, and controlled thermal conditions.

BAC Task 4: Full Scale Mockup Tests

Key Test Characteristics

- Design team collaboration
- Use existing BAC test facility
- Ultrasonic test (UT) monitoring of wastage during test
- Leak rate vs. crack geometry
- Extent of cooling

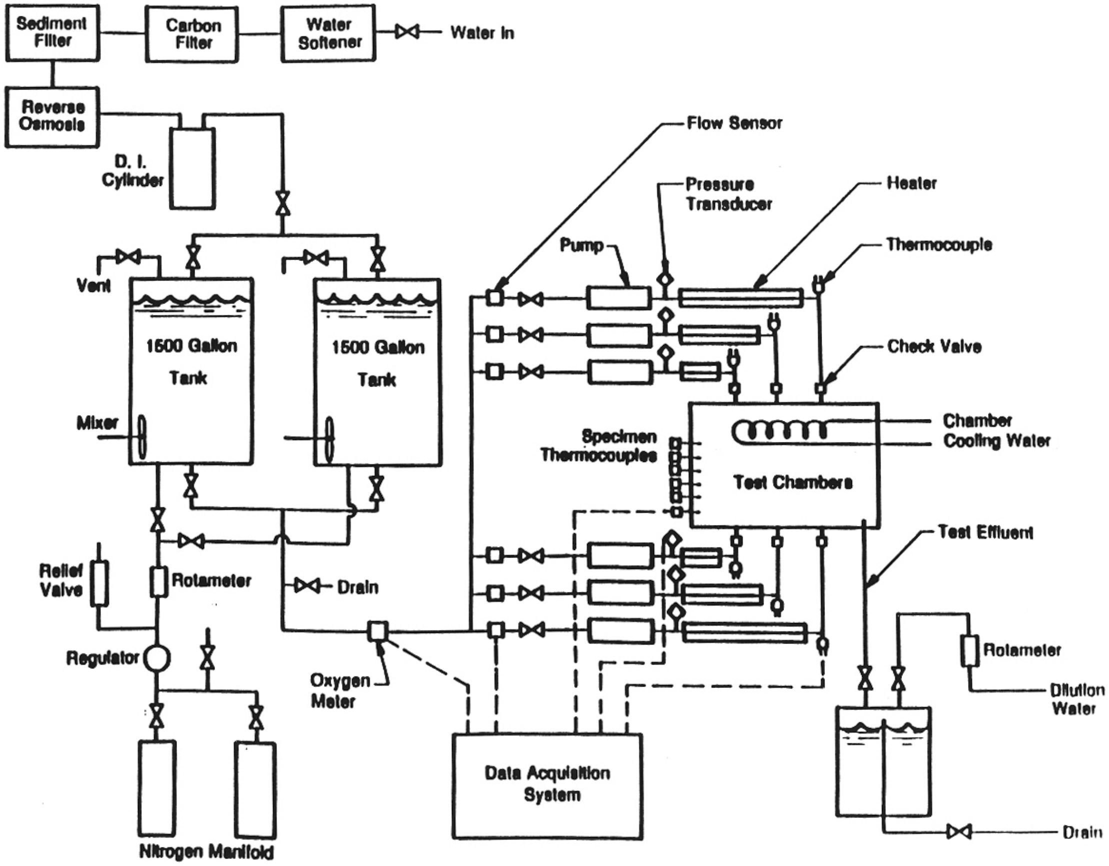
BAC Task 4: Full Scale Mockup Tests

Test Parameters for Possible Investigation

Nozzle geometry	Full size CRDM nozzle geometry
Leak rates	0.0001, 0.001, 0.01, 0.10, and 0.30 gpm
Crack lengths	0.25, 0.75, and 1.25 inch
Crack geometry	Simulated through-wall axial PWSCC crack (HIP'd EDM slit)
Nozzle fits	0.001" interference to 0.010" diametral clearance
Counterbore	No counterbore to 0.005" radial counterbore
Pre-existing cavity	No cavity, volume of 1 – 10 in^3
Temperature	550°F (288°C) to 605°F (318°C) (before cooling)
Insulation	Direct contact and stand-off

BAC Task 4: Full Scale Mockup Tests
Test Facility

- *Design for Previous 1996–97 Testing*



BAC Task 4: Full Scale Mockup Tests
Planned Test Section Configuration

- Goal is to select test specimen that
  - Represents prototypical conditions
  - Is easy to fabricate and of relatively low cost
  - Is of a size that would permit about five simultaneous tests
- Key features
  - Actual Alloy 600 CRDM nozzle dimensions
  - Modular design with bolted connections and gasket seals
  - Crack simulated by EDM slit subjected to Hot Isostatic Press (HIP) method to produce near prototypical crack exit velocities
  - Low alloy steel rings to simulate head
    - Large enough to simulate thermal conditions for wastage up to about ½-1" depth
  - Controlled leak rates
  - Volume of fluid under pressure kept low by use of sealed leakage annulus

BAC Task 4: Full Scale Mockup Tests
Questions Addressed

- The minimum leak rate at which high corrosion rates may occur
- The role of steam cutting and two phase jet impingement erosion
- The role of flow effects on the rate of corrosion and the shape of the developing cavity
- The relationship between crack/annulus geometry and leak rate
- The minimum leak rate leading to pooling / turbulent wetting of liquid on the head top surface
- The chemical environment that forms along the leak path
- The fraction of released boron that is transported to a remote location as opposed to forming deposits locally
- The effect of the initial nozzle fit
- The effect of the insulation configuration
- The effect of pre-existing boron deposits on the head top surface