

Technical Assessment of Davis-Besse Degradation

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 - Volume of boric acid deposits produced
 - Boric acid morphology and properties
 - Concentration of primary water
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 - Electrochemistry



Purpose and Approach

Purpose

- ▶ The purpose of the technical assessments is to complement plant experience in answering the following questions:
 - If a significant amount of RPV head material loss occurs, will it be detectable visually from above the head (either directly or through the presence of deposits)?
 - Could significant material loss occur during a single cycle?

- ▶ In addition, the technical assessments also address current questions regarding the progression of material loss mechanisms (i.e., understanding of degradation progression)

Approach

- The basic approach is to examine how the various potential material loss mechanisms vary as the leak rate is increased from 10^{-6} to 1.0 gpm and the initial tight nozzle annulus becomes a large cavity through material loss. Evaluations focus on:
 - Thermal-hydraulic environment
 - Chemical environment
 - Properties of boric acid and boron compounds
 - Relevant experimental results and plant experience

- The leak rate is expected to be the key parameter:
 - Expansion cooling increases with leak rate, potentially permitting a liquid film to reach the top head surface
 - Increasing leak rates result in higher velocities and potentially erosion or flow accelerated corrosion

Approach (continued)

- ▶ The leak rate also determines the amount of boric acid deposits that exit the pressure boundary

- ▶ The results of corrosion and erosion rate evaluations are used to bound:
 - The timeframe for significant degradation
 - The volume of low alloy steel material loss versus the volume of deposits produced



Material Loss Mechanisms

- Corrosion mechanisms
- Erosion mechanisms
- Flow accelerated corrosion

Material Loss Mechanisms

Overview

➤ Chemical Mechanisms

- Low-oxygen, boric acid corrosion (deaerated, concentrated boric acid solutions)
- Dry boric acid or boric oxide crystal corrosion
- Classic crevice corrosion (conductive liquid in the crevice forms an ionic path to allow dissolution deep in crevice remote from oxygen at crevice mouth)
- Galvanic corrosion (driving corrosion potential due to dissimilar metal couple between Alloy 600 nozzle and low-alloy-steel (LAS) head)
- “Classic” boric acid corrosion (aerated, concentrated boric acid solutions)
- Molten boric acid corrosion

Material Loss Mechanisms

Overview (continued)

- Flow-Enhanced Chemical Mechanisms
 - Two-phase flow accelerated corrosion (FAC) (low oxygen; boric acid not required)

- Mechanical Mechanisms
 - Droplet or solid particle impingement erosion
 - Flashing-induced erosion
 - Steam cutting erosion
 - Single-phase erosion

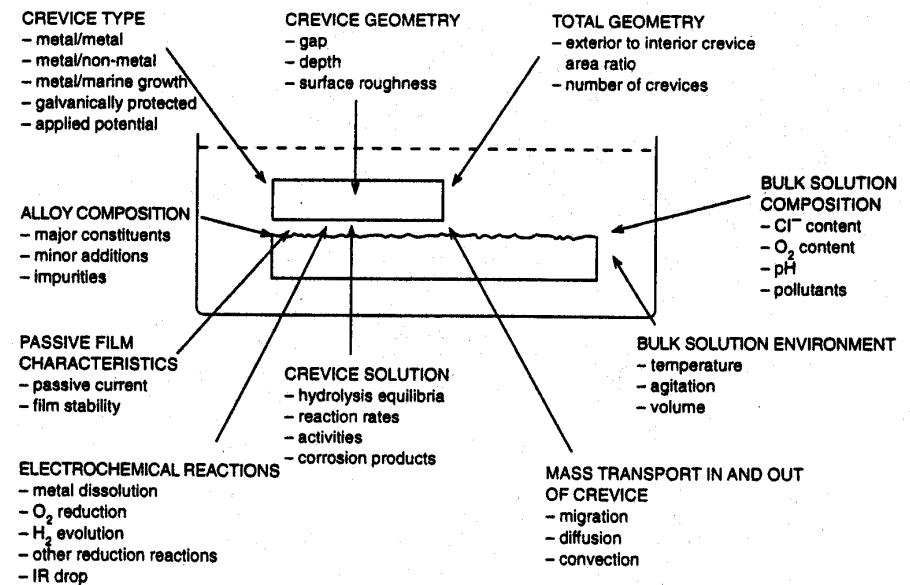
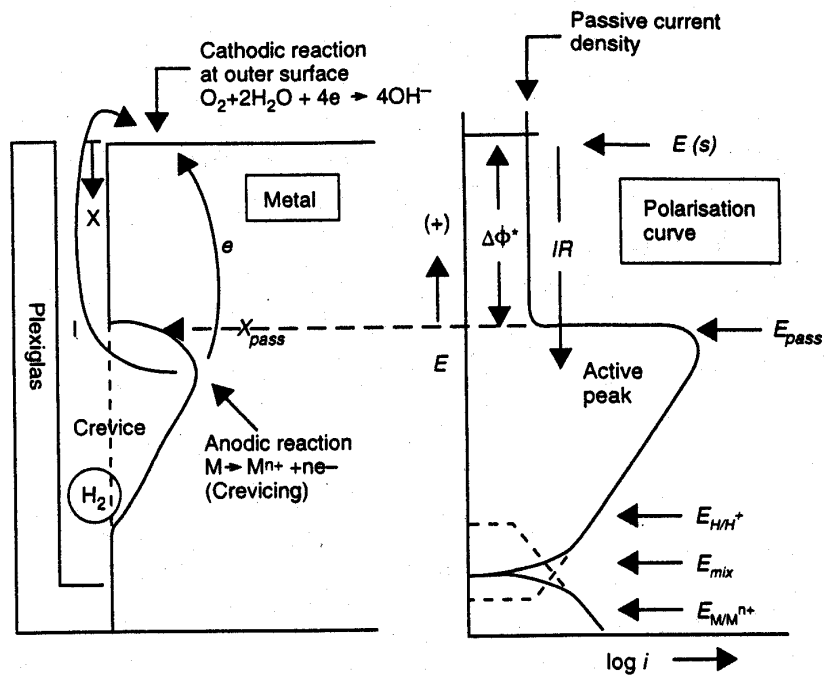
Material Loss Mechanisms

Matrix

PRELIMINARY		Extent of Wastage			
		Initial Tight Annulus	Enlarged Annulus	Small Cavity	Large Cavity
Possible Material Loss Mechanisms	Deaerated Boric Acid Corrosion Conc. Boric Acid Corrosion but DO ₂ ≈ 0-10 ppb	Low rates			
	Dry BA or Boric Oxide Crystal Corrosion Corrosion in Contact with Dry Crystals and Humidity	Low rates			
	Single-Phase Erosion Potential Erosion if High Steam Velocities	Possible for high leak rates	Less likely than for tight annulus		Large flow area precludes high velocities
	Flow Accelerated Corrosion (FAC) Low-Oxygen Dissolution through Surface Oxides	Possible if liquid velocities high enough and temperature low enough			Unlikely as oxygen stabilizes
	Impingement / Flashing-Induced Erosion Droplet and Particle Impact Opposite Crack Outlet	Possible if droplets right size and momentum			
	Crevice Corrosion Liquid Ionic Path from Top Head Surface	Believed not to be likely because low alloy steel does not passivate in an aerated, concentrated boric acid			Not possible because no crevice geometry
	"Occluded Region" Galvanic Corrosion Driven by Potential Difference Btw Dissimilar Metals	Possible at locations where liquid solution exists			
	"Molten" Boric Acid Corrosion Corrosion in Pure or Nearly Pure Melted BA Crystals	Possible but rate expected to be lower than for aerated BAC			
	Aerated Boric Acid Corrosion (BAC) Concentrated Boric Acid Solution with Oxygen	Not possible due to low oxygen deep in crevice	Unlikely	Possibly	Up to 1-5 inches per year

Chemical Mechanisms

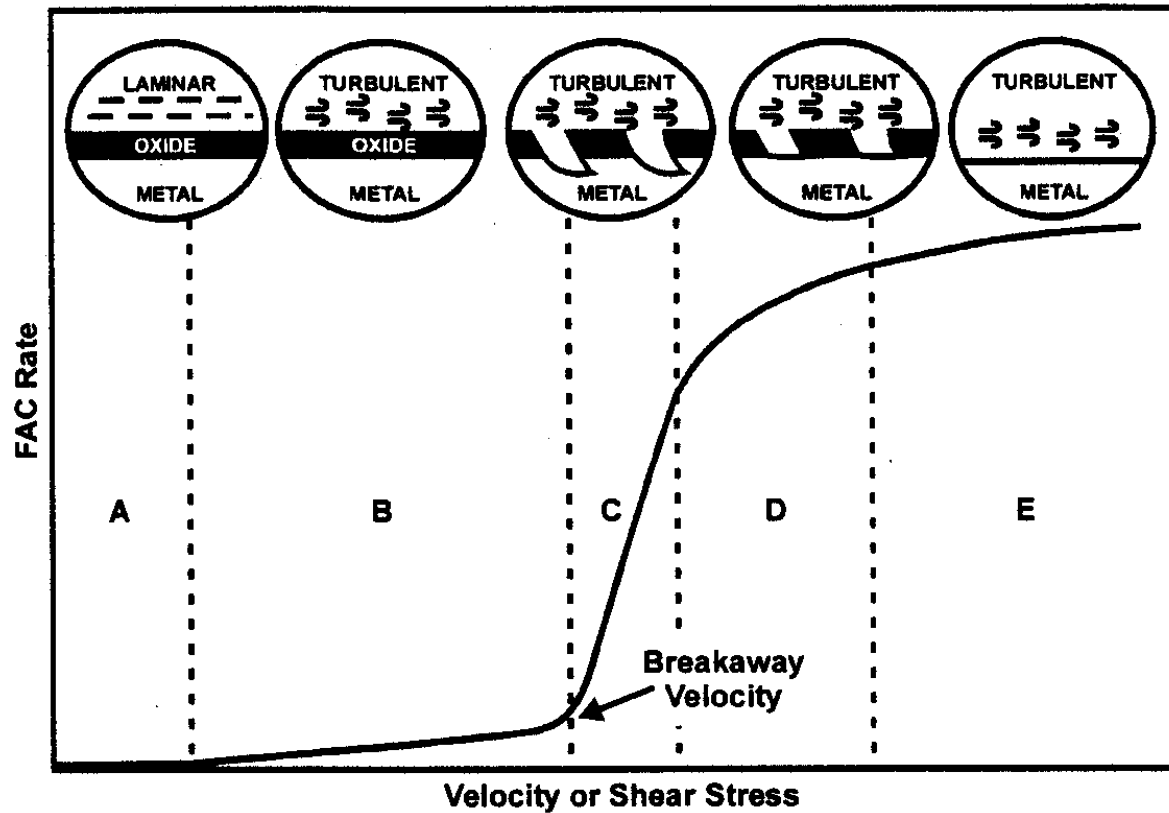
Classic Crevice Corrosion



Source: F.P. IJsseling. *Survey of Literature on Crevice Corrosion (1979-1998)*, IOM Communications Ltd., London, 2000.

Flow Accelerated Corrosion

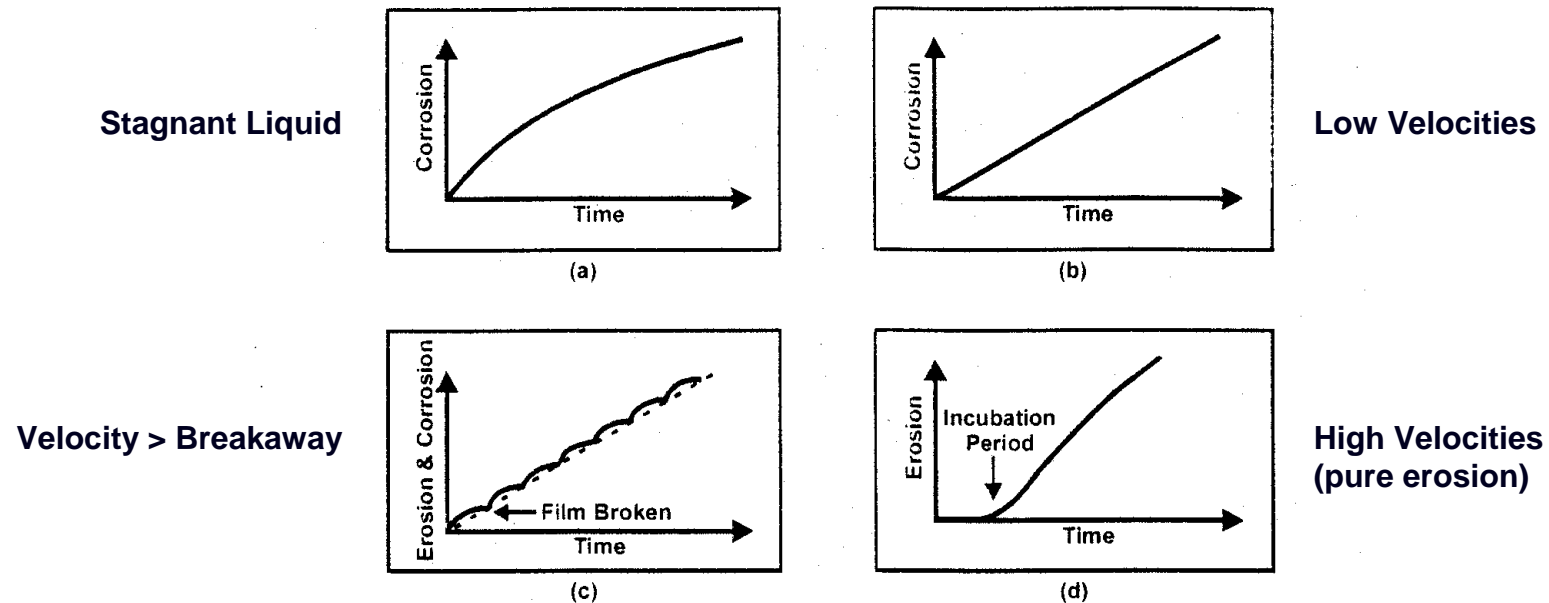
Effect of Velocity on FAC Rate



Source: B. Vyas, *Treatise on Materials Science and Technology*, vol. 16, 1979, p. 357.

Flow Accelerated Corrosion

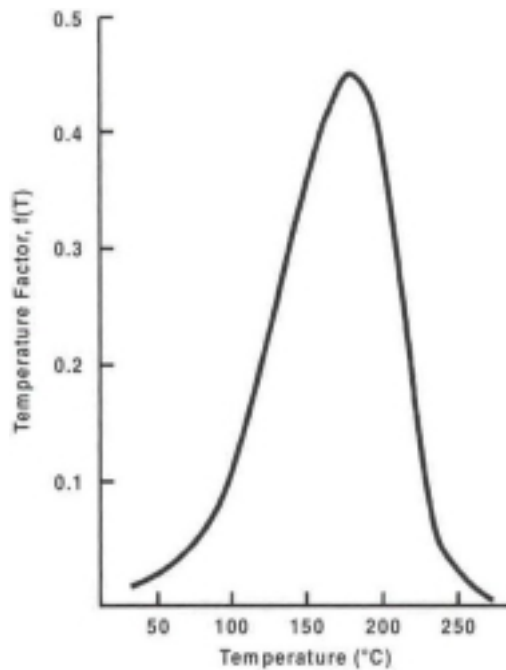
Time Dependencies of FAC Processes



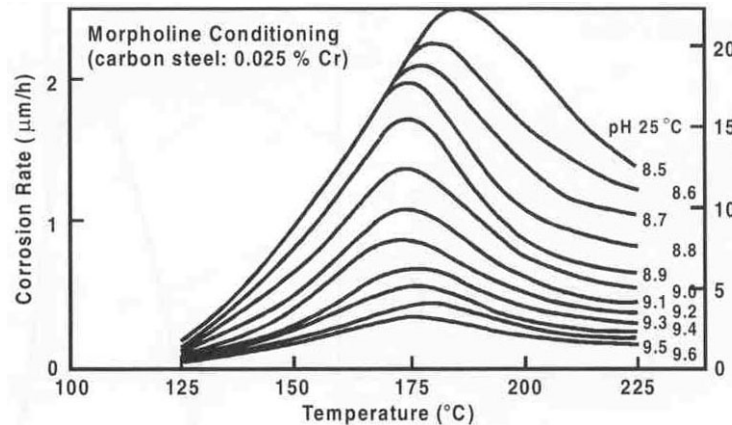
Source: B. Chexal, et al., *Flow-Accelerated Corrosion in Power Plants*, TR-106611, EPRI, Palo Alto, CA, 1996.

Flow Accelerated Corrosion

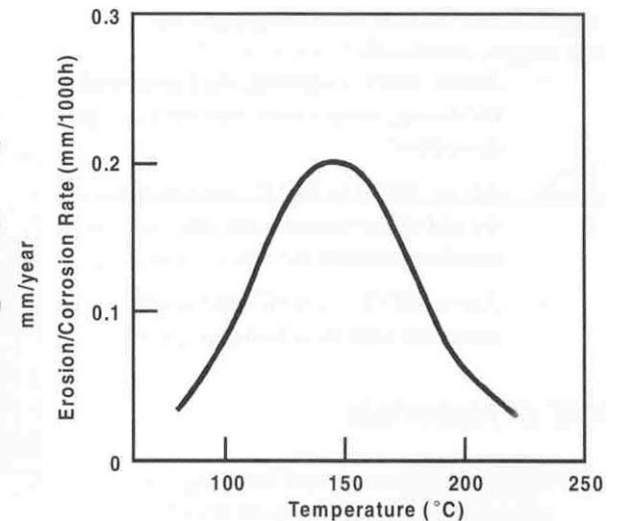
Effect of Temperature for Two-Phase Flows



Temperature Dependence of Two-Phase FAC
 From Keller, H., *VGB Kraftwerkstechnik*,
 54, (1974), p. 292.



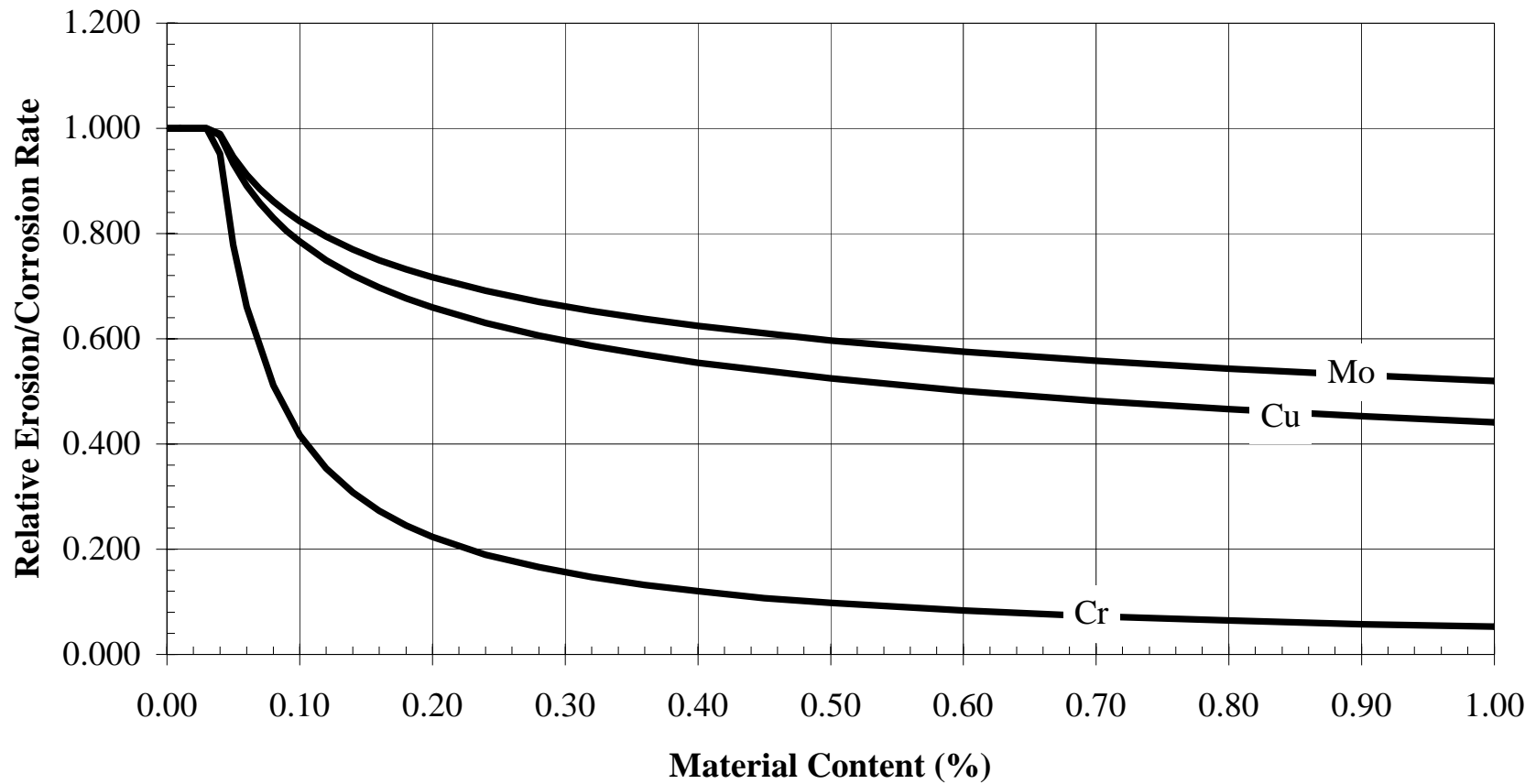
Temperature Dependence of Two-Phase FAC with a Steam Quality of 65% and a Velocity of 185 ft/s
 From Bouchacourt, M., *EDF Internal Report*, (1982),
 Ref.: HT-PVD. XXX MAT/T.42.



Temperature Dependence of Two-Phase FAC
 From Izumiya, M., *Water Chemistry and Corrosion Products in Nuclear Power Plants*, International Atomic Energy Agency, Vienna (1983), p. 61.

Flow Accelerated Corrosion

Effect of Alloy Content on Erosion / Corrosion Rate

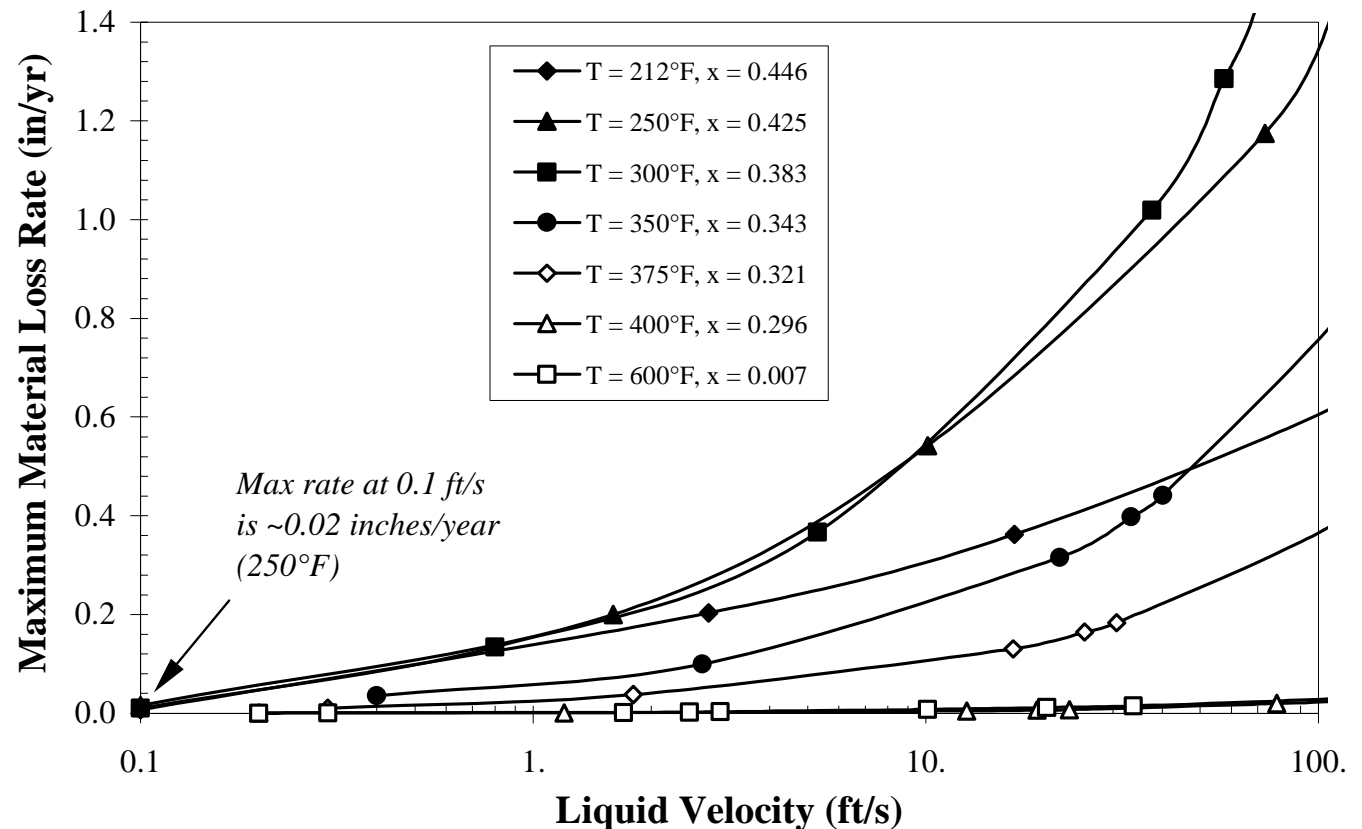


Source: EPRI CHECWORKS

Flow Accelerated Corrosion

EPRI CHECWORKS FAC Predictions

- Predictions for saturated two-phase water flow through a 2-inch Sch 80 90° elbow with R/D = 1.5
- No Cr assumed but 0.5% Mo
- Dissolved $O_2 = 0$
- $pH_{RT} = 7$



NOTE: CHECWORKS is intended to be used to model FAC in secondary cycle piping systems and not in situations such as leaking crevices. These calculations show the rough effects of liquid velocity and temperature that may be expected for leaking CRDM nozzles.

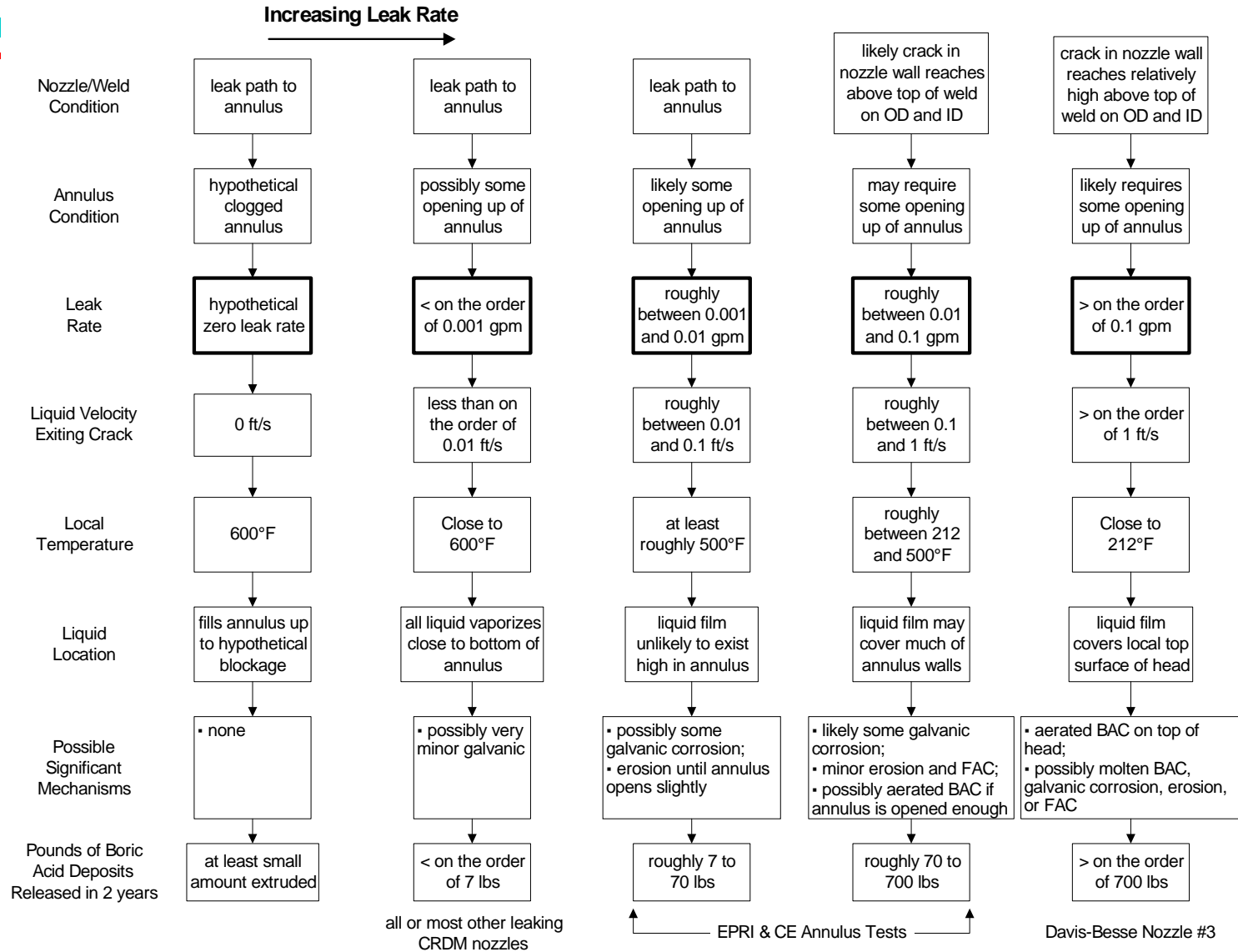


Degradation Progression

Degradation Progression

Leak Rate is Main Controlling Parameter

PRELIMINARY



Degradation Progression

- Condition 1a. If—contrary to plant experience—a leak path crack forms in the absence of leakage to the top surface of the head
 - There will be low oxygen, zero velocity, and no vaporization-driven concentration mechanism, so material loss rates will be small

- Condition 1b. For tight nozzle cracks that allow a leak path
 - The leak rate will be limited and the annulus downstream of the crack will boil dry within a short distance
 - Erosion and FAC will not be active due to very low liquid velocities
 - Small amounts of boric acid or boric oxide crystals will accumulate on the top head surface

Degradation Progression (continued)

- Condition 2. As the crack widens and the minimum leak path flow area increases
 - Flashing-induced erosion or FAC may initiate the material loss process
 - Galvanic corrosion may be important if cooling is sufficient to allow liquid to exist over a significant height in the annulus
 - These mechanisms could be expected to produce greater relative material loss deep in the annulus, consistent with Davis-Besse Nozzle #2 and the EPRI BAC leaking annulus tests

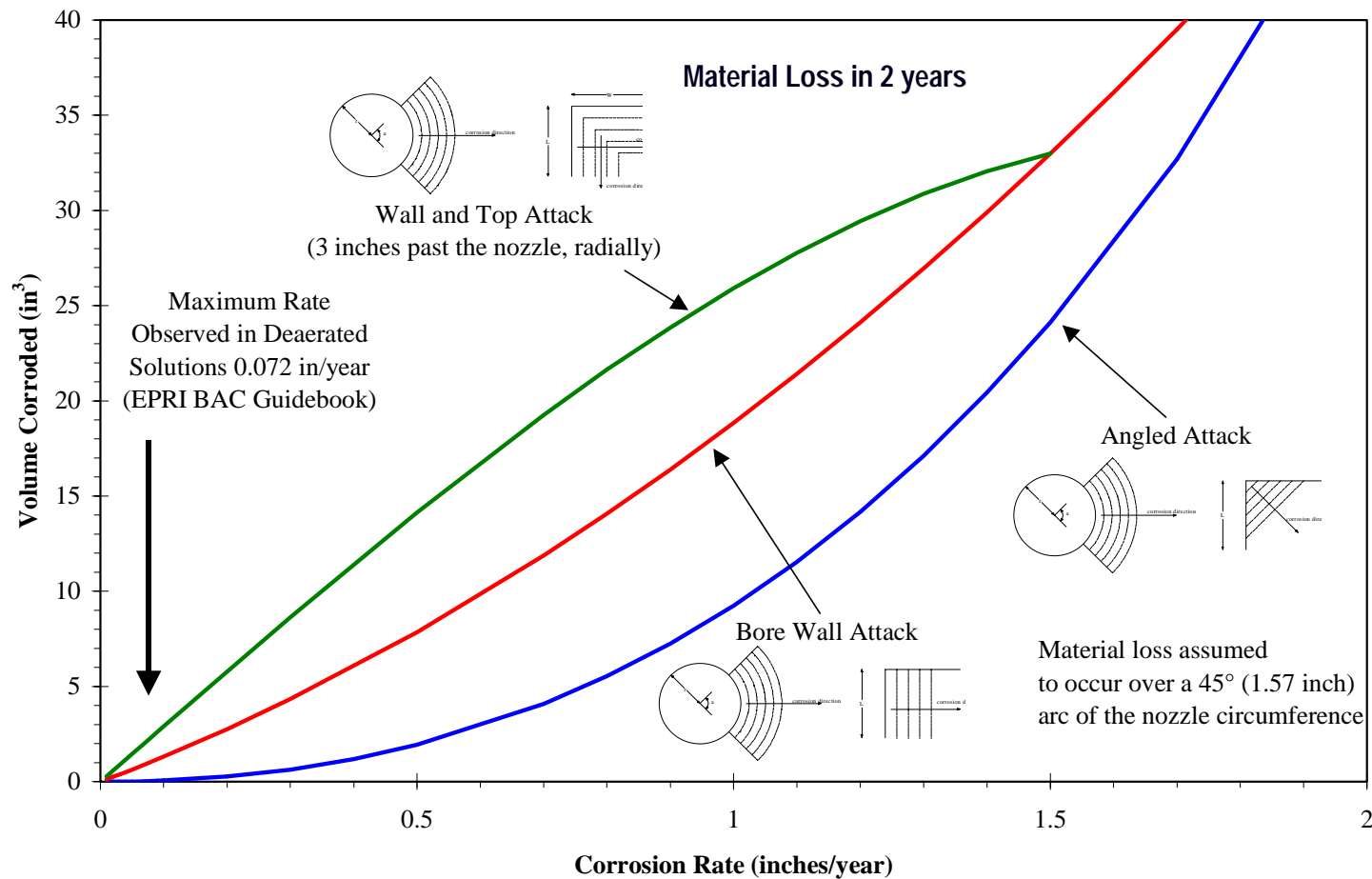
- Condition 3. As the leak rate increases and the wastage area grows from a small cavity to a large, open cavity
 - Aerated boric acid corrosion (up to 1-5 inches per year) may occur

Degradation Progression (continued)

- The geometry of the Davis-Besse Nozzle #3 cavity may indicate that aerated BAC removing material from the top surface down toward the cladding replaced corrosion and/or erosion deep down in the annulus as the dominant degradation mode
 - The slope of the walls of the cavity change with distance from the top head surface
 - Heat transfer calculations show considerable local cooling of the head for the range of leak rates believed to apply to this nozzle, indicating an aerated, concentrated liquid boric acid solution film on the top head surface adjacent to this nozzle
 - Laboratory tests and plant experience indicate relatively high corrosion rates for low alloy steel exposed to aerated, concentrated liquid boric acid solution in comparison to other material loss mechanisms
 - Gravity-driven flow of this liquid film would tend to produce the observed oblong shape of the Nozzle #3 cavity

Degradation Progression

Relating Linear Loss Rate to Volume Loss (Example Calcs)

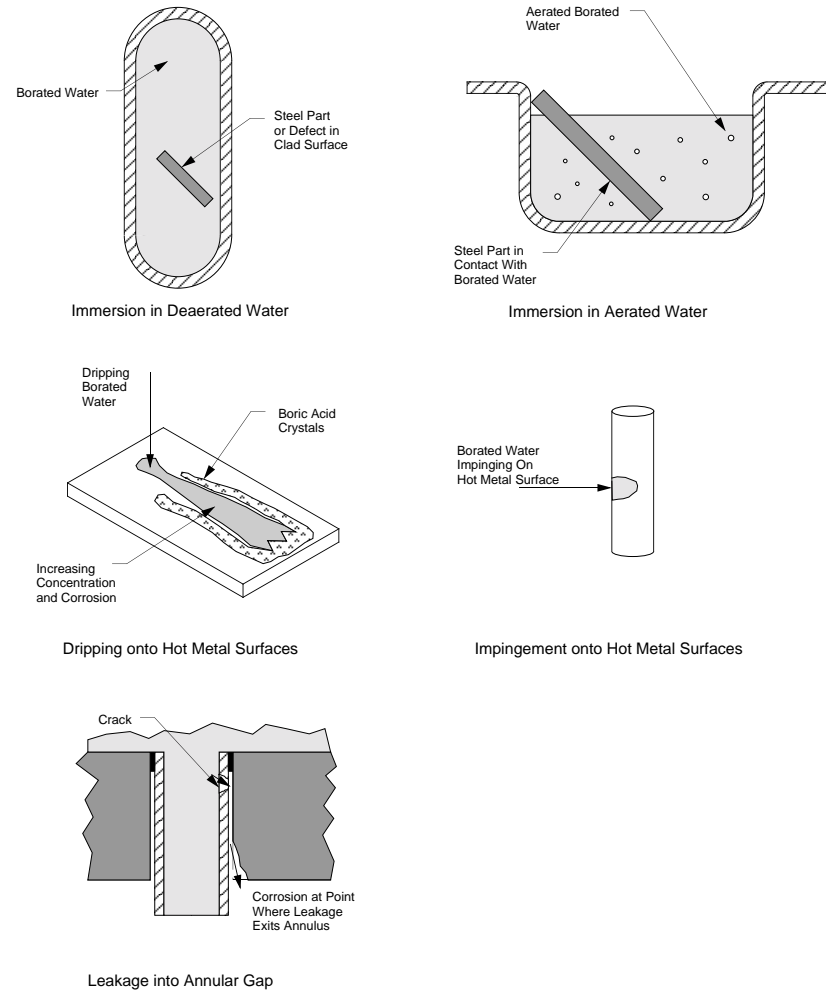




Boric Acid Corrosion Tests Simulating Nozzle Leakage

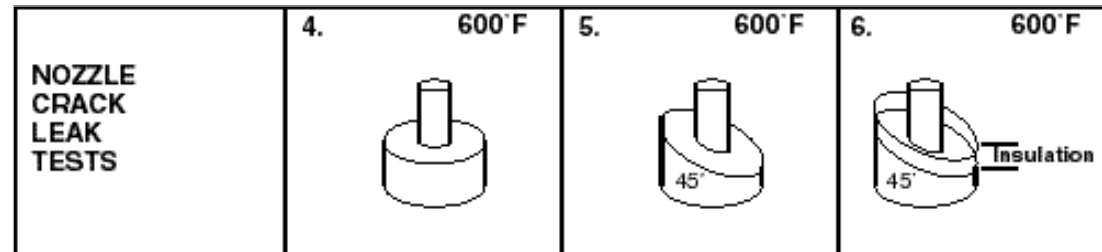
BAC Tests Simulating Nozzle Leakage *Overview*

- An extensive set of experimental data has been compiled and reported in the EPRI *Boric Acid Corrosion Guidebook, Revision 1*
 - Tests by several organizations prior to 1995
 - Tests of a range of conditions
 - Deaerated water
 - Aerated water
 - Dripping
 - Impingement
 - Leakage into annulus
 - Tests performed by EPRI at Southwest Research Institute in 1996/97
- Results of additional tests performed by CEA in France have been made available to EPRI



BAC Tests Simulating Nozzle Leakage

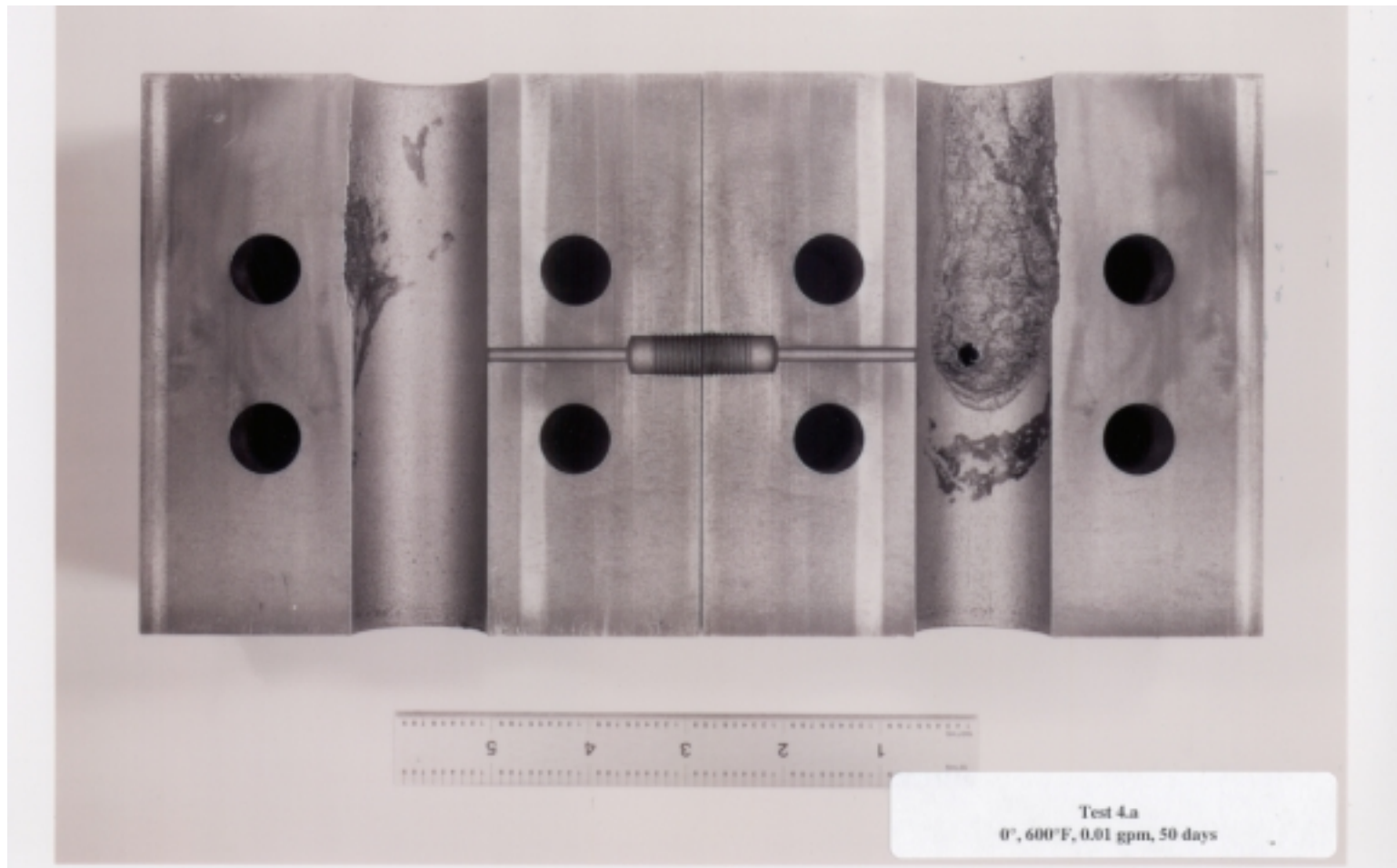
EPRI Annulus Test Matrix



Test Number	Temperature (F)	Flow Rate (gpm)
4a	600	0.01
4b	600	0.10
5a	600	0.01
5b	600	0.10
6a	600	0.01
6b	600	0.10

BAC Tests Simulating Nozzle Leakage

Typical Sectioned EPRI Test Specimen



BAC Tests Simulating Nozzle Leakage

Test Conclusions

- The maximum corrosion rates in both the EPRI and CE tests were about 2.0 – 2.5 in/yr
- The maximum corrosion rates occurred at leak rates of about 0.01 gpm with decreasing corrosion rate as leak rate was increased above 0.01 gpm
 - However, one test by CE at a low leak rate (0.002 gpm) showed a very low corrosion rate
- While the tests may not represent the initial conditions of a very tight fit, they are considered to represent anticipated conditions once the annulus opens up to about 0.005”
- While the corrosion depth can be greater below the exposed surface than at the surface, the tests showed relatively large amounts of boric acid deposits for the range of flow rates tested



Thermal-Hydraulic Environment

- Leak rate
- Expansion cooling
- Velocity and wall shear stress

Leak Rate Calculations

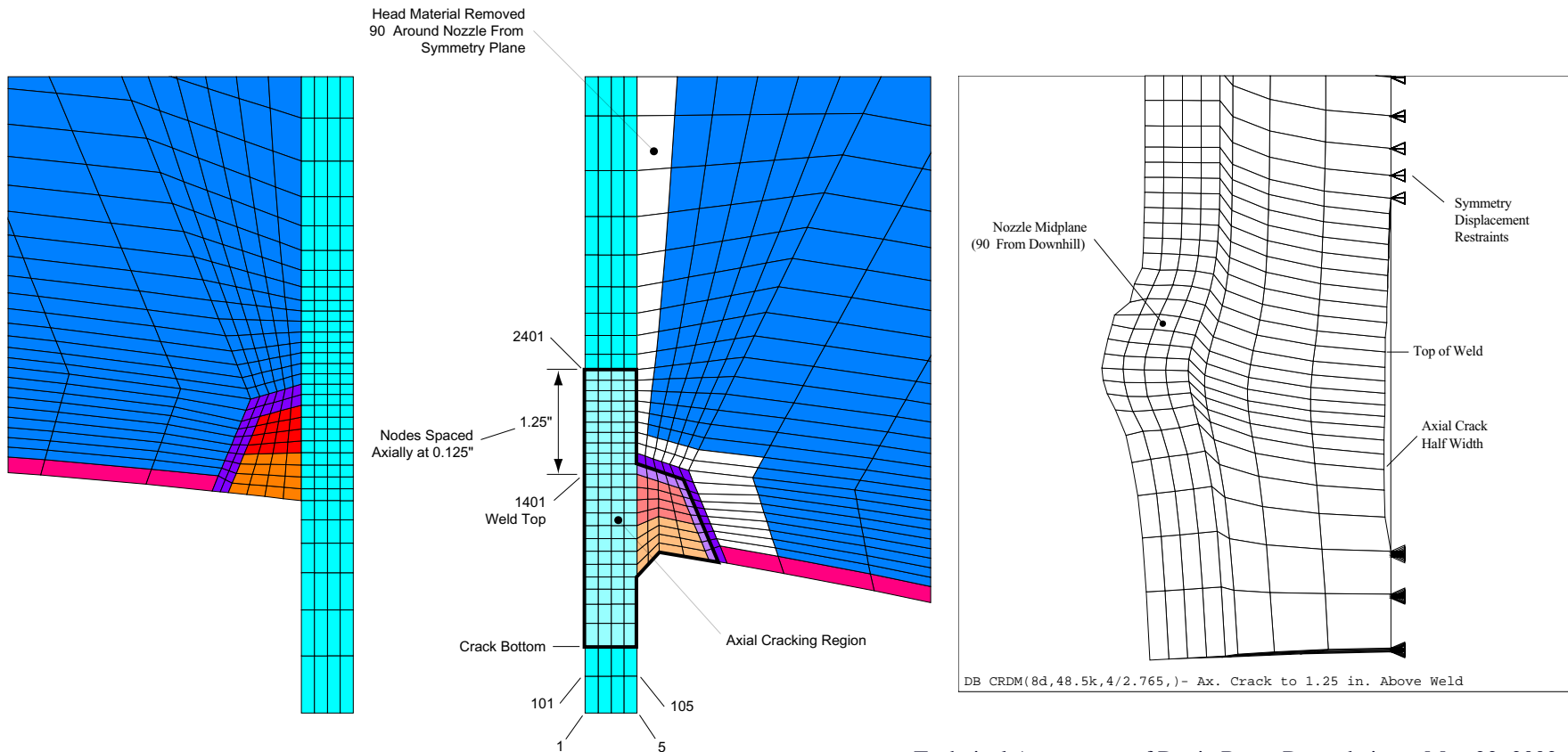
Method

- Calculate axial crack length and opening area above the top of the weld using welding residual stress FEA or an available analytical expression from fracture mechanics
- Calculate the leak rate based on industry correlations for choked flow through a crack in a steam generator tube
- Consider the potential additional flow resistance of a tight annulus downstream of the crack

Leak Rate Calculations

Crack Opening Displacement and Area

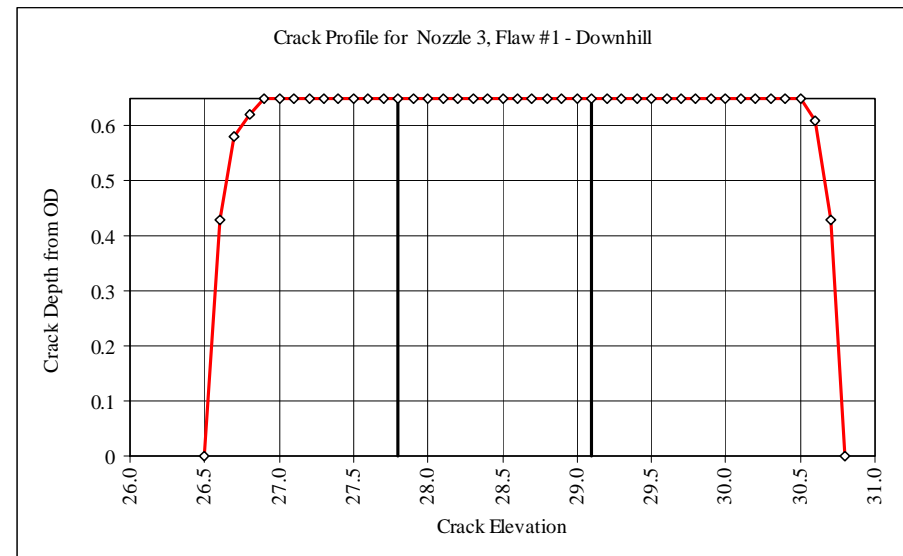
- Crack opening displacement and area determined using finite element models with welding residual and operating stresses



Leak Rate Calculations

Effect of Actual Crack Front Profile

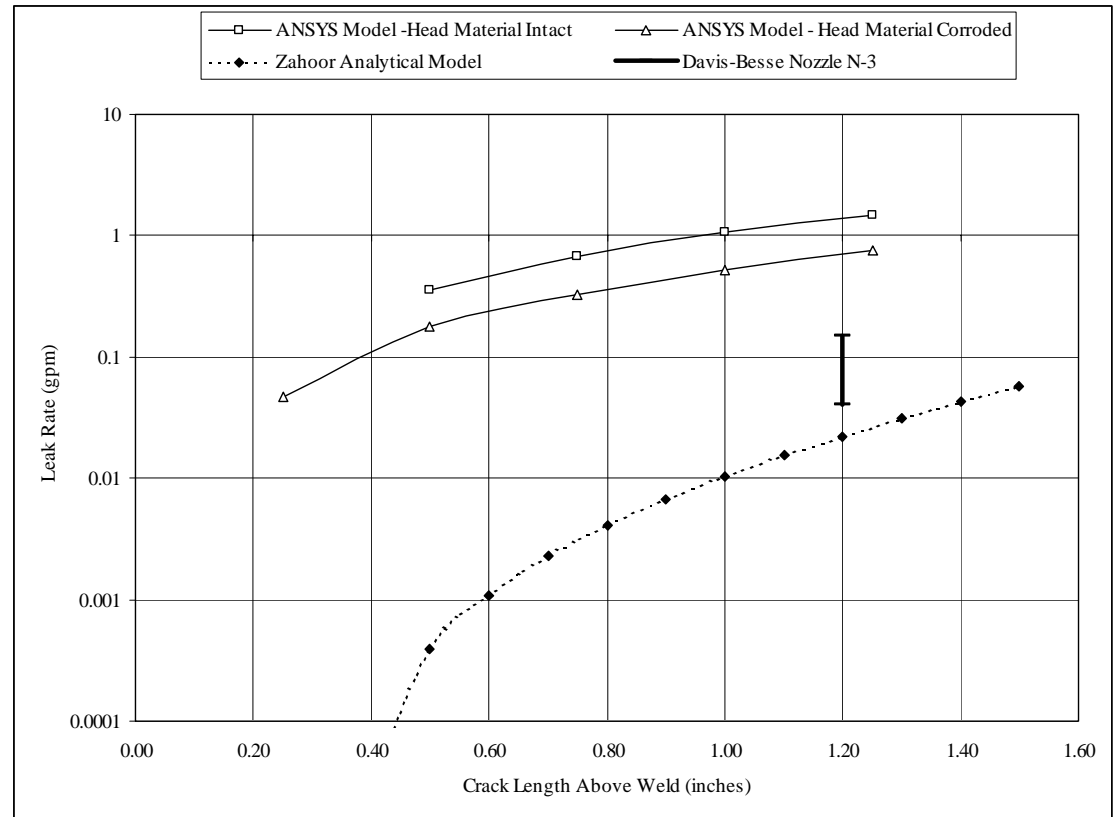
- Crack opening displacement calculations have assumed crack cuts completely through the nozzle wall, and J-groove weld, from the reported crack bottom to top
- Subsequent to initial leak rate calculations, the actual crack profiles at Davis-Besse have been determined from top-down UT data



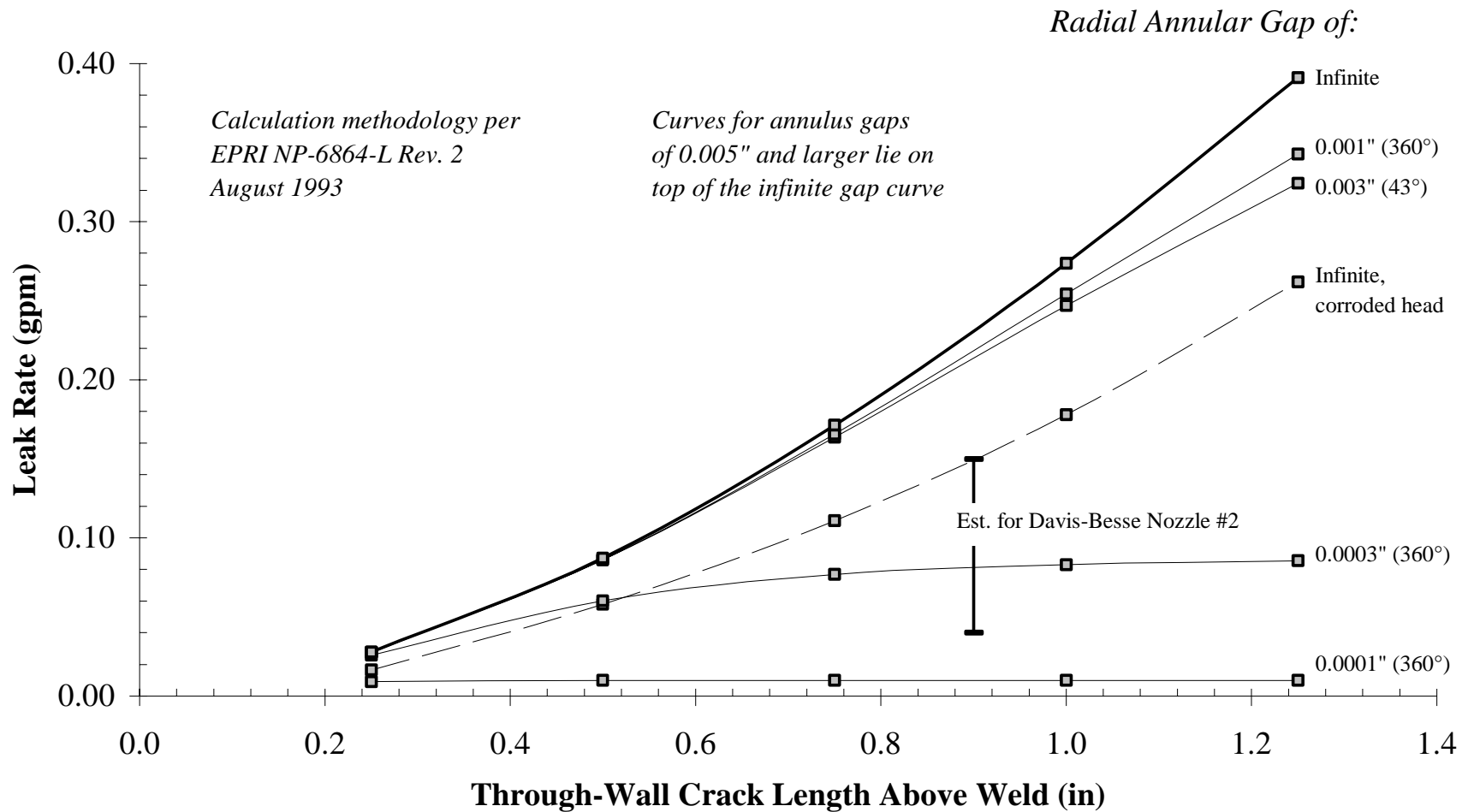
Leak Rate Calculations

Typical Results

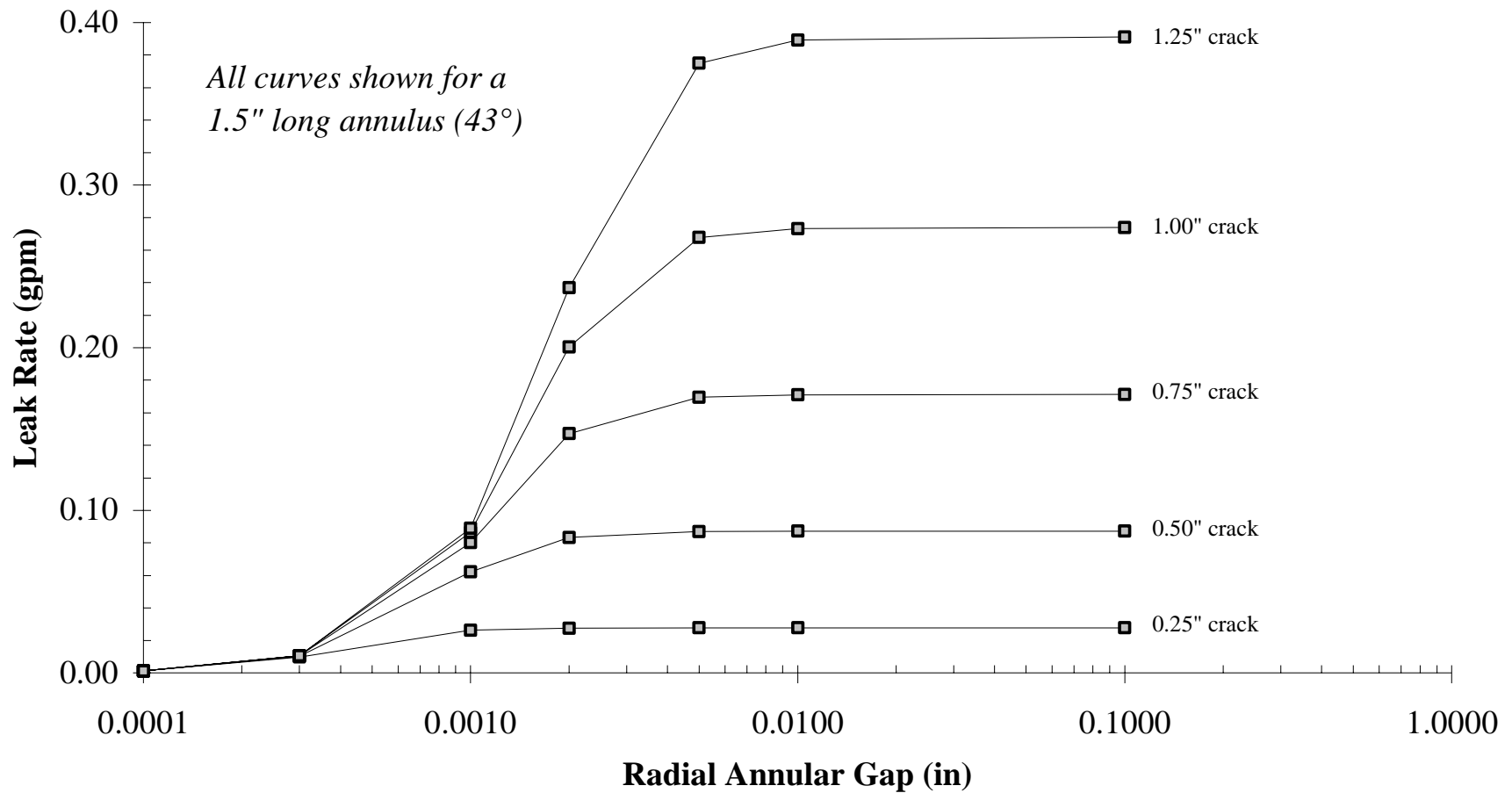
- ▶ Actual unidentified leak rate is bounded by leak rates calculated using
 - Crack opening area for a through-wall axial crack in a pipe with length equal to the length that the axial crack extends above the top of the J-groove weld
 - Crack opening area determined using the finite element method for an ideal through-wall crack
- ▶ Calculations show leak rate increases quickly with crack length above the top of the J-groove weld



Leak Rate Variation with Crack Length



Leak Rate Variation with Annular Gap Width



Expansion Cooling Modeling

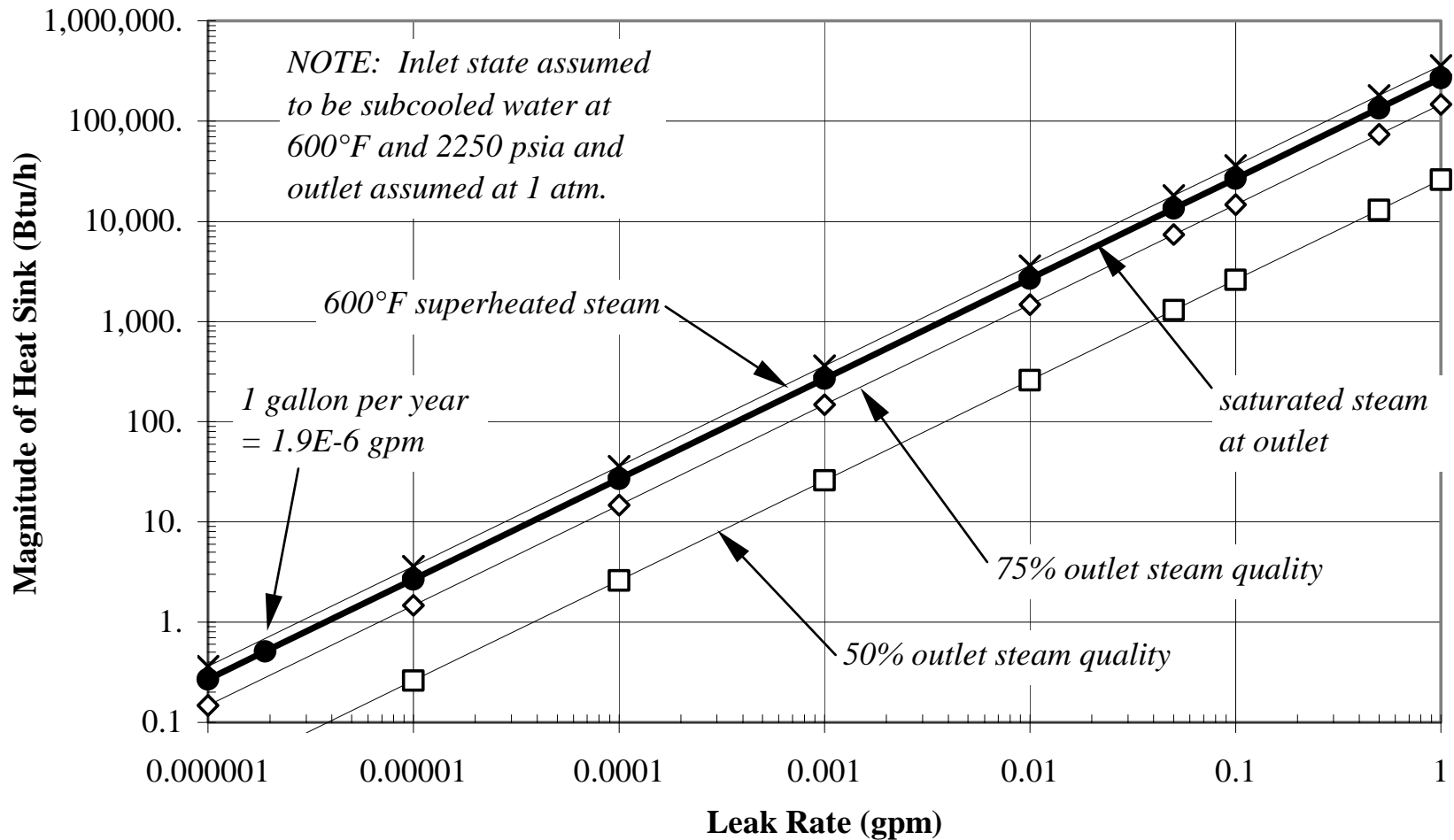
Overview

- Approach is to determine extent of cooling along the leak path as a function of leak rate using
 - Heat required to vaporize all leaking liquid is the leak rate times the enthalpy increase (from primary water at 613 Btu/lb to saturated steam at atmospheric pressure at 1150 Btu/lb)
 - FEA heat transfer model of conduction within head materials with convection boundary conditions from primary coolant and to space above
 - Correlations for two-phase and single-phase heat transfer coefficients along the leak path

- Extent of cooling affects important parameters including
 - Location of concentrated liquid
 - pH
 - FAC susceptibility

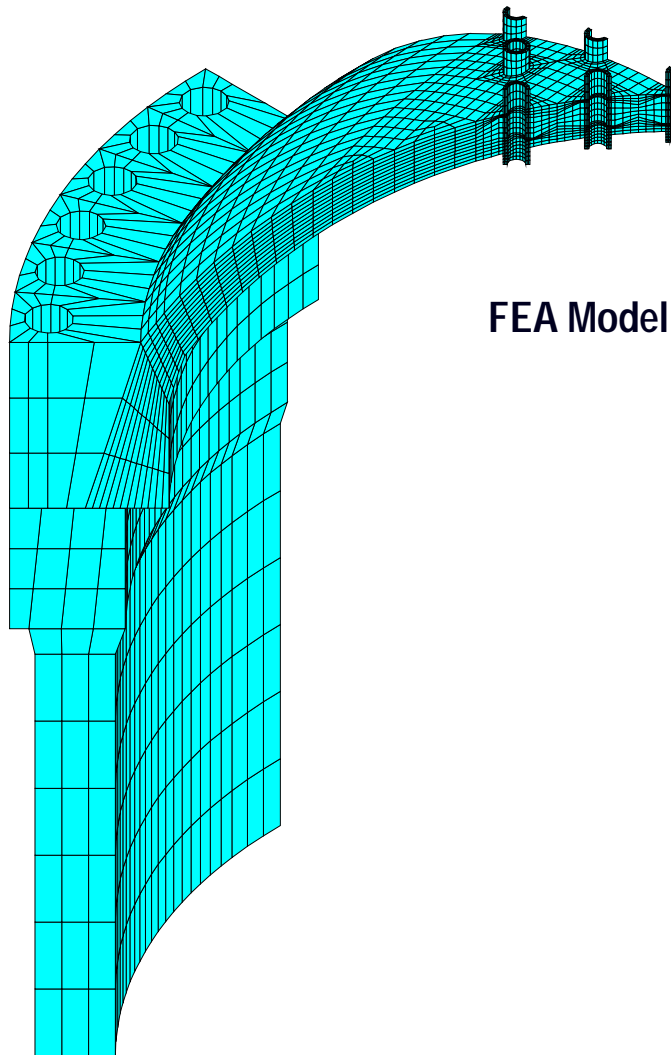
Expansion Cooling Modeling

Magnitude of Heat Sink



Expansion Cooling Modeling

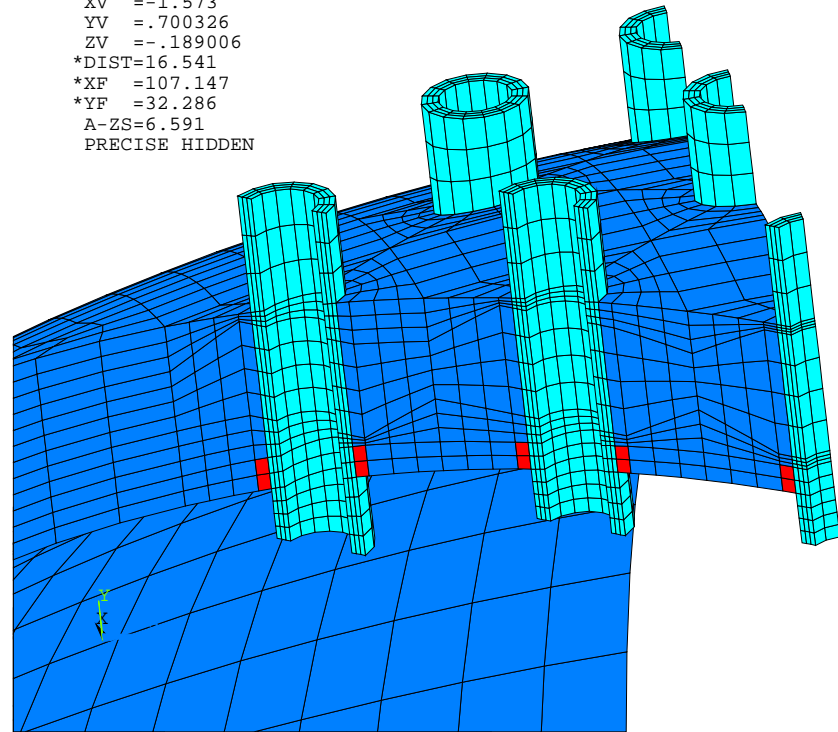
Finite Element Analysis of Head Heat Transfer



FEA Model

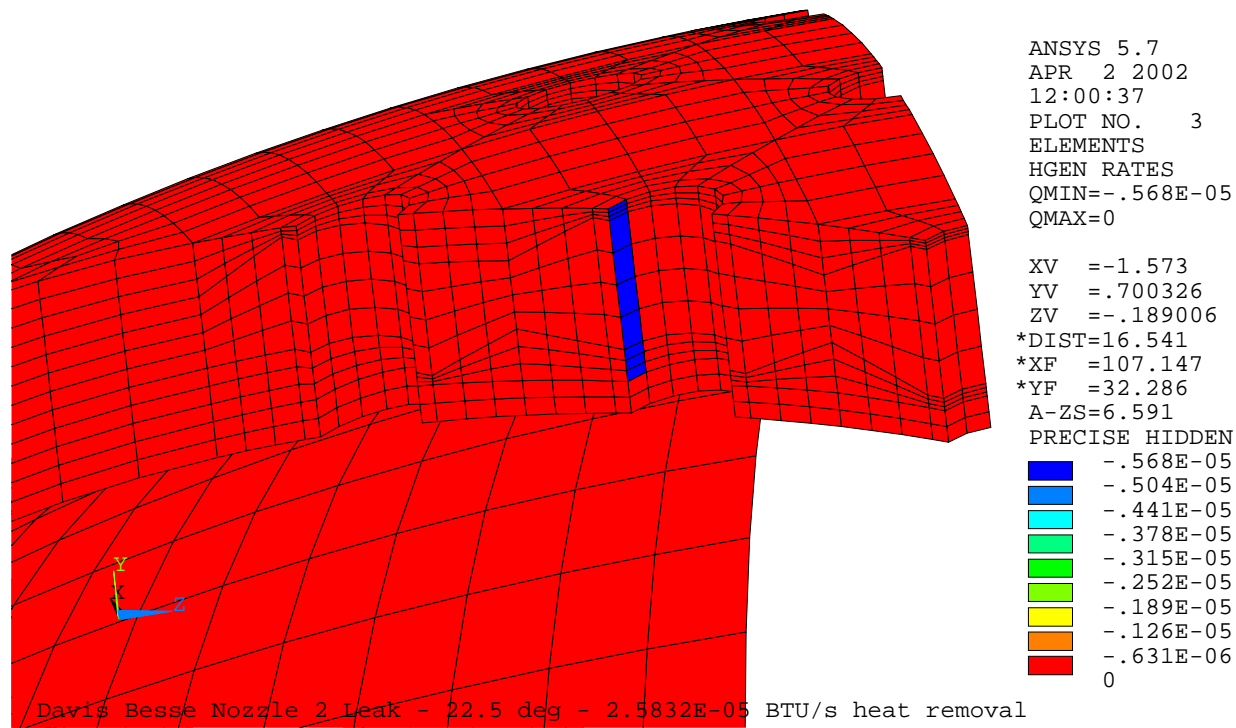
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APR 2 2002  
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MAT NUM
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ZV =-.189006  
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*YF =32.286  
A-ZS=6.591  
PRECISE HIDDEN
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Expansion Cooling Modeling

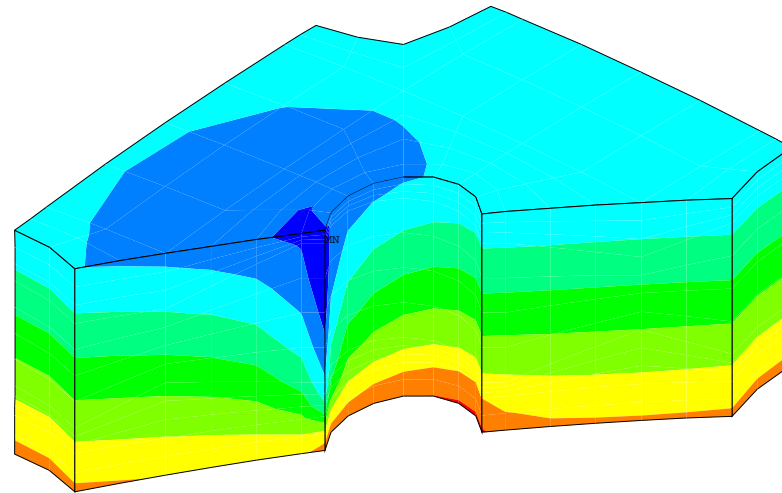
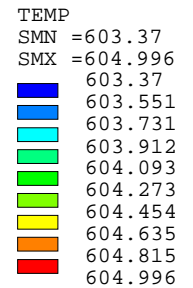
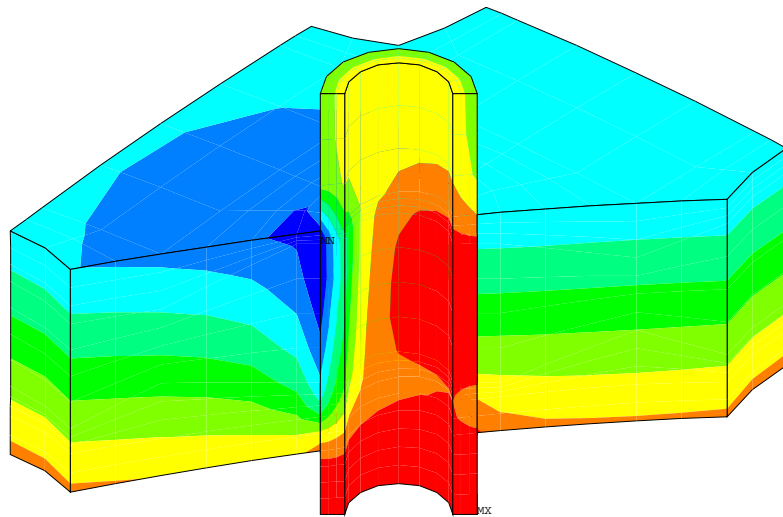
Finite Element Analysis of Head Heat Transfer



Uniform Surface Heat Sink Along the Leak Path Assumed

Expansion Cooling Modeling

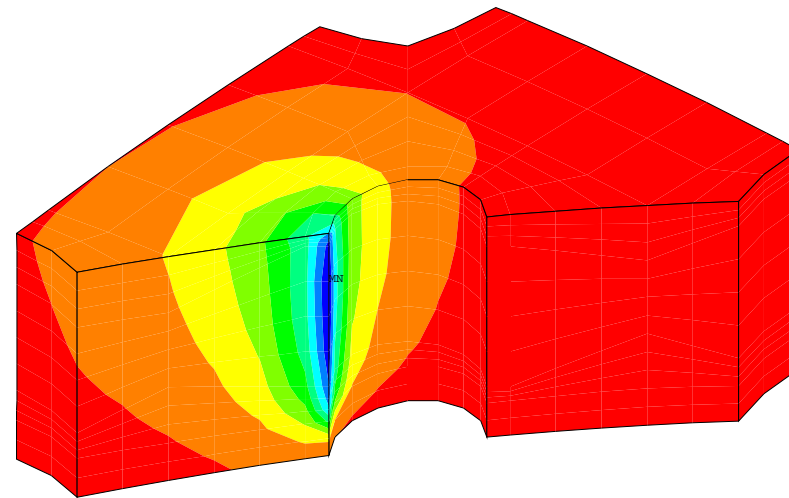
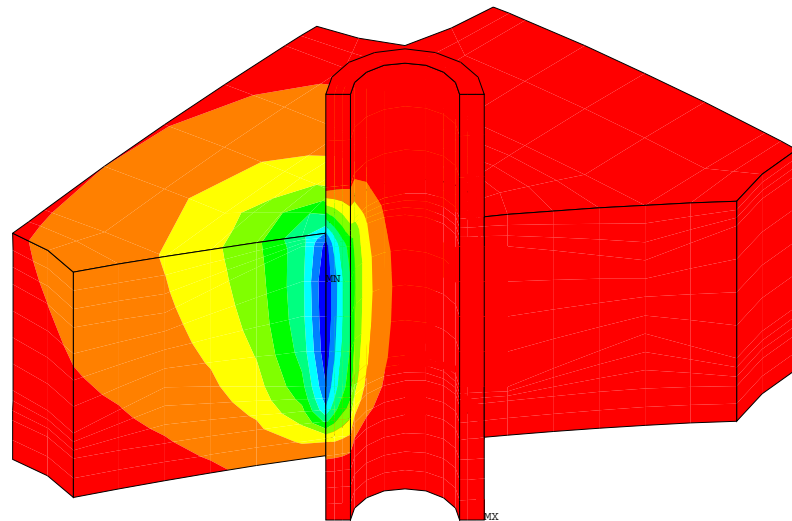
Finite Element Analysis of Head Heat Transfer



Example Calculation for Low Leak Rate
(18.6 Btu/h Heat Sink:
complete vaporization of 7×10^{-5} gpm leak)

Expansion Cooling Modeling

Finite Element Analysis of Head Heat Transfer



TEMP

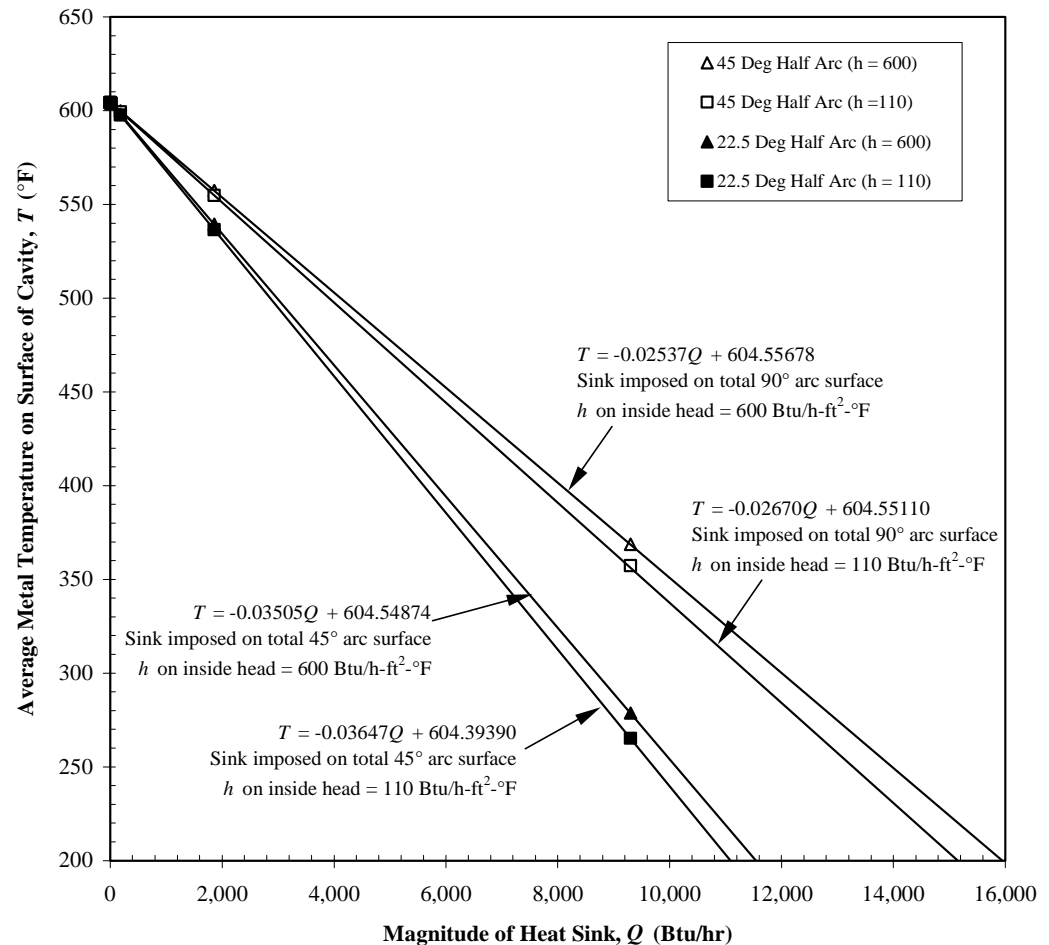
SMN	=	514.122
SMX	=	604.939
		514.122
		524.212
		534.303
		544.394
		554.485
		564.576
		574.667
		584.758
		594.849
		604.939

**Example Calculation for Moderate Leak Rate
(1860 Btu/h Heat Sink:
complete vaporization of 0.007 gpm leak)**

Expansion Cooling Modeling

Finite Element Analysis of Head Heat Transfer

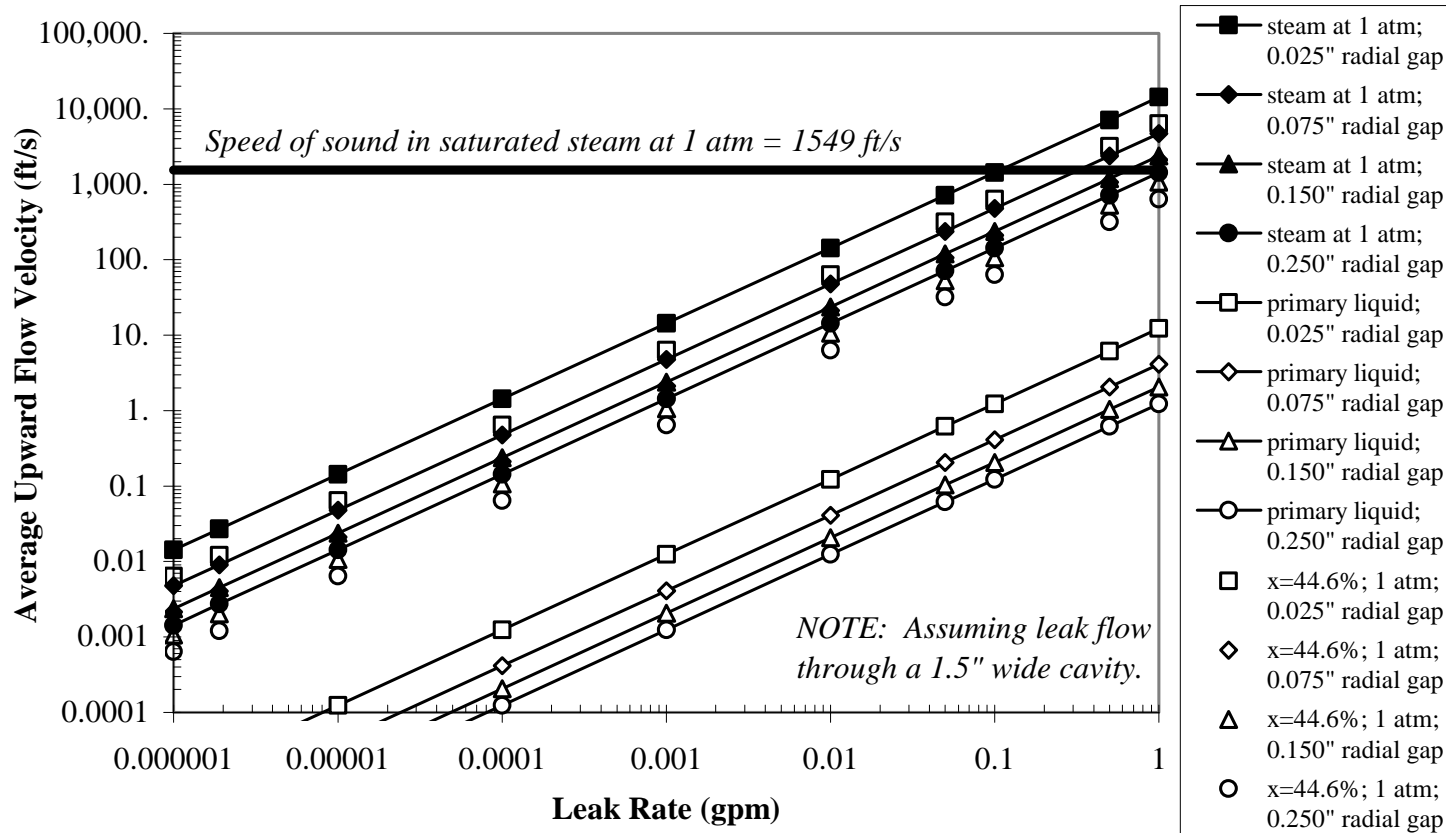
Average Metal Surface Temperature Along the Leak Path



Effluent Velocity

Average Velocities Up Through a 1.5-inch Wide Cavity

- ▶ Calculations for a uniform cavity with 1.5-inch circumferential extent

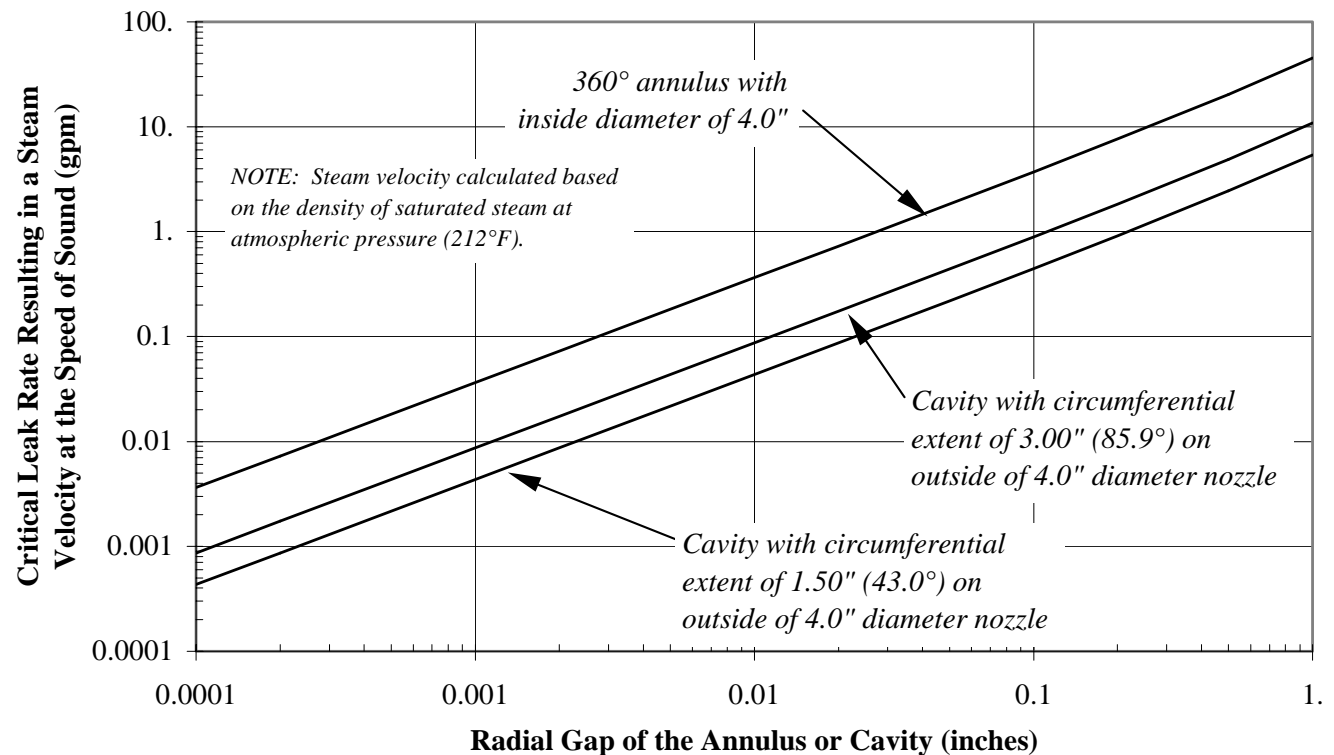


Effluent Velocity

Single-Phase Steam Critical (Choked) Velocity

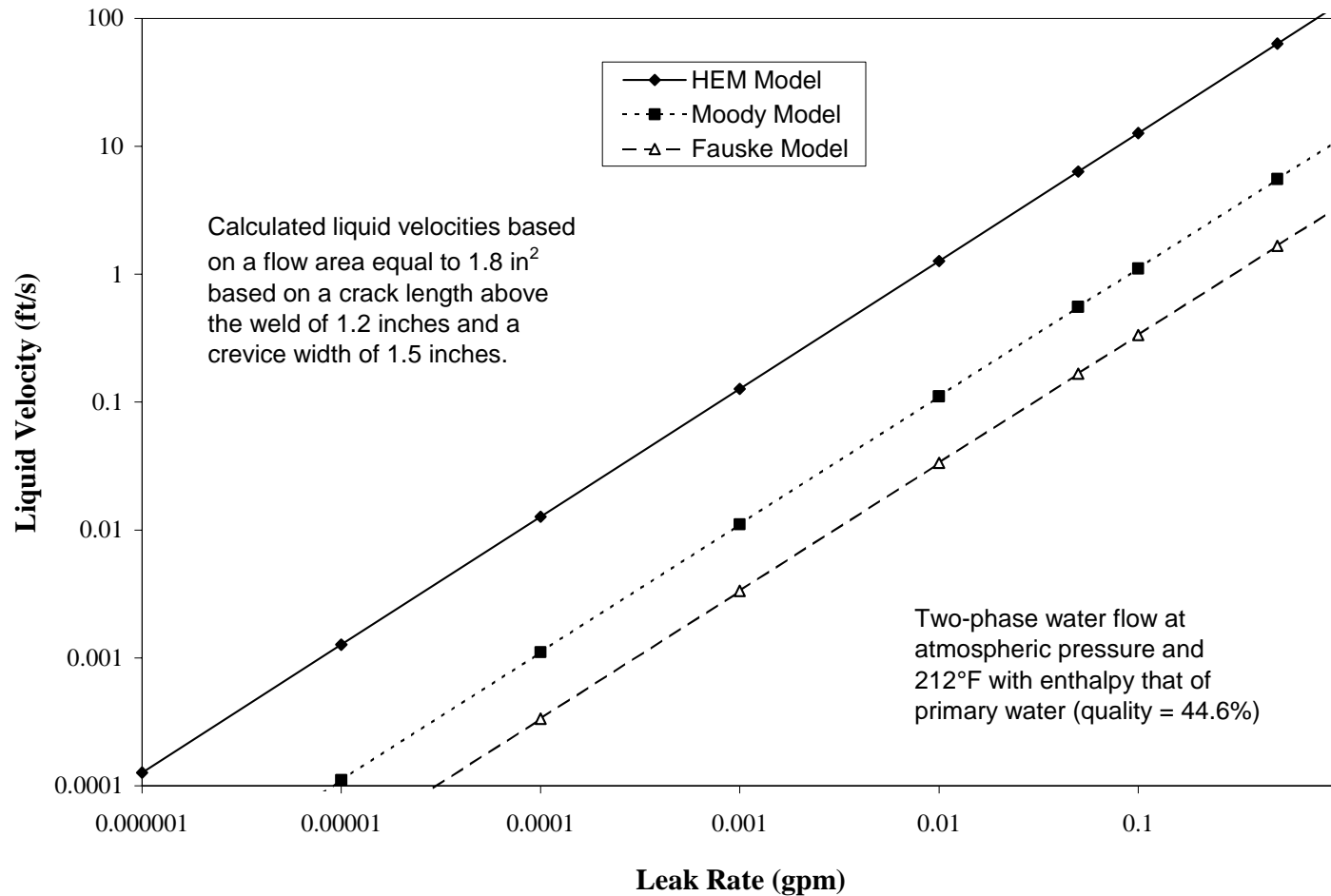
➤ Figure shows the gap size resulting in sonic steam velocities at the annulus/cavity exit for

- 360° uniform annulus
- 3-inch wide cavity
- 1.5-inch wide cavity



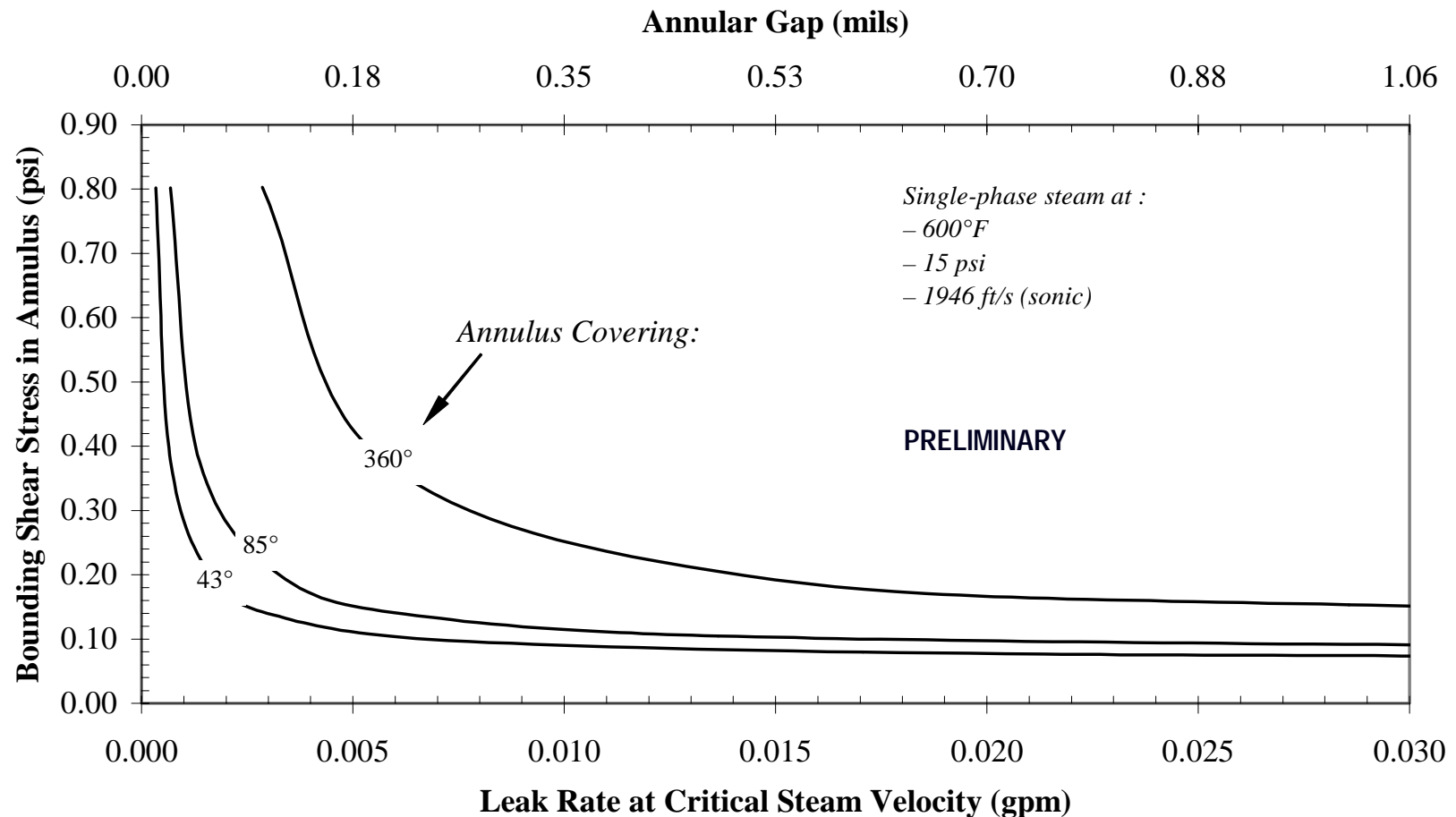
Effluent Velocity

Liquid Velocity Estimates at Exit of Crack



Wall Shear Stress Calculation

(Single-Phase Steam, 1.25-inch Crack Length Above Top of Weld)



Single-Phase Erosion in Steam

Experimental Data

- Data available from testing of turbine materials in 1950s
(*Trans. ASME*, v. 80, 1958)

- Erosion tests carried out for a number of materials:
 - 430°F / 350 psia
 - 9% moisture
 - 460 ft/s steam velocity
 - 1000 h duration

- Key result: 3–4 mils erosion in carbon and ½-Mo steels
 - Represents a rate of 0.025–0.035 inches per year
 - Erosion could be due principally or partly to presence of liquid (9%)

Chemical Environment

- Volume of boric acid deposits produced
- Boric acid morphology and properties
- Concentration of primary water
- pH
- Electrochemistry

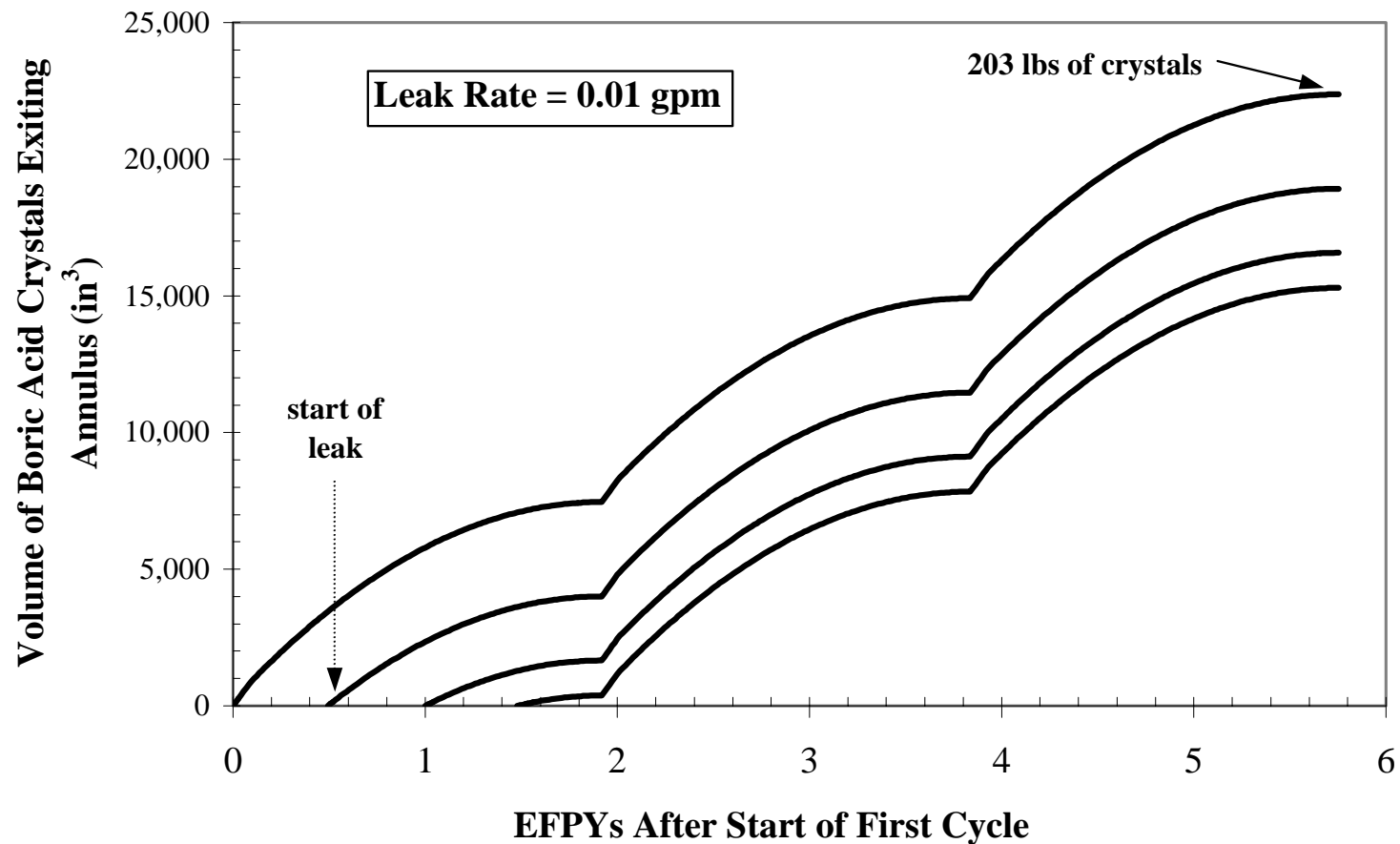
Volume of Boric Acid Deposits on the Vessel Head

Methodology

- Integrate the leaking boron mass over the fuel cycle
- Calculate the volume of leaked boron based on the density of boric acid (H_3BO_3) or boric oxide (B_2O_3) crystals, conservatively assuming no porosity
- The fraction of precipitated boron compounds that deposits on the head adjacent to the leaking nozzle may be affected by
 - Droplet entrainment into the steam flow
 - Boric acid volatility (10% or less)

Volume of Boric Acid Deposits on the Vessel Head

Example Integration of Boron Mass



Boric Acid Morphology and Properties

Boron 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 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

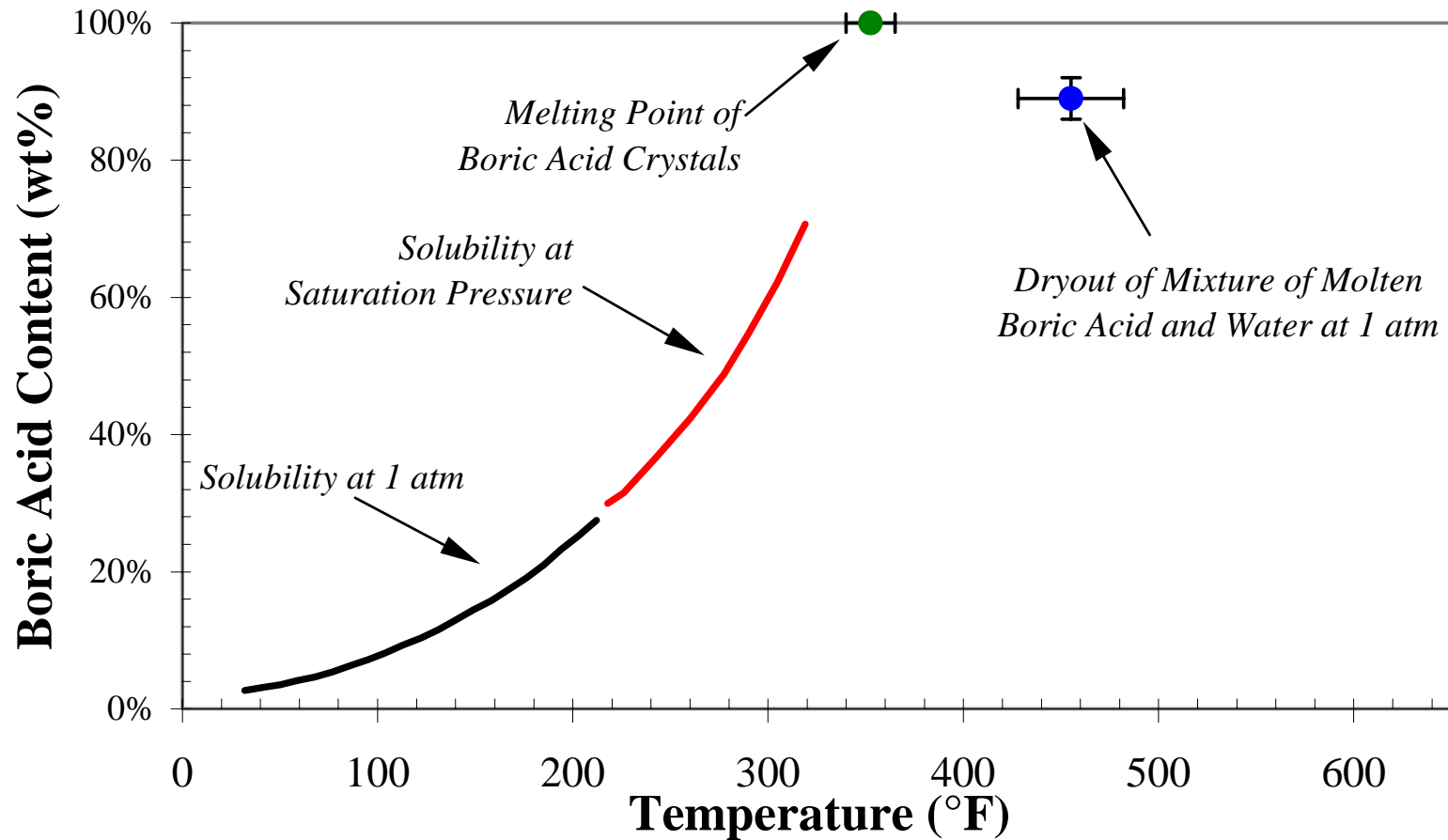
- Above 302°F boric acid is subject to a dehydration reaction to form boric oxide
- The resultant crystalline mass is an anhydrous, white, opaque, non-glasslike, stony solid

➤ Molten boric oxide

- Above 617°F boric oxide begins to soften and at about 842°F becomes a highly viscous liquid

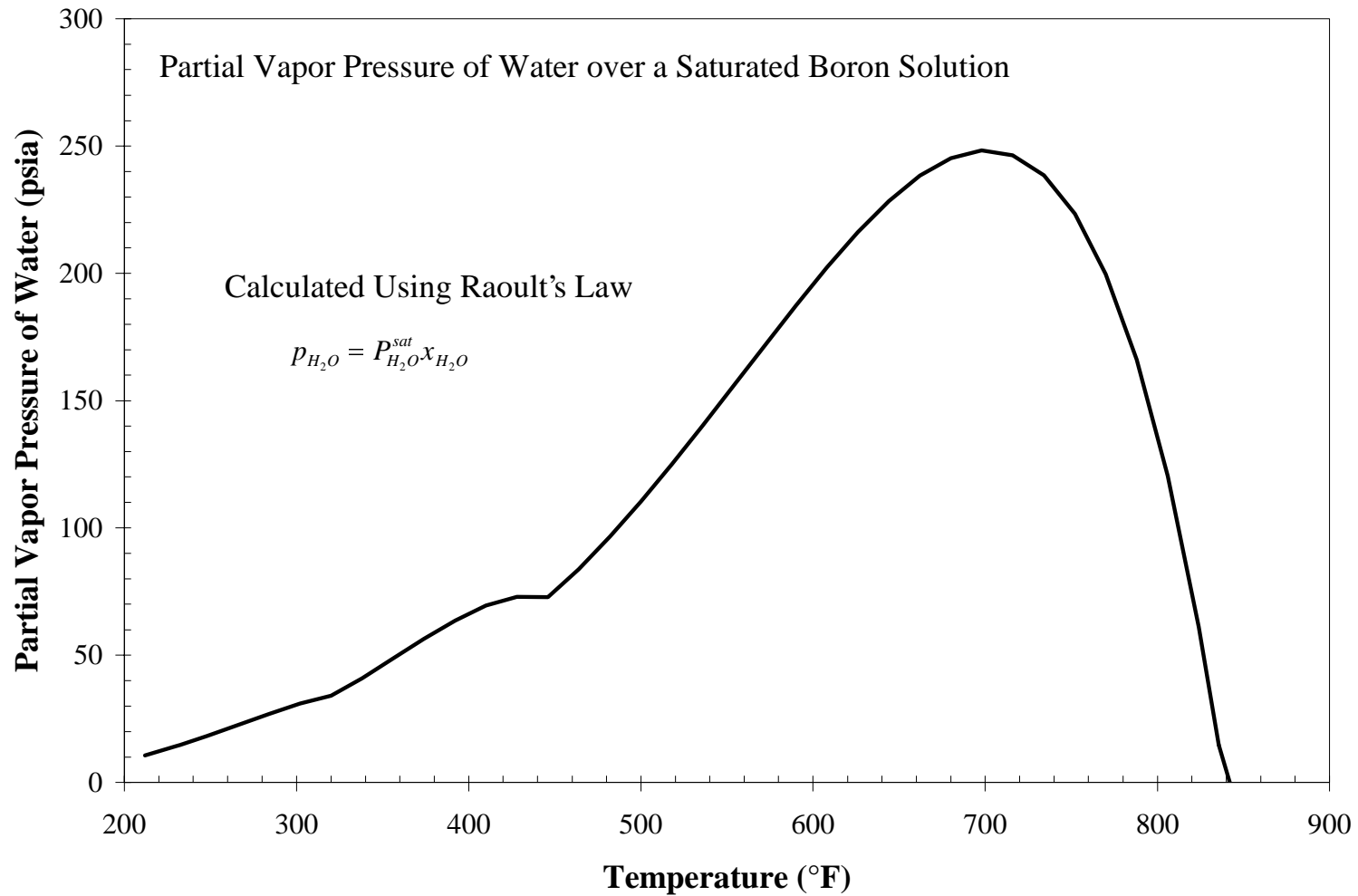
Boric Acid Morphology and Properties

Key Temperature Behavior



Boric Acid Morphology and Properties

Partial Vapor Pressure



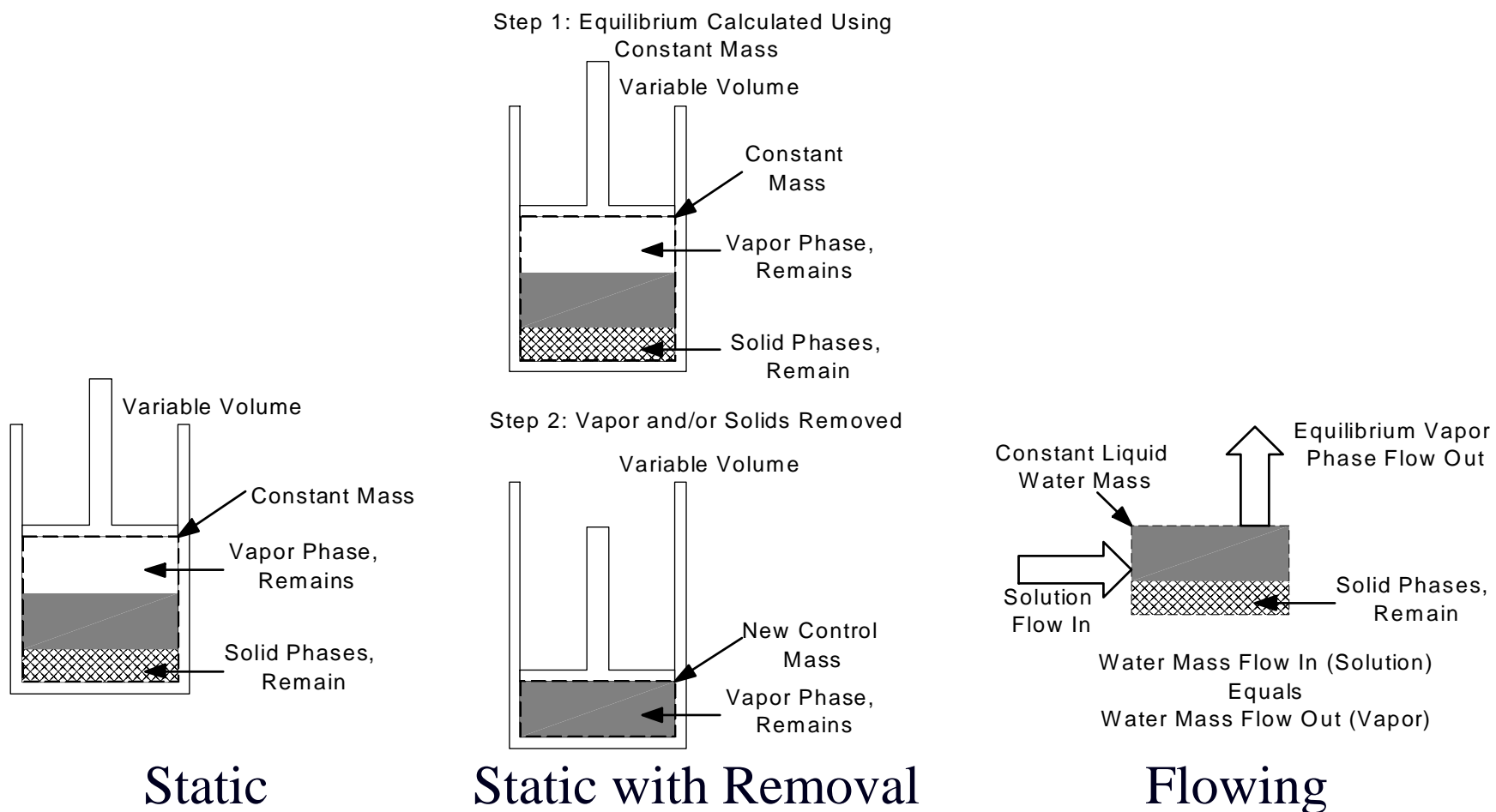
Boric Acid Morphology and Properties

General pH Effects without Large Local Cooling

- For low concentration factors, the solution becomes slightly alkaline, having a small effect on crack growth rates
- For high concentration factors, the solution becomes acidic with a high-temperature pH of 4.5 according to MULTEQ calculations
- The initial high ratio of crevice surface area to volume may allow some buffering by the iron in the head material
- Precipitation of complex lithium and boron compounds occurs and tends to limit pH swings

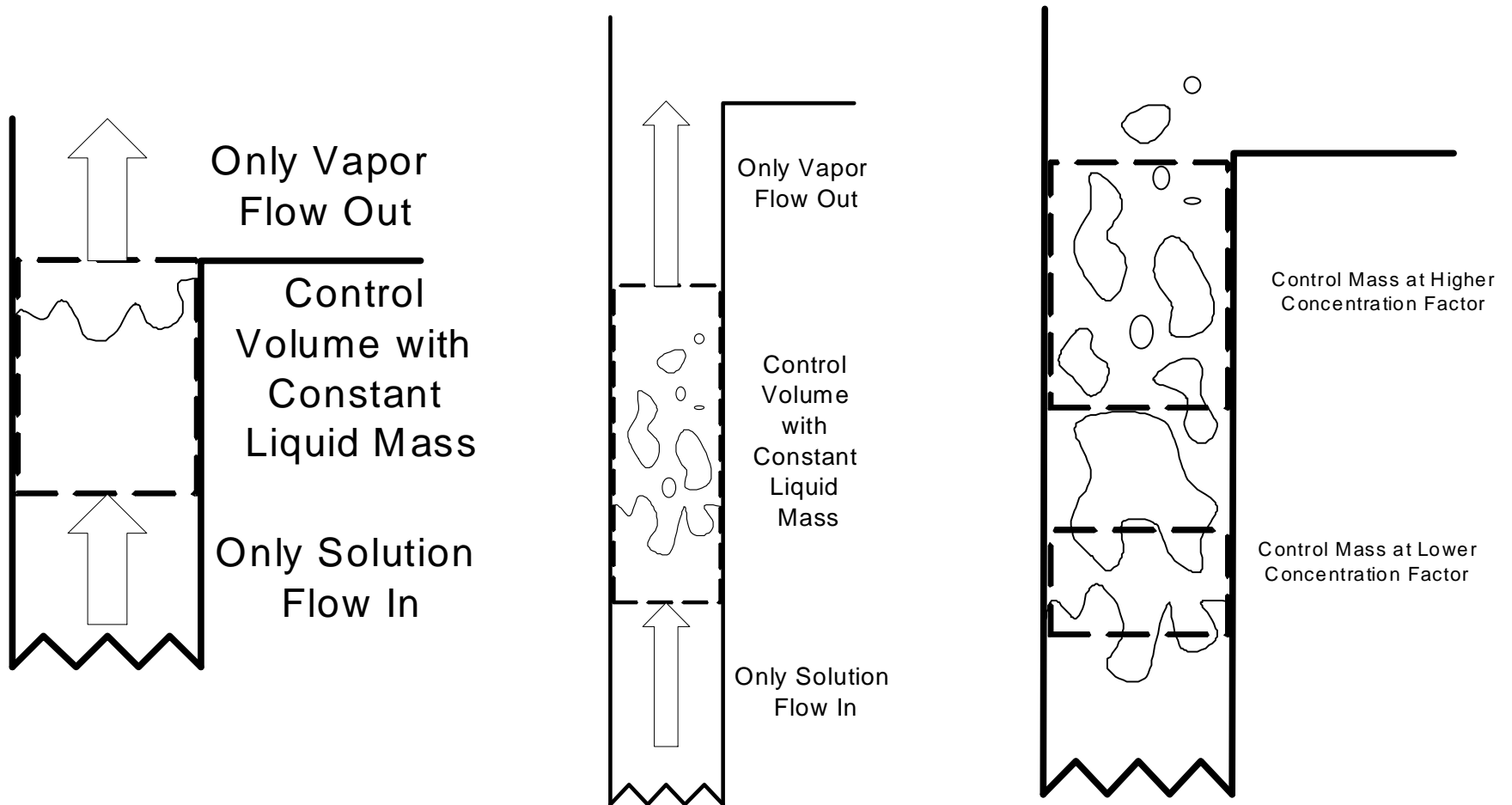
MULTEQ Modeling

Three Main Flow Models Available



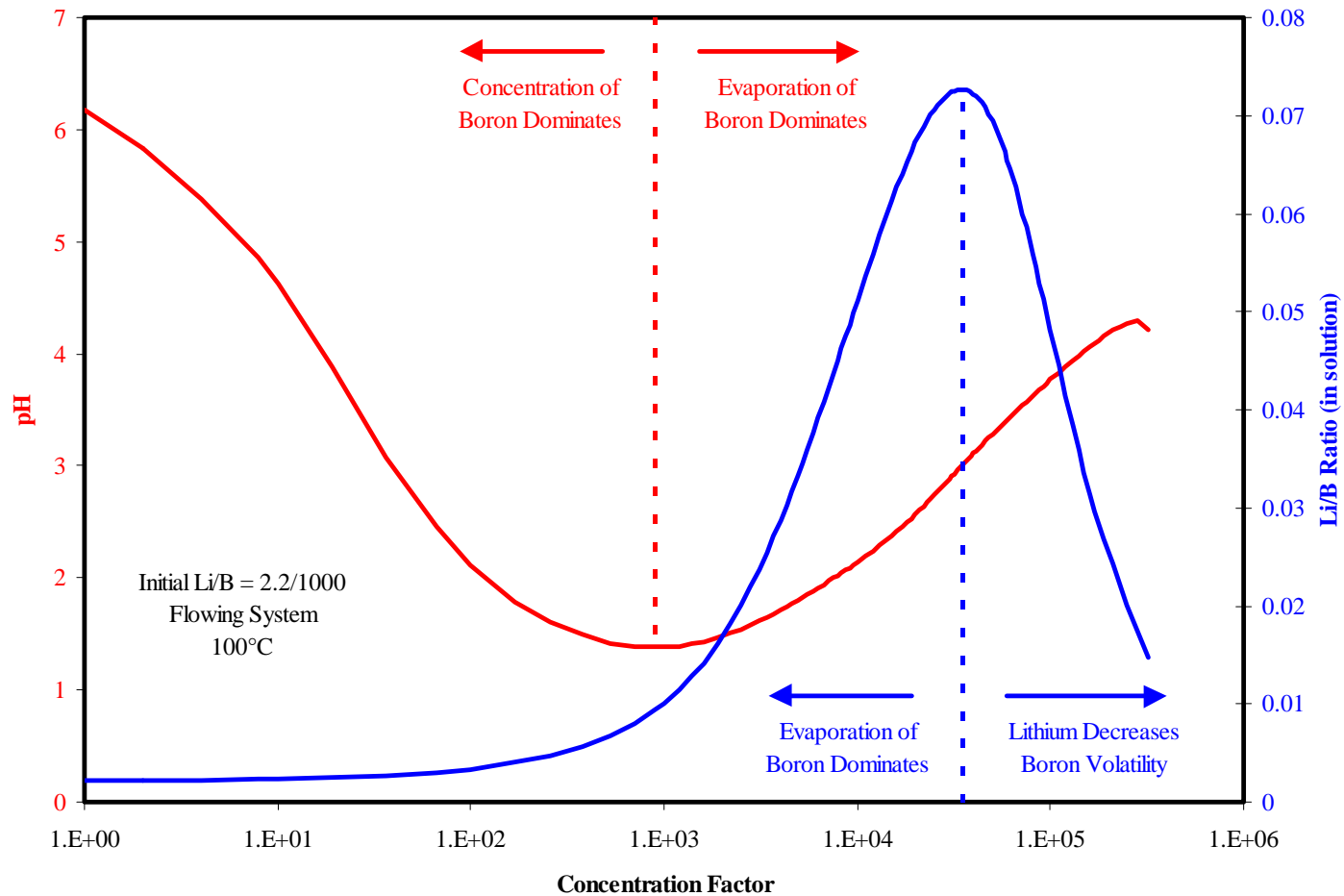
MULTEQ Modeling

Available Control Volumes



Example MULTEQ Calculation

pH in a Flowing System at 100°C



Molten Boric Acid

Orthoboric Acid- H_3BO_3 Metaboric Acid- HBO_2 Boric Oxide B_2O_3

- Corrosion in molten boric acid largely unstudied

- Degradation:
 - Melting point above the degradation point
 - Orthoboric acid: melts at 170.9°C (340°F); degrades to metaboric acid at 169.6°C (337°F)
 - Metaboric acid: melts at 236°C (457°F); degrades to boric oxide at 235°C (455°F)
 - Degradation reaction is slow
 - Effect of degradation products on corrosion largely unknown
 - (degradation probably lower in boric oxide, B_2O_3 , than in either acid)
 - Degradation products highly hygroscopic
 - Analysis of deposits not likely to indicate their at-temperature composition

- Solubility issues largely unstudied
 - Miscibility limits unknown
 - For pH calculations, molten boric acid could be an additional precipitate
 - Degradation products not included in MULTEQ

Molten Boric Acid

Molten Salt Corrosion

- Molten salt corrosion is electrochemically very similar to aqueous corrosion, depending on a reaction couple:
 - $\text{Fe} \rightarrow \text{Fe}^{2+}$ anodic reaction
 - $\text{O}_2 \rightarrow \text{OH}^-$ or $\text{H}^+ \rightarrow \text{H}_2$ cathodic reaction
 - Additional cathodic reactions unlikely in molten boric acid
 - Typical molten salt corrosion occurs through de-passivation
 - Not relevant since LAS and CS are not passive in acidic media

- Acceleration possible due to high conductivity of molten salts
 - Unlikely to lead to a qualitative difference relative to highly concentrated solutions

Molten Boric Acid Issues

Molten Salt Corrosion (continued)

- Solubility of corrosion products likely to be less in molten boric acid than in water
 - Leads to lower corrosion rates

- Molten boric acid corrosion likely to be significantly slower than corrosion in aqueous solution
 - Lower O₂ and H⁺ concentrations (slower cathodic reactions)
 - Possibly lower conductivity
 - Likely lower corrosion product solubility (slower anodic reactions)

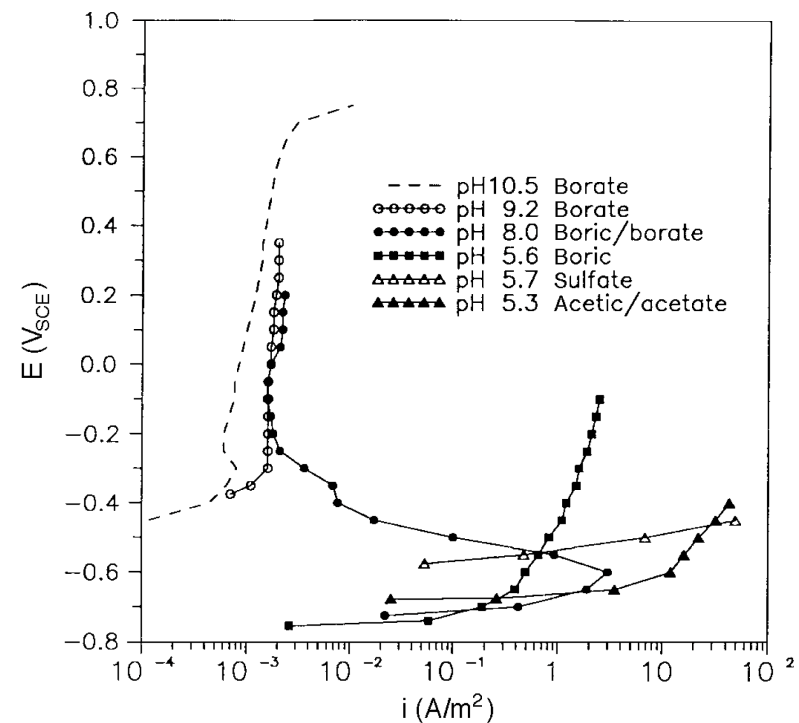
- Corrosion in molten boric acid is a particular case of corrosion in boric acid solutions, not a separate phenomenon

Crevice Corrosion Mechanism

Classic Crevice Corrosion is Not Believed to be Active

- Crevice corrosion typically requires a passivating material in order to allow separation of cathodic and anodic zones
- Carbon and low alloy steels generally do not passivate in acidic media
- Corrosion testing in boric acid solutions indicates that general corrosion is much greater in aerated environments—*i.e.*, there is no passivation

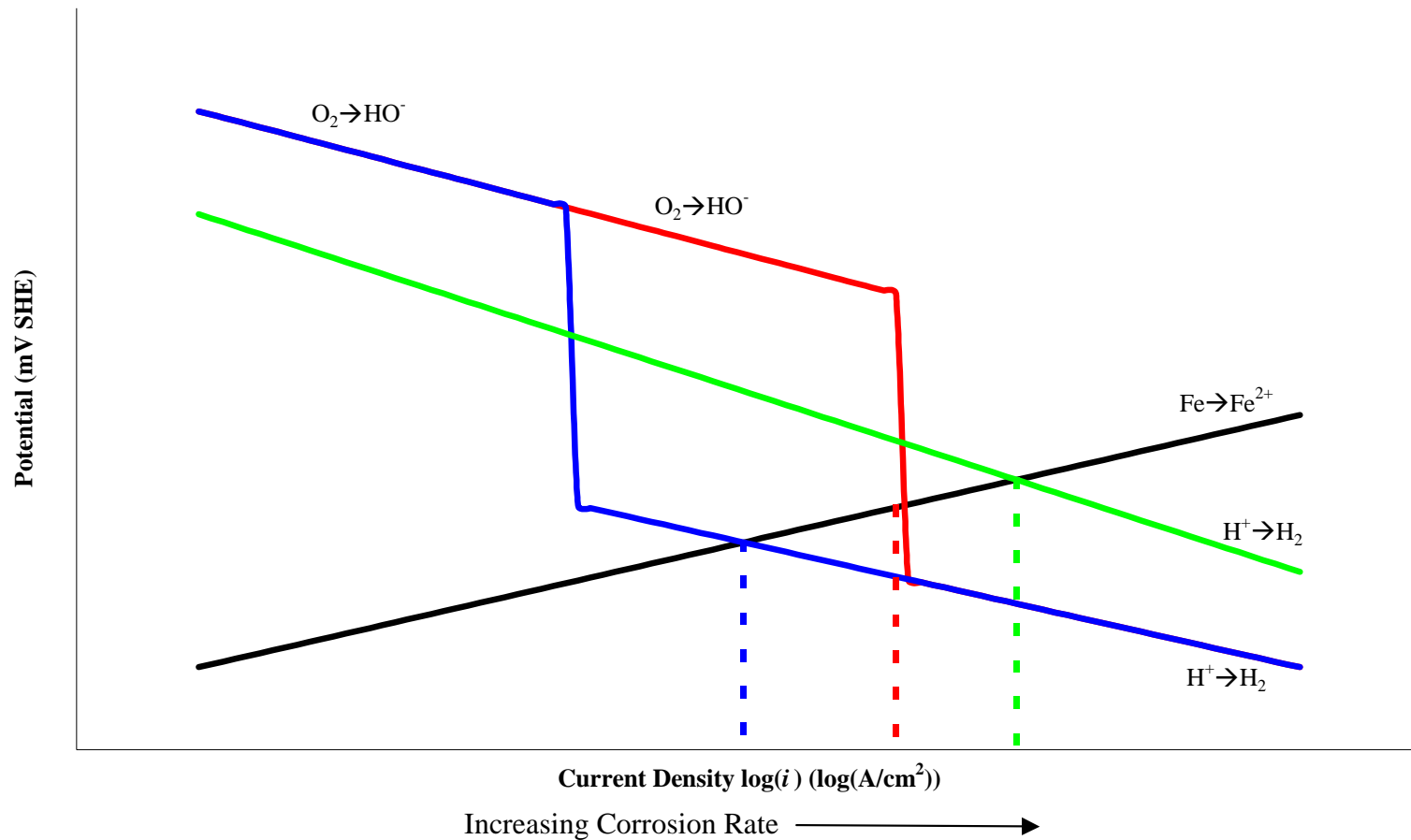
Iron Corrosion Rates in Various Solutions



Makar and Tromans, *Corrosion* 52:4 p.250, 1996

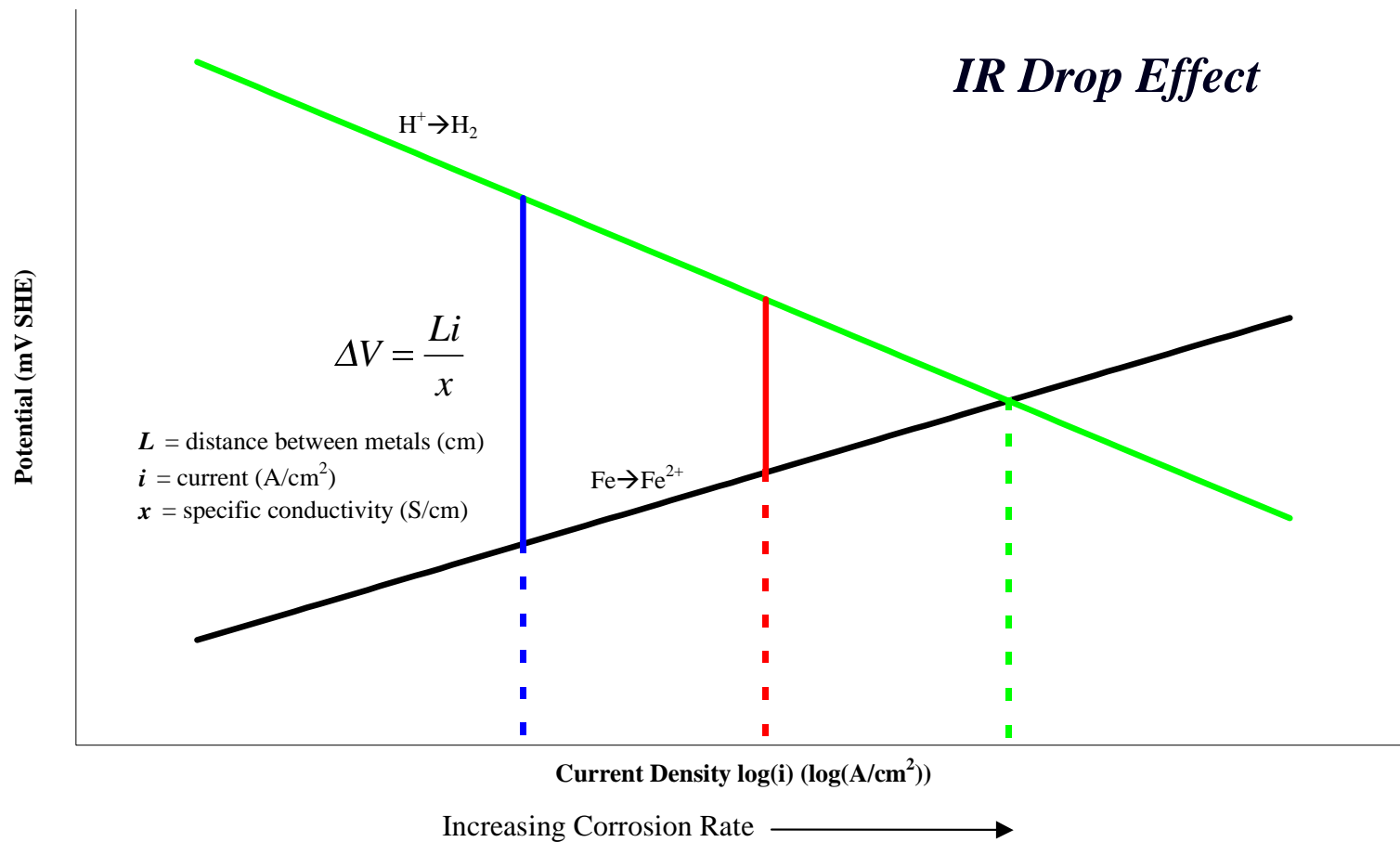
Electrochemistry of Corrosion

Galvanic Corrosion Electrochemistry for a Non-Passivating Metal



Electrochemistry of Corrosion

Galvanic Corrosion Electrochemistry for a Non-Passivating Metal



Degradation Progression

Leak Rate is Main Controlling Parameter

PRELIMINARY

