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

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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 (H₃BO₃) or boric oxide (B₂O₃) 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

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• Boric acid volatility (10% or less)

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Volume of Boric Acid Deposits on the Vessel Head *Example Integration of Boron Mass*

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Boric Acid Morphology and Properties Boron Phases

- ► <u>Boric acid solutions</u> 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

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- 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
- 🕻 \succ 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 \checkmark
 - 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

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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

Step 1: Equilibrium Calculated Using **Constant Mass** Variable Volume Constant Mass Vapor Phase, Remains Solid Phases, Remain Variable Volume Step 2: Vapor and/or Solids Removed Equilibrium Vapor **Constant Liquid** Phase Flow Out Variable Volume Water Mass Constant Mass Vapor Phase, Solid Phases, Remains Solution Remain Flow In New Control Solid Phases, Water Mass Flow In (Solution) Mass Remain Equals Vapor Phase, Water Mass Flow Out (Vapor) Remains Flowing Static with Removal Static

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MULTEQ Modeling • Available Control Volumes

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Example MULTEQ Calculation pH in a Flowing System at 100°C

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Inter statistic constraint of the data of the statistic transferred and the second statistic statistics of 0.08 7 Evaporation of Concentration of 0.07 Boron Dominates **Boron Dominates** 6 1 0.06 5 Δ Hq 3 2 Initial Li/B = 2.2/1000 0.02 Flowing System 100°C 1 0.01 Evaporation of Lithium Decreases Boron Volatility Boron Dominates 0 n 1.E+03 1.E+04 1.E+05 1.E+06 1.E+02 1.E+00 1.E+01 **Concentration Factor**

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Molten Boric Acid

Orthoboric Acid-H₃BO₃ Metaboric Acid-HBO₂ 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

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- 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

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Molten Boric Acid Molten Salt Corrosion

- Molten salt corrosion is electrochemically very similar to aqueous corrosion, depending on a reaction couple:
 - Fe \rightarrow Fe²⁺ anodic reaction
 - $O_2 \rightarrow OH^-$ or $H^+ \rightarrow H_2$ 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)

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- 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

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- 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