

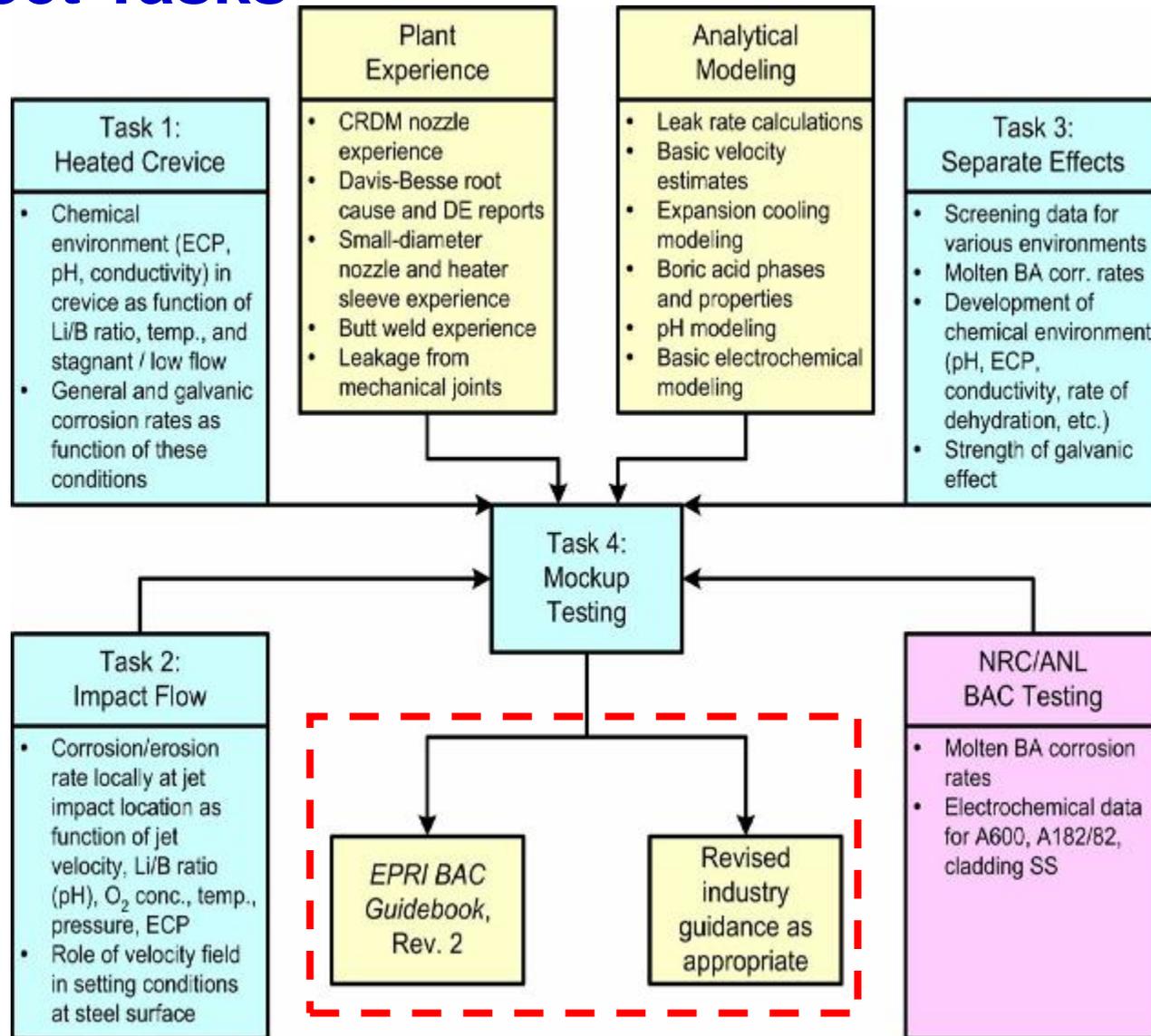


# **Boric Acid Corrosion Testing Program Overview**

**NRC/EPRI MRP Meeting  
Rockville, MD  
February 29, 2012**

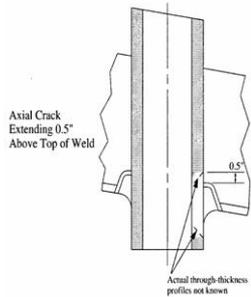
**Rick Reid  
EPRI**

# Project Tasks



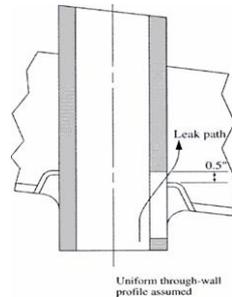
# Implications Assessment of BAC Testing

## Overview of BAC Test Programs



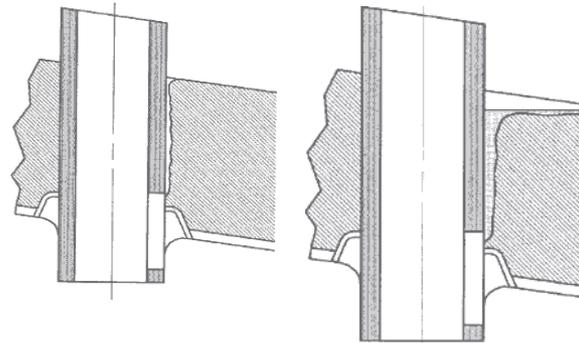
**Task 1**

**Stagnant/Low Flow  
Corrosion**



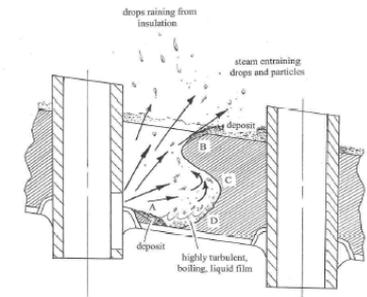
**Task 2**

**Flowing/Impingement  
Corrosion**



**Task 3**

**Separate Effects:  
*Immersion Tests*  
*Electrochemical Tests*  
*Chemical Concentration Tests***



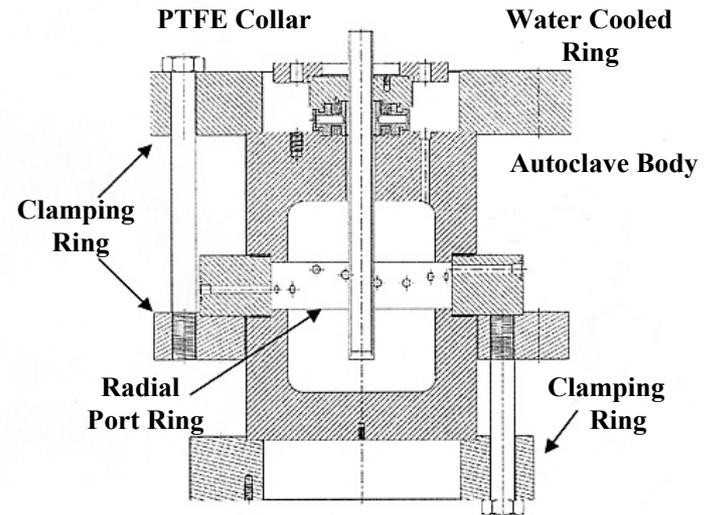
**Task 4**

**Full-Scale Mockup Testing**

- Task 1: Rockwell Scientific performed corrosion tests in stagnant and low flowing (<0.005gpm) primary water simulating early stages of degradation
- Task 2: University of New Brunswick performed primary water impingement corrosion tests
- Task 3: Dominion Engineering, Inc. measured corrosion rates in immersion corrosion environments including concentrated boric acid and wetted molten boric acid, among other tests
- Task 4: DEI and SwRI designed and conducted tests with full-scale mockups of leaking CRDM nozzles and BMNs that simulated a range of operating conditions

# Task 1: Heated Crevice Tests (1/2)

- Objectives:
  - Quantify corrosion rates likely to occur in the early stages of a CRDM nozzle leak
- Methodology:
  - Simulated annulus between Alloy 600 and LAS RPV Head
    - Crevice device to simulate the corrosion of (1) low alloy steel and (2) high chromium steel exposed to stagnant or low flow primary coolant
  - Volumetric flow rate: 2 liters/hr
  - Water chemistry: 3.5 ppm Li - 2000 ppm B, 0.5 ppm Li – 200 ppm B
  - Temperatures: 200°C, 250°C, and 280°C



# Task 1: Heated Crevice Tests (2/2)

- Results and Findings:
  - Rapid corrosion does not occur at test conditions
  - Beginning of cycle chemistry slightly more aggressive (~0.10 mm/yr (4 mpy) versus ~0.03 mm/yr (1 mpy))
  - Corrosion rate is insensitive to test temperature changes
  - Most pronounced corrosion rate change occurred when 25 cc/kg H<sub>2</sub> change to air at 200°C (near zero to 0.13 mm/yr (5 mpy) in RPV steel and 0.08 mm/yr (3 mpy) in 5% Cr steel).
  - Galvanic coupling the LAS to Alloy 600 does not result in significant increases to the corrosion rate for the conditions tested
- Report: Reactor Vessel Head Boric Acid Corrosion Testing (MRP-163)  
*Task 1: Stagnant and Low Flow Primary Water Tests (2005)*

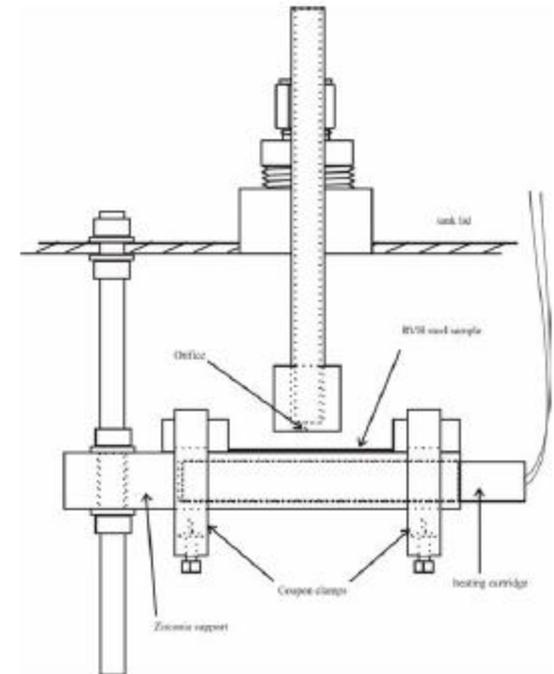
# Task 2: Jet Impingement Tests (1/2)

- Objectives:

- Investigate corrosion of low-alloy steel by primary water jet impingement

- Methodology:

- Impinge water jet onto a RPV low-alloy steel heated plate
- Temperature: 325°C; Pressure: 2200 psig
- Test parameters investigated:
  - Test duration
  - Initial chemistry
  - Flow characteristics
  - Heating
  - Purge gas
  - Jet orientation
  - Jet length
- Electrical resistance and electrochemical potential measured.
- Scanning electron microscopy and surface profilometry measurements for calculated wastage rates



Impingement Test Assembly

## Task 2: Jet Impingement Tests (2/2)

- Results and Findings:
  - Heat flux, water chemistry, flow rate, jet velocity and oxygen are all important parameters affecting LAS corrosion
  - Damage at jet impingement is minimal
  - Corrosion rates are markedly higher at higher coolant boron to lithium ratios (lower pH) and higher levels of dissolved oxygen.
  - Corrosion rates – 0.002 to 0.2 in<sup>3</sup>/yr
- Report: Reactor Vessel Head Boric Acid Corrosion Testing (MRP-164) *Task 2: Jet Impingement Studies (2006)*

# Task 3: Separate Effects Tests (1/3)

- Objective

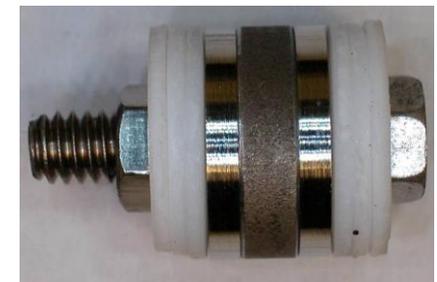
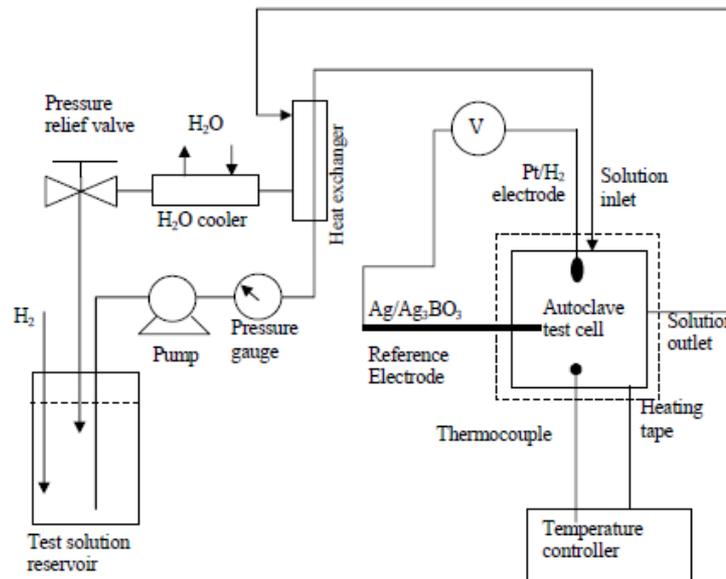
- Investigate the separate effects of chemistry, temperature, and sample configuration on corrosion rates

- Methodology

- Immersion tests using low alloy steel corrosion coupon in an autoclave with a liquid/slurry phase and a gas phase



Crevice Specimen



Galvanic Specimen

# Task 3: Separate Effects Tests (2/3)

- Methodology (continued)

- Test conditions tested included the following parameters:
  - Temperature: 100°C, 200°C, or 315°C
  - Boron concentration: 2000 ppm as boron, 1000 g boric acid per 1 kg of water, or 9000 g of boric acid per 1 kg of water
  - Lithium to boron ratio: no lithium, Li/B = 0.002, or Li/B = 0.05
  - Gas composition: oxygen or a mix of hydrogen (10%) and nitrogen (90%)
  - Sample configuration: uncoupled (free), creviced (with PTFE), or galvanically coupled (to Alloy 600)
- Corrosion rates determined by the mass and the test duration using the initial dimensions to determine the surface area.

Plant Chemistry: B – 500 to 2000 ppm; Li/B – 0.002 to 0.007

# Task 3: Separate Effects Tests <sup>(3/3)</sup>

- Results and Findings:
  - pH is the most significant parameter – temperature, galvanic coupling, crevice geometry, and oxygen are secondary effects to pH.
  - Slurries of hydrated molten boric acid can corrode LAS at up to 5 in/yr
  - Dynamic concentration tests indicated that molten boric acid mixtures are unlikely to retain the moisture necessary for high corrosion rates
  - Lithium concentration could lower corrosion rates by 10X or greater
- Report: Reactor Vessel Head Boric Acid Corrosion Testing (MRP-165)  
*Task 3: Separate Effects Testing (2005)*

# ANL Test Program (1/3)

- Objective
  - Determine the electrochemical potentials (ECPs) and corrosion rates of RPV head and CRDM nozzle materials in boric acid solutions at varying temperatures and environmental conditions.
- Methodology
  - Three different environments designed to simulate the postulated stages of corrosion attack were investigated:
    - High pressure/high temperature aqueous solutions
    - High temperature/atmospheric pressure hydrogen-boron-oxygen environments (Hydrated and Dry)
    - Low temperature saturated boric acid solutions

# ANL Test Program (2/3)

- Results
  - 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. However, it may be very difficult under plant conditions to keep molten boric acid hydrated.
    - Maintaining heads clean eliminates potential for development of hydrated molten boric acid conditions

# ANL Test Program (3/3)

- Results (continued)
  - Corrosion significantly slowed by the presence of lithium, with effect most apparent at high temperatures. Increased boric acid volatility at higher temperatures limits ability to concentrate, increasing Li/B ratio and lowering corrosion rate
  - 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

# Full-scale CRDM Mock-up BAC Tests

- Objectives:

- Perform full-scale CRDM BAC tests with prototypic geometries, materials, thermal-hydraulic conditions and primary coolant chemistries

- Approach:

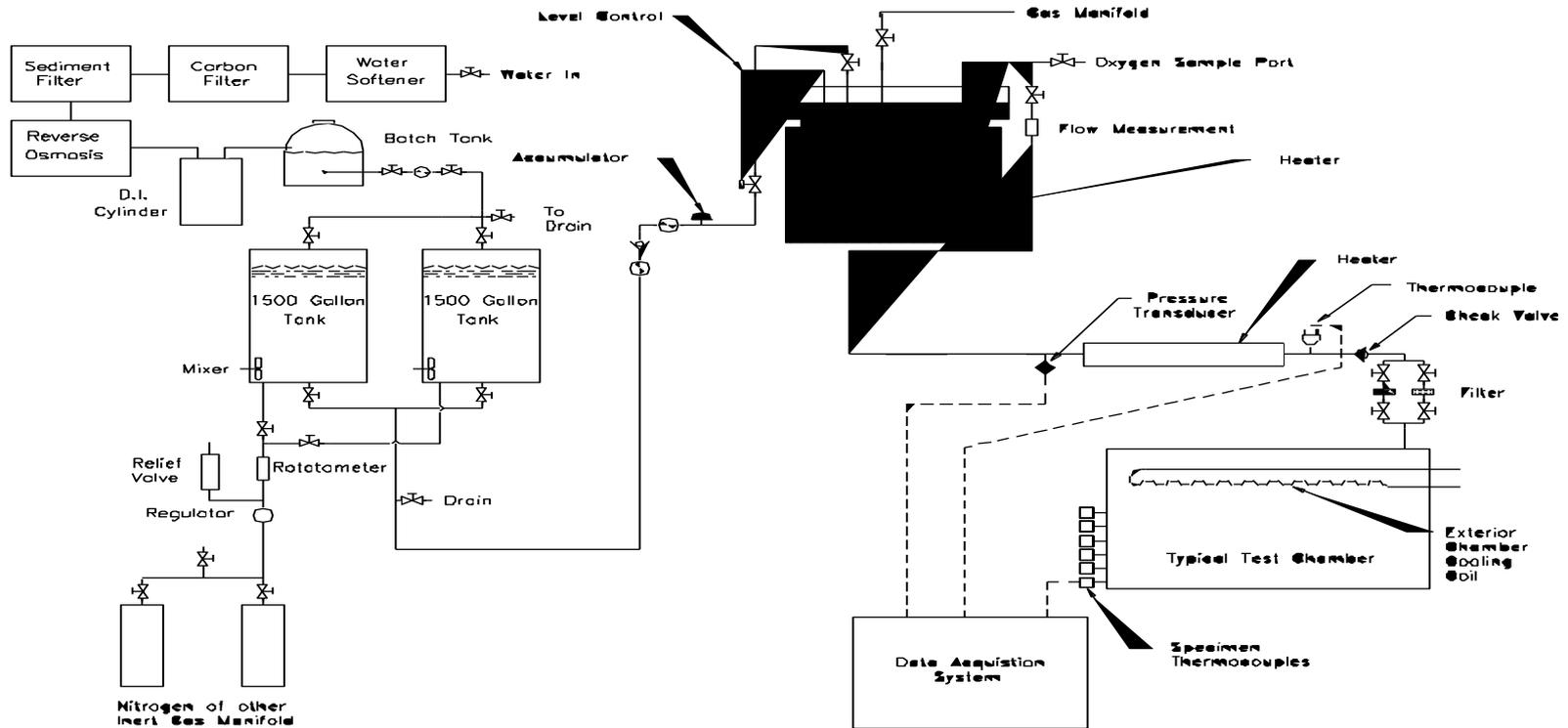
- A modular CRDM mockup fabricated from low-alloy steel and alloy 600 materials. With capability to vary:

- Flow rate, Temperature, Pressure, Chemistry
    - LAS-Nozzle annulus gap width and geometry

- Testing Completed and Report Issued December 2009

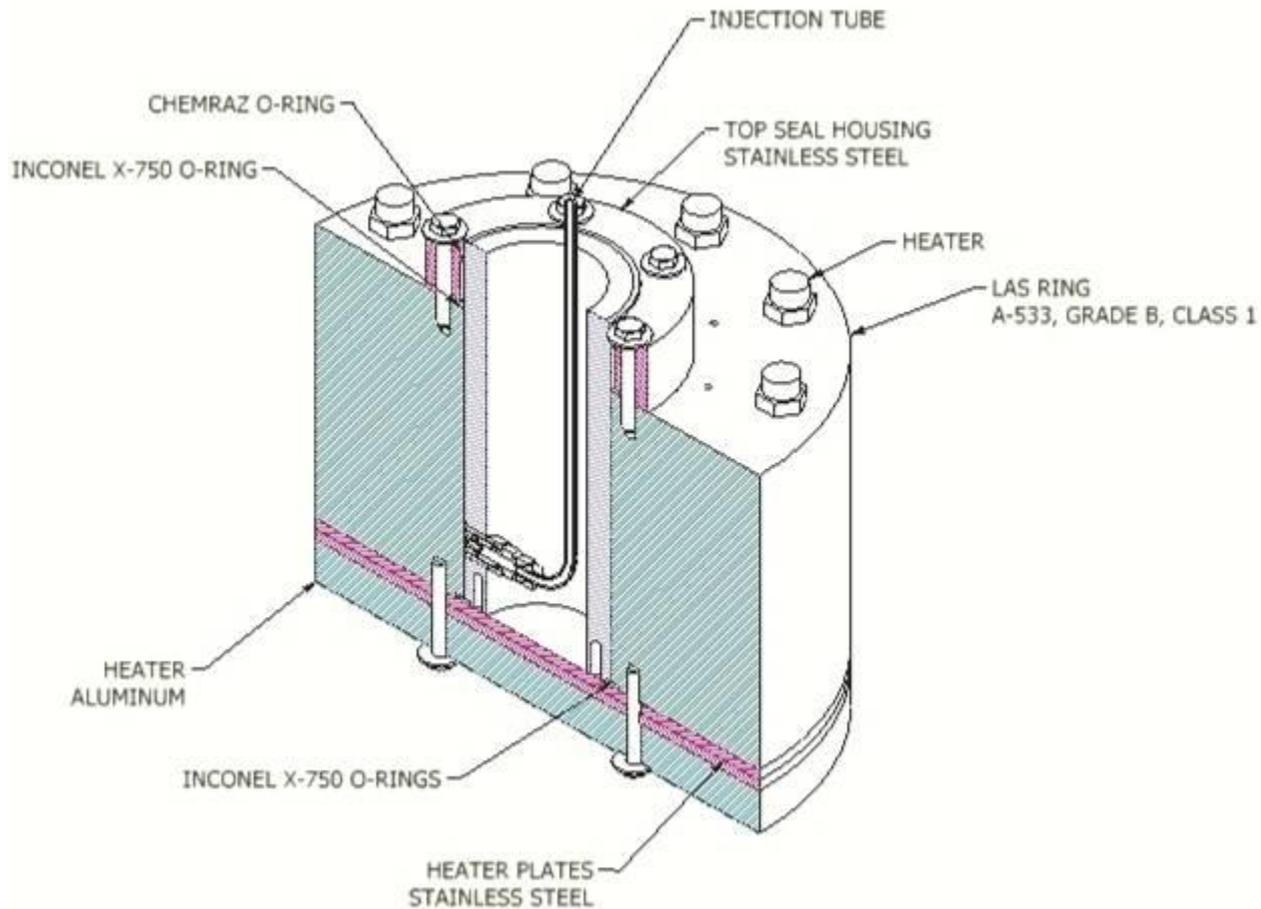
- EPRI 1019085 (MRP-266): Full-Scale CRDM Mockup Boric Acid Corrosion Testing

# Test Assembly Schematic



12105-01REV

# CRDM Mock-Up



# CRDM Test Results Summary (1/4)

Test No.	Ave. Flow Rate [gpm]	Gap [mil]	Total Material Wastage [in <sup>3</sup> /yr]	Area-Avg Wastage Rate [in/yr]	General Observations	Photo of Post-Test Annulus
01	0.0114	1	0.10	0.015	<ul style="list-style-type: none"> <li>(-) Localized impingement with no wastage</li> <li>(-) Tenacious deposits around injection site</li> <li>(-) Single flow channel to top of annulus</li> <li>(-) Localized (irregular) wastage at top of annulus</li> </ul>	
02	0.0015	10	0.00	0.002	<ul style="list-style-type: none"> <li>(-) LAS annulus was still clean</li> <li>(-) Insignificant wastage observed</li> <li>(-) Small pit directly beneath injection site</li> <li>(-) Small amount of loose white deposits located at injection site and top of annulus</li> </ul>	
03	0.0110	10	0.24	0.034	<ul style="list-style-type: none"> <li>(-) Annular flow path was originally upward (evidence of pitting)</li> <li>(-) Tenacious deposits formed around the entire injection site</li> <li>(-) No wastage at local injection site</li> <li>(-) Wastage was observed around injection site and within deposit ring</li> <li>(-) Effluent passed through restrictive passage along bottom of annulus</li> </ul>	
04	0.0920	10	4.10	0.214	<ul style="list-style-type: none"> <li>(-) Few deposit were formed in the annulus</li> <li>(-) Flow fanned out vertically above injection site</li> <li>(-) Coloration of deposits on top of LAS indicated corrosion products</li> <li>(-) Minimal wastage at local injection site</li> <li>(-) Significant wastage observed around and below injection site</li> </ul>	

# CRDM Test Results Summary (2/4)

Test No.	Ave. Flow Rate [gpm]	Gap [mil]	Total Material Wastage [in <sup>3</sup> /yr]	Area-Avg Wastage Rate [in/yr]	General Observations	Photo of Post-Test Annulus
06a	0.0100	10	0.93	0.189	<ul style="list-style-type: none"> <li>(-) Minimal wastage at injection site</li> <li>(-) Measurable wastage around and below injection site</li> <li>(-) Defined horizontal boundary - Top 2" of LAS appear to have not been exposed to effluent</li> </ul>	
07a	0.1000	10	16.30	0.290	<ul style="list-style-type: none"> <li>(-) No evidence of injection site on the cavity surface</li> <li>(-) Few deposits formed in annulus</li> <li>(-) Wastage was around and below cavity</li> <li>(-) Wastage was observed at the top of the annulus at both 90° locations from the injection site</li> <li>(-) Evidence of possible leakage at lower o-ring</li> </ul>	
08a	0.0100	10	0.90	0.183	<ul style="list-style-type: none"> <li>(-) Minimal wastage at injection site</li> <li>(-) Measurable wastage around and below injection site</li> <li>(-) Defined horizontal boundary - Top 2" of LAS appear to have not been exposed to effluent</li> </ul>	

# CRDM Test Results Summary (3/4)

Test No.	Ave. Flow Rate [gpm]	Gap [mil]	Total Material Wastage [in <sup>3</sup> /yr]	Area-Avg Wastage Rate [in/yr]	General Observations	Photo of Post-Test Annulus	Back of Annulus or Exit Plane Photo (if needed)
09a	0.1000	10	17.70	0.242	<ul style="list-style-type: none"> <li>(-) Rust-colored deposits evident on mockup and in test box</li> <li>(-) Evidence of wastage-induced leak at bottom weld seal (90° from injection site)</li> <li>(-) Minimal wastage at injection site</li> <li>(-) Measurable wastage around injection site</li> </ul>		
10a	0.0010	1	0.00	0.024	<ul style="list-style-type: none"> <li>(-) LAS annulus was still clean</li> <li>(-) Insignificant wastage observed</li> <li>(-) Small pit directly beneath injection site</li> <li>(-) Small amount of loose white deposits located at injection site and top of annulus</li> </ul>		—
11a	0.0100	10	2.10	0.070	<ul style="list-style-type: none"> <li>(-) Rust colored deposits on outside of deposit</li> <li>(-) Localized impingement with no wastage</li> <li>(-) Tenacious deposits around injection site</li> <li>(-) Deposits form flow path to top of annulus</li> </ul>		—

# CRDM Test Results Summary (4/4)

Test No.	Ave. Flow Rate [gpm]	Gap [mil]	Total Material Wastage [in <sup>3</sup> /yr]	Area-Avg Wastage Rate [in/yr]	General Observations	Photo of Post-Test Annulus	Back of Annulus or Exit Plane Photo (if needed)
12a	0.1000	10	16.83	0.346	<ul style="list-style-type: none"> <li>(-) No evidence of injection site on the cavity surface</li> <li>(-) Few deposits formed in annulus</li> <li>(-) Deep channel wastage around and below cavity and engineered channel</li> <li>(-) Wastage was observed at the top of the annulus at both 90° locations from the injection</li> </ul>		
Inverted 01	0.0136	10	1.90	0.158	<ul style="list-style-type: none"> <li>(-) Localized impingement with no wastage plateau</li> <li>(-) Wastage around plateau region</li> <li>(-) Two flow channels formed by deposits guided flow to top of annulus</li> <li>(-) Localized (irregular) wastage at top of annulus</li> </ul>		—
Inverted 02	0.1000	10	10.60	0.357	<ul style="list-style-type: none"> <li>(-) Notable impingement damage with no wastage plateau</li> <li>(-) Deep attack around a 3-inch x 2-inch oval about the injection location, especially close to top hot plate area.</li> <li>(-) Diffus attack fanning out toward the bottom exit of the annulus</li> </ul>		

# Deposit Formation



0.01gpm



0.1gpm



0.1gpm

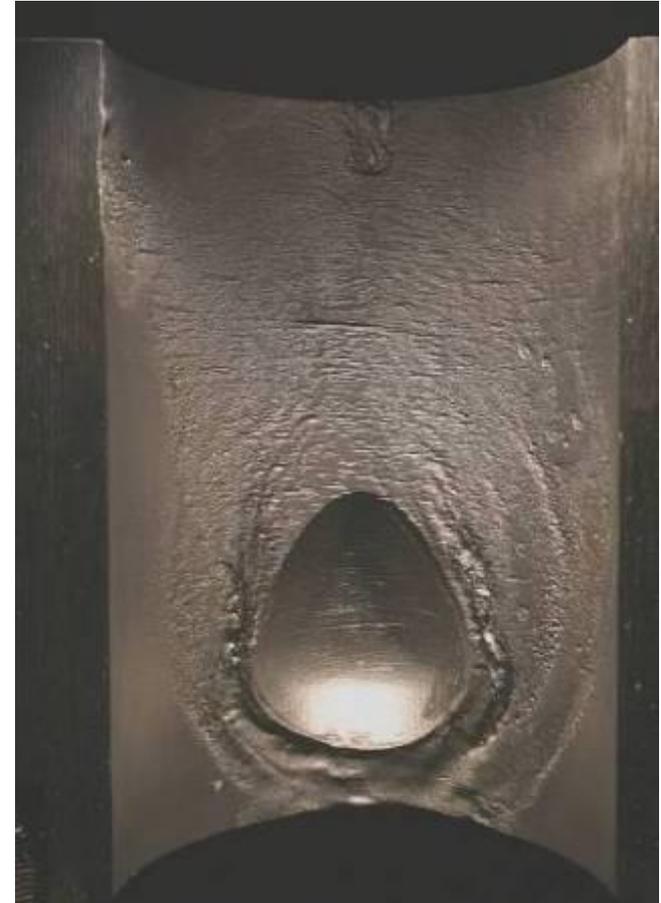
# Pre-machined Cavity Effect

#4



0.1 gpm, 10 mil  
Wastage – 4.1 in<sup>3</sup>/yr

#7a



0.1 gpm, 10 mil  
Wastage – 14.86 in<sup>3</sup>/yr

# Pre-machined Cavity Effect

#8a



0.01 gpm, 10 mil  
Wastage – 0.90 in<sup>3</sup>/yr

#6a



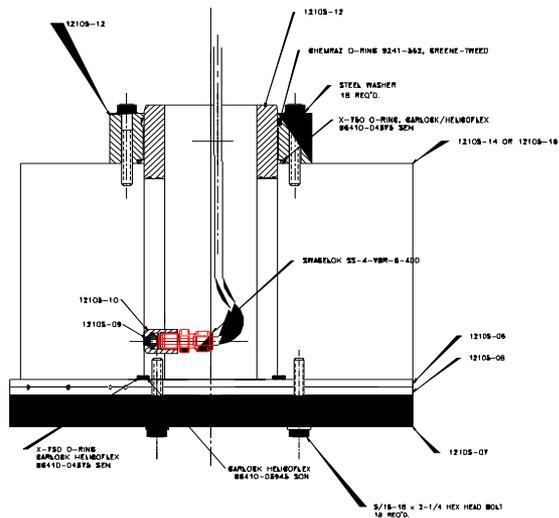
0.01 gpm, 10 mil  
Wastage – 0.93 in<sup>3</sup>/yr

# Bottom Mounted Instrument Nozzle Mock-Up Testing

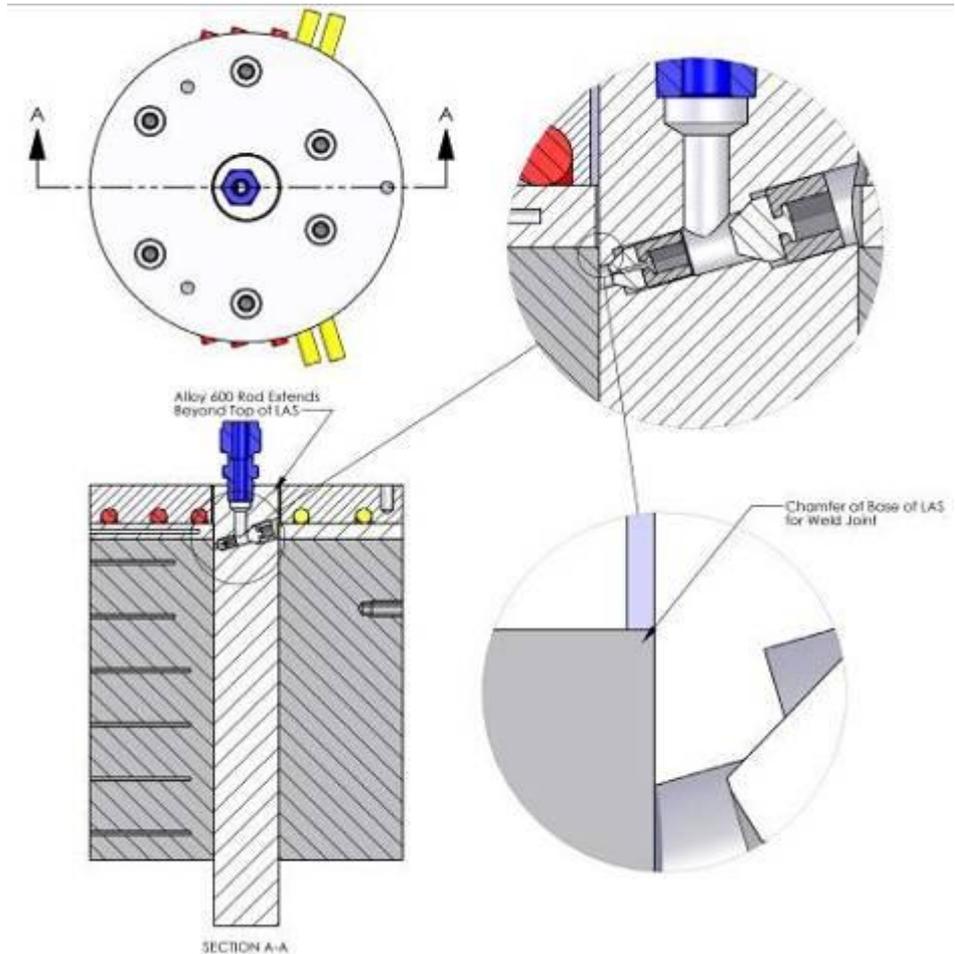
# Full-Scale BMI Nozzle BAC Testing

## Injection Design

- Design uses a replaceable orifice
- Allows extended duration tests
- Possibility of running tests with increasing leak rates



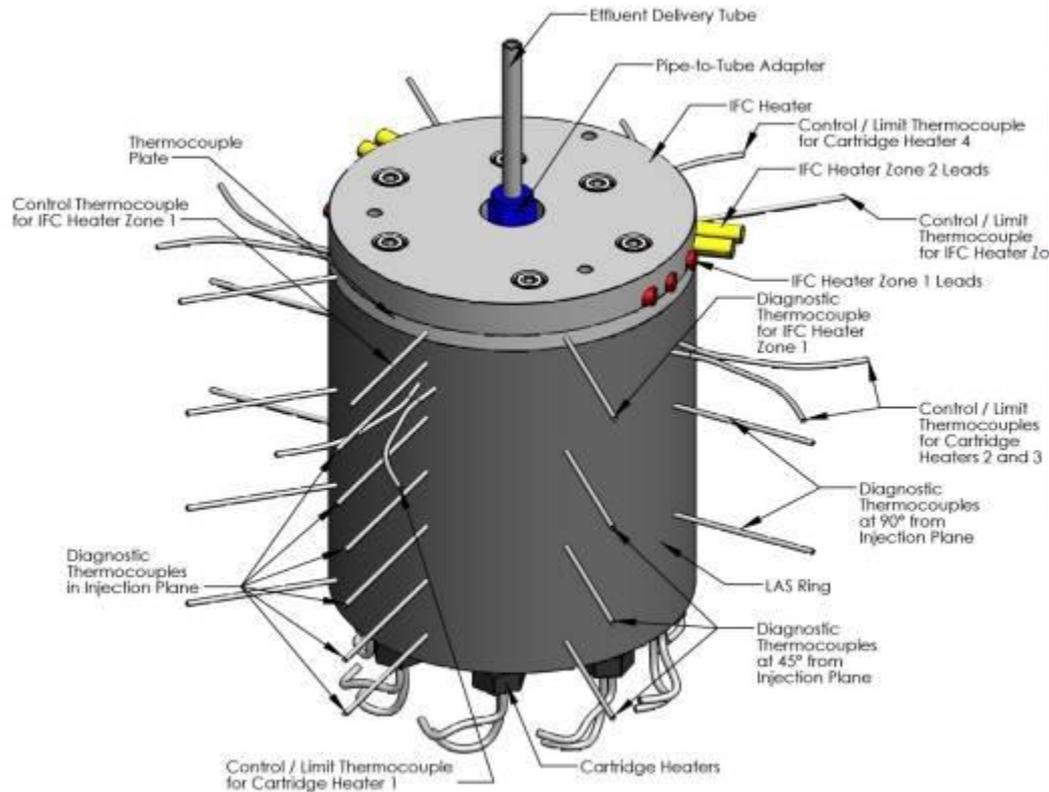
CRDM Mock-Up Design



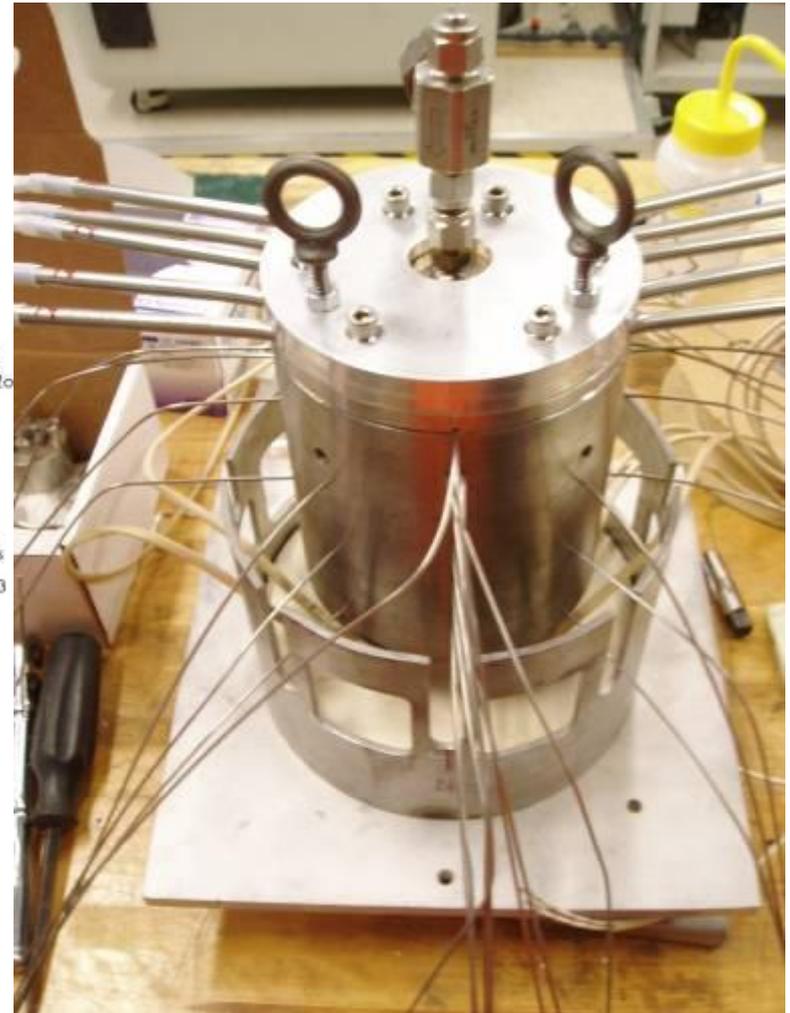
BMN Mock-Up Design

# Full-Scale BMI Nozzle BAC Testing

*Mockup Assembly – Thermocouples, Bottom Insulation and Support Installed*



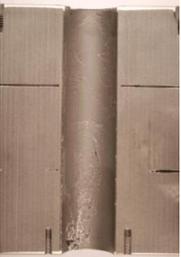
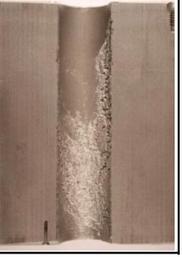
Mockup Symmetric About Vertical Plane Aligned with Injection Location



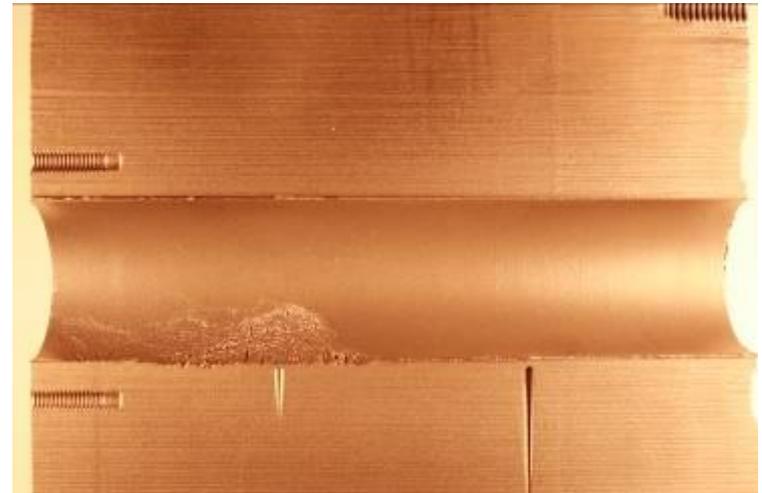
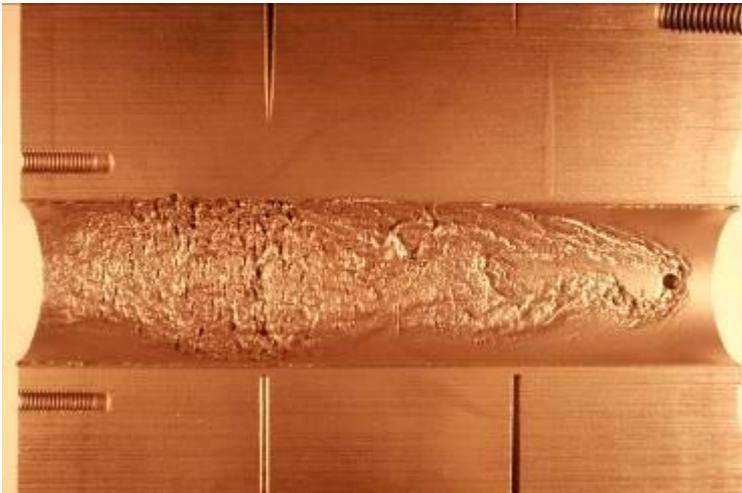
# BMN Test Results Summary (1/2)

Test No.	Ave. Flow Rate [gpm]	Gap [mil]	Total Material Wastage [in <sup>3</sup> /yr]	Area-Avg Wastage Rate [in/yr]	General Observations	Photo of Post-Test Annulus	Back of Annulus or Exit Plane Photo (if needed)
1	0.0099	10	2.26	0.383	<ul style="list-style-type: none"> <li>(-) Notable impingement damage with small plaeau</li> <li>(-) Flow path restricted to front of annulus</li> <li>(-) Wastage is distributed axially with increased wastage closer to annulus exit</li> </ul>		—
2	0.0060	10	1.69	0.693	<ul style="list-style-type: none"> <li>(-) Minimal impingement damage</li> <li>(-) Minimal damage around inject or upper half of annulus</li> <li>(-) Limited flow arc twists around annulus to 90°</li> <li>(-) All damage located on lower half of annulus</li> </ul>		
3	0.0055	10	4.84	0.744	<ul style="list-style-type: none"> <li>(-) Notable impingement damage at injection</li> <li>(-) Minimal damage around injection location</li> <li>(-) Flow restricted to front of annulus</li> <li>(-) Damage in lower two-thirds of annulus</li> </ul>		—

# BMN Test Results Summary (2/2)

Test No.	Ave. Flow Rate [gpm]	Gap [mil]	Total Material Wastage [in <sup>3</sup> /yr]	Area-Avg Wastage Rate [in/yr]	General Observations	Photo of Post-Test Annulus	Back of Annulus or Exit Plane Photo (if needed)
4	0.0010	10	0.26	0.085	<ul style="list-style-type: none"> <li>(-) No damage at impingement or upper part of annulus</li> <li>(-) Flow path restricted to 1/2-inch front half of annulus</li> <li>(-) Damage is very localized near exit of annulus.</li> </ul>		—
5a	0.0058	1	2.42	0.235	<ul style="list-style-type: none"> <li>(-) Minimal impingement damage with no wastage plateau</li> <li>(-) Minimal wastage in upper one-third of annulus</li> <li>(-) Flow twisted around annulus and most damage is on backside lower two-thirds of annulus</li> <li>(-) Flow area restricted to ~1/2 annulus arc</li> </ul>		
7a	0.0280	10	3.43	0.313	<ul style="list-style-type: none"> <li>(-) Notable impingement damage at injection</li> <li>(-) Some Plateau</li> <li>(-) Extensive damage over entire length of annulus</li> <li>(-) Flow are restricted to ~1/2 annulus arc</li> <li>(-) Flow twisted to exit at 90°</li> <li>(-) Damage on exit plan of LAS</li> </ul>		

# BMN Test 1 Cross Section



# BMN Test Results: Test 1 (10-mil gap; 0.01 gpm leak rate)

Low Alloy Steel  
("reactor vessel")

Inconel Tube



Deposits clearly visible after two days



Very heavy deposits after ~one month

# BMN Test 5

- Long-term test (164 days)
  - 0.006 gpm leakage rate; 1-mil annulus gap
  - Boric acid deposits visible after just one day



# Together...Shaping the Future of Electricity