Recent Results and Future GSI-191 Research

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Outline

- **Future Research Plans**
  - Latent Debris Characterization
  - Additional Head-loss Testing
  - HPSI Throttle Valve Blockage
    - Sump Screen Debris Penetration
    - Surrogate Chamber Blockage
- **Recent Results**
  - Chemical Test Program
    - Review of Concerns and Test Procedure
    - Review of Previous Results
      - Head-loss from metallic precipitants
      - Low-temperature zinc corrosion
    - Discussion of new Results
      - High-temperature zinc corrosion
      - Corrosion product composition
      - Zinc paint chip leaching
      - Non qualified paint immersion
      - Debris-bed degradation

Future Research Projects (1)

- **Latent Debris Characterization**
  - Objectives:
    - Plant-wide inventory – based on condition assessments
    - Physical characteristics
      - fiber/particulate mass ratio
      - size ranges for transportability
    - Hydraulic properties
      - specific surface area
      - porosity

Define a ‘recipe’ for PWR dirt surrogate that can be produced in quantity for large-loop head-loss testing

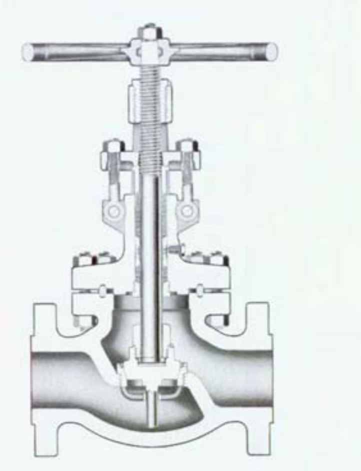
  - Procedure: (under development)
    - Microscopic physical examination
    - Pre-filter fiber from particulate
    - Surface area measurement by nitrogen condensation
    - Porosity by micro head-loss measurement
  - Scope: Approximately 5 samples from 5 volunteer plants
  - Status: Preparing to receive samples from first 2 volunteers

Future Research Projects (2)

- **Additional Large-Loop Head-loss Tests**
  - Fill gaps in earlier Cal-Sil test data
    - High flow rate compression
    - Low flow rate hydraulic parameters
  - Confirm large-loop head-loss properties of surrogate PWR debris
    - Characterization project will provide physical description of a appropriate surrogate test material
    - Identify any discrepancies between PWR surrogate and typical fiber/particulate combinations

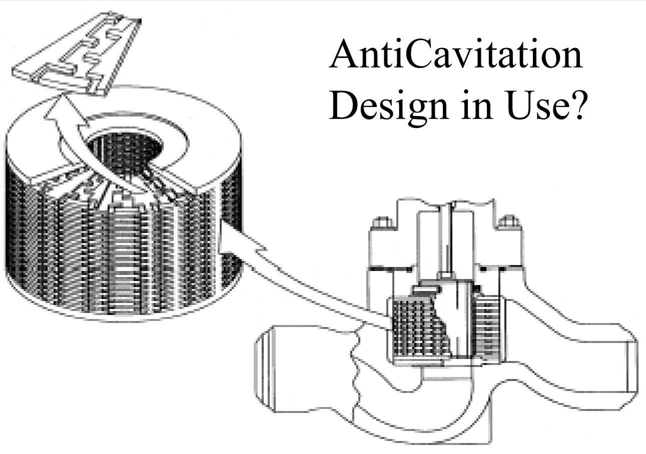
Future Research Projects (3)

- **HPSI Throttle Valve Blockage**
  - Sump-screen debris penetration
    - Horizontal Flume with typical screen sections and downstream capture system
    - Separate debris types and combinations
  - Valve chamber blockage tests
    - Design surrogate valve bodies and/or obtain substandard valves
    - Design pressurized pumping system or charging tank for ? P
    - Introduce ‘penetrable’ debris in pressurized flow and examine internal blockage mechanisms
      - Geometric and/or Buildup



Basic Globe Valve design may be manual, pneumatic or hydraulic

Variety of seat and seal designs



AntiCavitation Design in Use?

UNITED STATES NUCLEAR REGULATORY COMMISSION

HPSI Valve Operating Conditions

Plant Design Type	HPI Pump Head, psig	HPI Pump Flow, GPM[1]
W – 2 Loop (low flow)[2]	1170	300
W – 2 Loop (high flow)[2]	1750	700
W – 3 Loop (low flow)[2]	2514	150
W – 3 Loop (high flow)[2]	1750	375
W – 4 Loop (low flow)[2]	1170	425
W – 4 Loop (high flow)[2]	1235	800
Commanche Peak (W – 4 Loop)[3]	715	650
CE – 2 Loop (low flow)[2]	1214	150
CE – 2 Loop (high flow)[2]	1227	415
CE – 3 Loop[2]	2850	150
B&W – 2 Loop (low flow)[2]	2514	150
B&W – 2 Loop (high flow)[2]	1170	500

- Need to know maximum pressure drop when HPSI valve is in use
    - Defines max pressure for debris integrity considerations
    - Defines safety requirements of test apparatus
- ? P may not be as extreme as available pump head
- Flow volume and turbulence may be more important for some types of debris

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[1] flow at stated head (rated conditions)

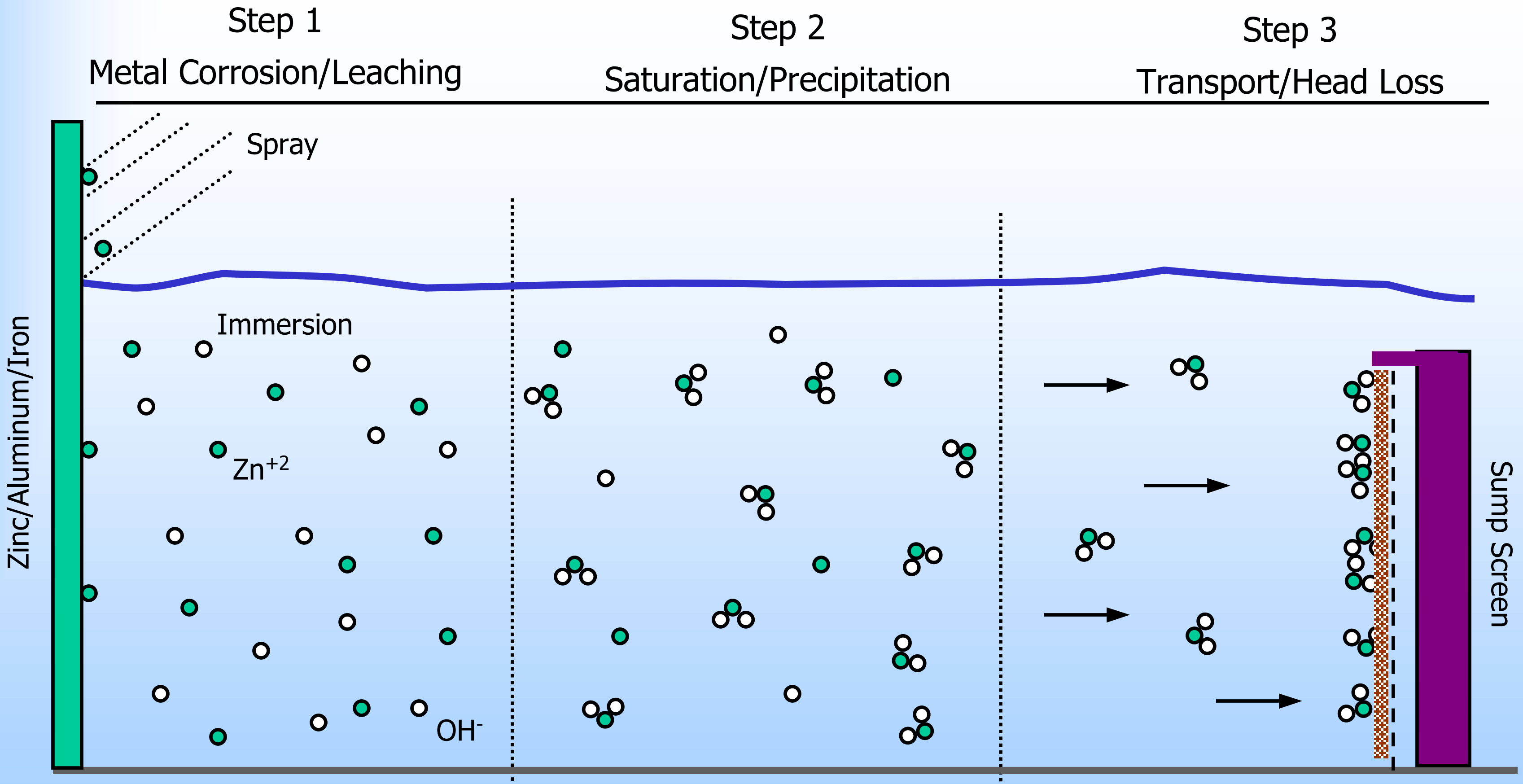
[2] Source: NUREG/CR-5640, "Overview and Comparison of U.S. Nuclear Power Plants

[3] Source: Commance Peak Nuclear Plant FSAR

Chemical Effects Test Objectives

- **Motivation:**
  - ACRS concern regarding "gelatinous" material reported in TMI containment
  - Estimates of bulk corrosion using previously reported corrosion rates
- **Scope potential chemical/temperature induced degradation mechanisms contributing to debris generation and head loss**
- **Investigation tasks:**
  - Review existing literature and establish chemical test conditions
  - Corrosion of metals with precipitation of flocculant
    - Rate of corrosion for iron, zinc, aluminum
    - Head-loss effects of chemical precipitation
  - Chemical degradation of fibrous debris beds leading to slow compaction and increasing head loss (none observed in one pre-immersion fiber test)
  - Degradation nonqualified coatings (none observed in one 6-day test)

Corrosion/Precipitation Concern



Free metal ions released from solids and dissolved in water

Saturation Limit Exceeded Suspended Solids Form

Migration to Sump and Collection on Fiber

Summary of Results

- **Metal corrosion credible for exposure to borated cooling water**
  - UNM tests confirm literature reports at low temp
  - High-temp immersion tests inconclusive
    - Max rate (0.04 $g/hr/m^2$) 4 times higher than low temp rate (0.01 $g/hr/m^2$)
    - MUCH lower than reported max rate of (11.3 $g/hr/m^2$)
    - Secondary corrosion observed but no precipitation
- **Low solubility can lead to precipitation at low concentrations**
- **Precipitated flocculant can induce significant head-loss in combination with fiber debris beds**
- **Plant vulnerability depends on:**
  - Ultimate formation of the flocculant (not confirmed)
  - Surface area of exposed metal and exposure time
  - Post-LOCA chemical balance

LOCA Chemical Conditions

Parameters	T = 0 sec	T = 10 sec	T = 23 sec	T = 15 min	T = 24 hr	T = 48 hr
Lithium (ppb)	1400	1400	1400	630	115	115
Borate (ppm)	800	800	800	1400	2070	2070
Temperature °C (°F)	40 (104)	124 (255)	128 (262)	118 (244)	63 (145)	63 (145)
pH	7.7	7.0	7.2	8.4	7.9	7.8

- Radiolytic and thermal decomposition products evolved in severe accident scenarios *not* considered as precursor to sump failure
- Phosphate baskets designed for iodine sequestration not utilized in all plants, so not considered for test chemistry

Head-loss Test Apparatus

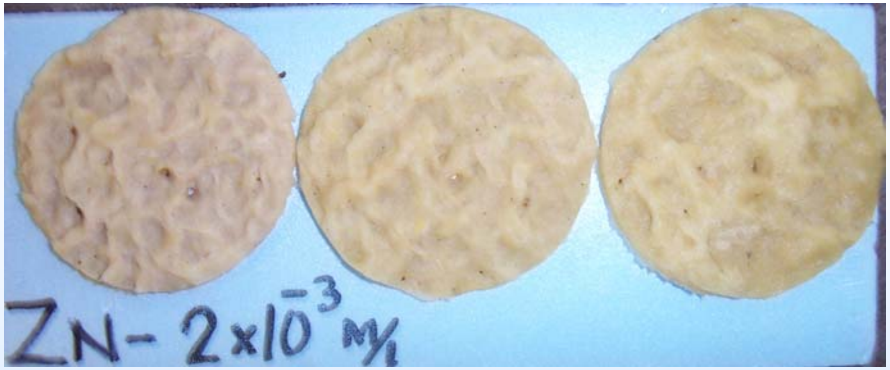
- Diameter 1/3 of large setup
- Flow meter has 20gpm max
- 10 liter total volume
- Online temperature probe
- Flow valve in the pump outlet
- Continuous pH control
- Pump heats water to ~47 °C
- Replicate measurements with tap water and fiber confirm same response between large and small loops

Head Loss in Different Chemical Environments

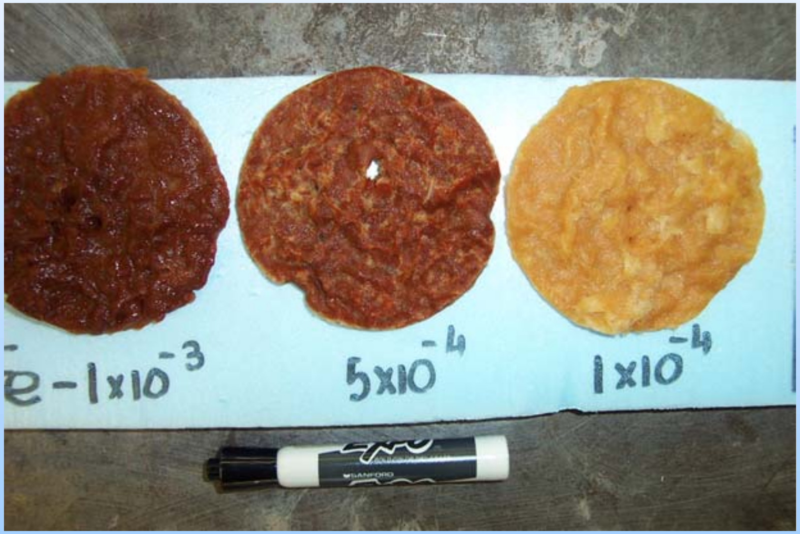
- **Tests done in deionized water supplemented by strongly buffered stock solution of boric acid and lithium hydroxide (some Calcium hydroxide [$Ca(OH)_2$] added to simulate concrete ablation)**
- **Fiber bed established**
- **Metallic salts (representative concentrations) used to artificially induce precipitation**
  - Iron nitrate nanohydrate [$Fe(NO_3)_3 \cdot 9\ H_2O$]
  - Aluminum nitrate nanohydrate [$Al(NO_3)_3 \cdot 9\ H_2O$]
  - Zinc nitrate hexahydrate [$Zn(NO_3)_3 \cdot 6\ H_2O$]
- **Head loss measurement**

Sample Debris Beds

Zinc

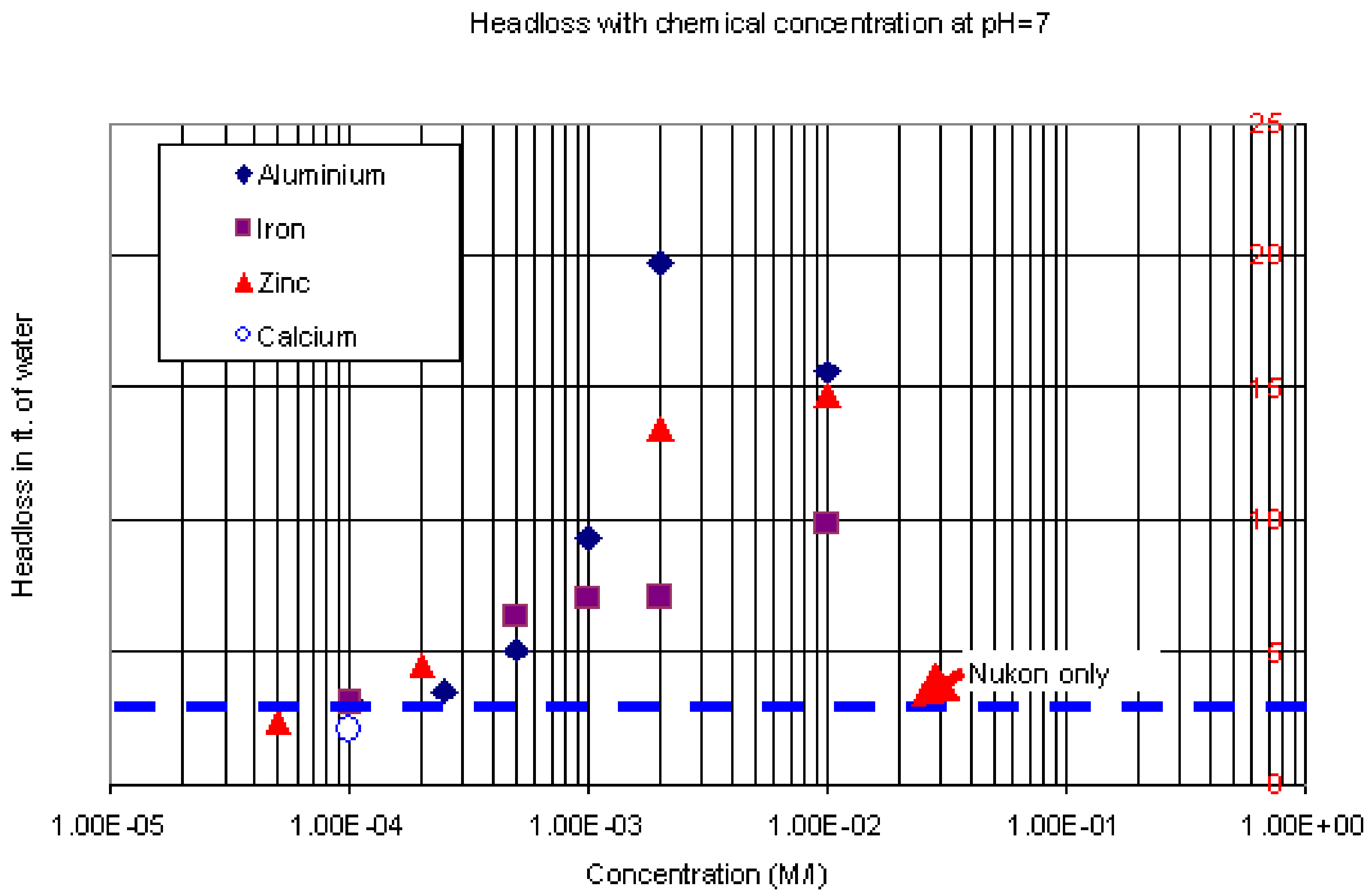


Iron



Iron Close up

Head-Loss Observations



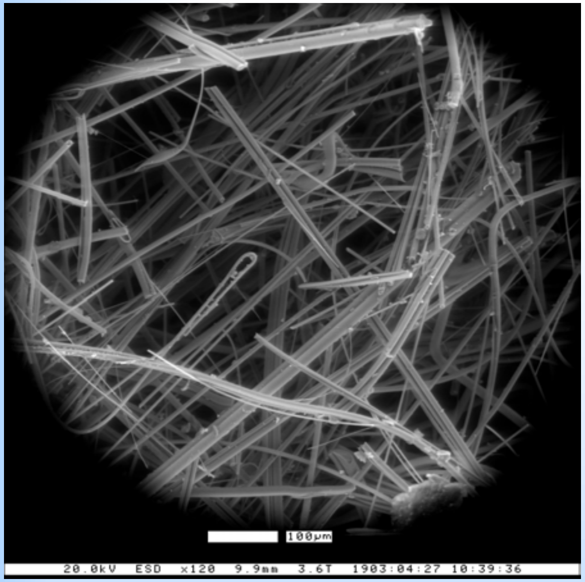
Engineering Chemistry Facts

- **Atomic Weights:**
  - Al = 27 g/mole
  - Fe = 56 g/mole
  - Zn = 65 g/mole
- **10^{-4} M (moles/liter)**
  - Al = 23 lb/10^6 gal
  - Fe = 47 lb/10^6 gal
  - Zn = 55 lb/10^6 gal

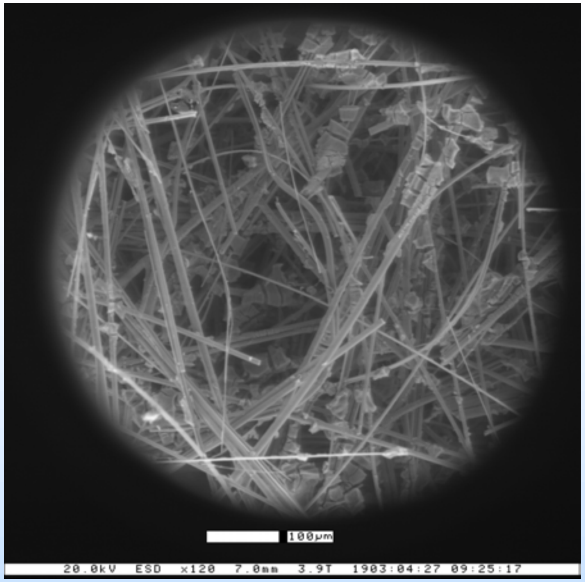
- **Threshold of measurable ΔP increase at 10^{-4} M**
- **7 to 10 ft of additional head loss at 10^{-3} M**
- **10^{-3} M (moles/liter)**
  - Al = 0.27 g/10 liter
  - Fe = 0.56 g/10 liter
  - Zn = 0.65 g/10 liter

- Thresholds for precipitation *may not* be independently additive
- Poor solubility of metals reaches saturation at low concentration
- Aluminum nitrate commonly used as water clarity coagulant
- Head-loss *much* more severe than equal mass of particulate
- Electrochemical binding of water molecules displaces large volume

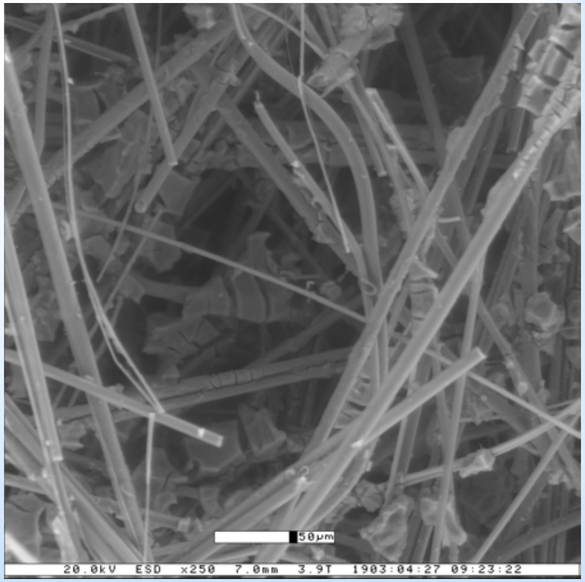
ESEM Images of Dry Samples



Pure Fiber



Iron Bed



Iron-bed Close Up

Apparent adhesion of amorphous material may not permit application of NUREG 6224 head-loss correlation

Dissolved Metal Source Terms (Leaching Tests)

- **STUK reports Zn corrosion rates between 0.01 $g/m^2/hr$ and 11.3 $g/m^2/hr$ under mixed temps and pH**
- **UNM 11-day immersion tests of zinc granules and bulk coupons confirms lower rate at room temp, pH 7**
  - Measured sample mass before and after with immersion time averaging
  - Analytic concentration measurement of solution confirms dissolution
  - Never reached saturation limit
- **UNM 11-day immersion tests of zinc granules and primer chips at 80°C, pH 7 were inconclusive (max average corrosion rate 0.04 $g/m^2/hr$)**
  - All Zinc samples turn black and gain mass
  - Primer chips discolored gain mass (water retention or reaction with paint?)
  - Concentration measurement of solution confirms dissolution/leaching
  - Rapid dissolution suspected to reach solubility limit
  - Hard crystalline particulate formed on surfaces (frangible)
  - Secondary reaction products different from precipitation in form
  - Daily test intervals unsuccessful to isolate corrosion rate
  - Composition of crystalline product and formation process uncertain

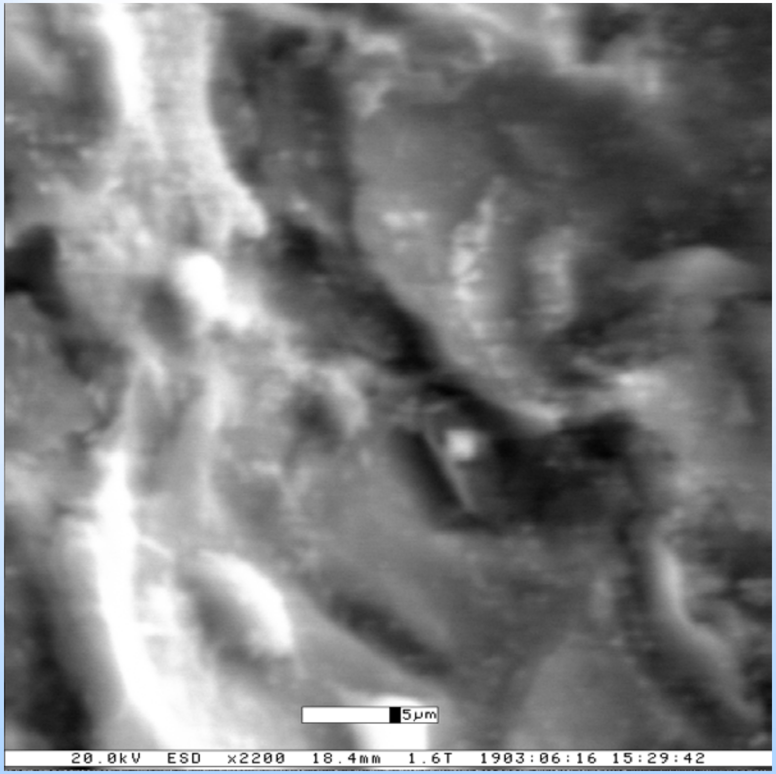
Samples Before/After Immersion

Zinc Granules

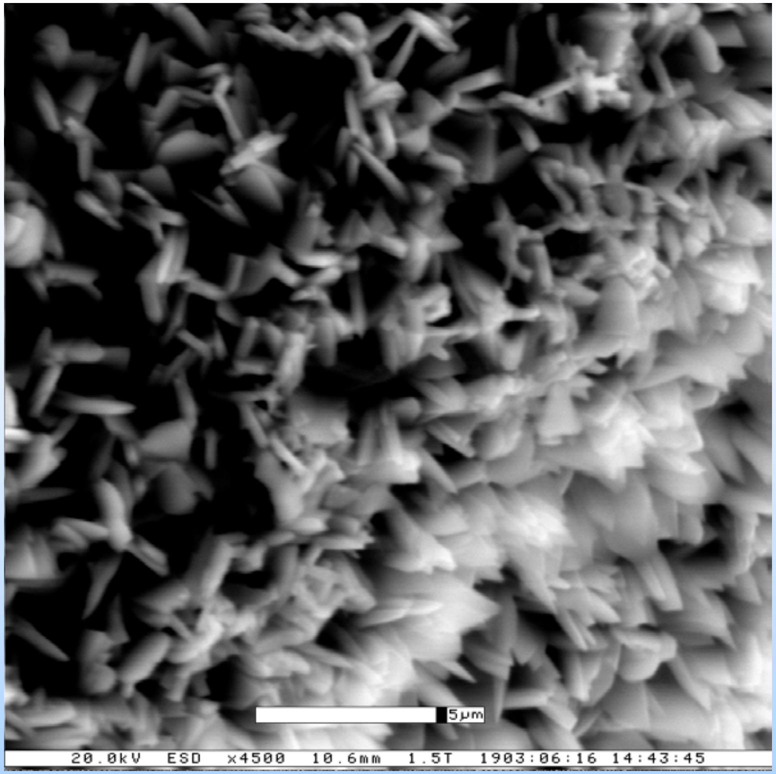
Unqualified Alkyde Paint

Zinc Coupon

ESEM of Secondary High-Temp Surface Reaction/Deposition

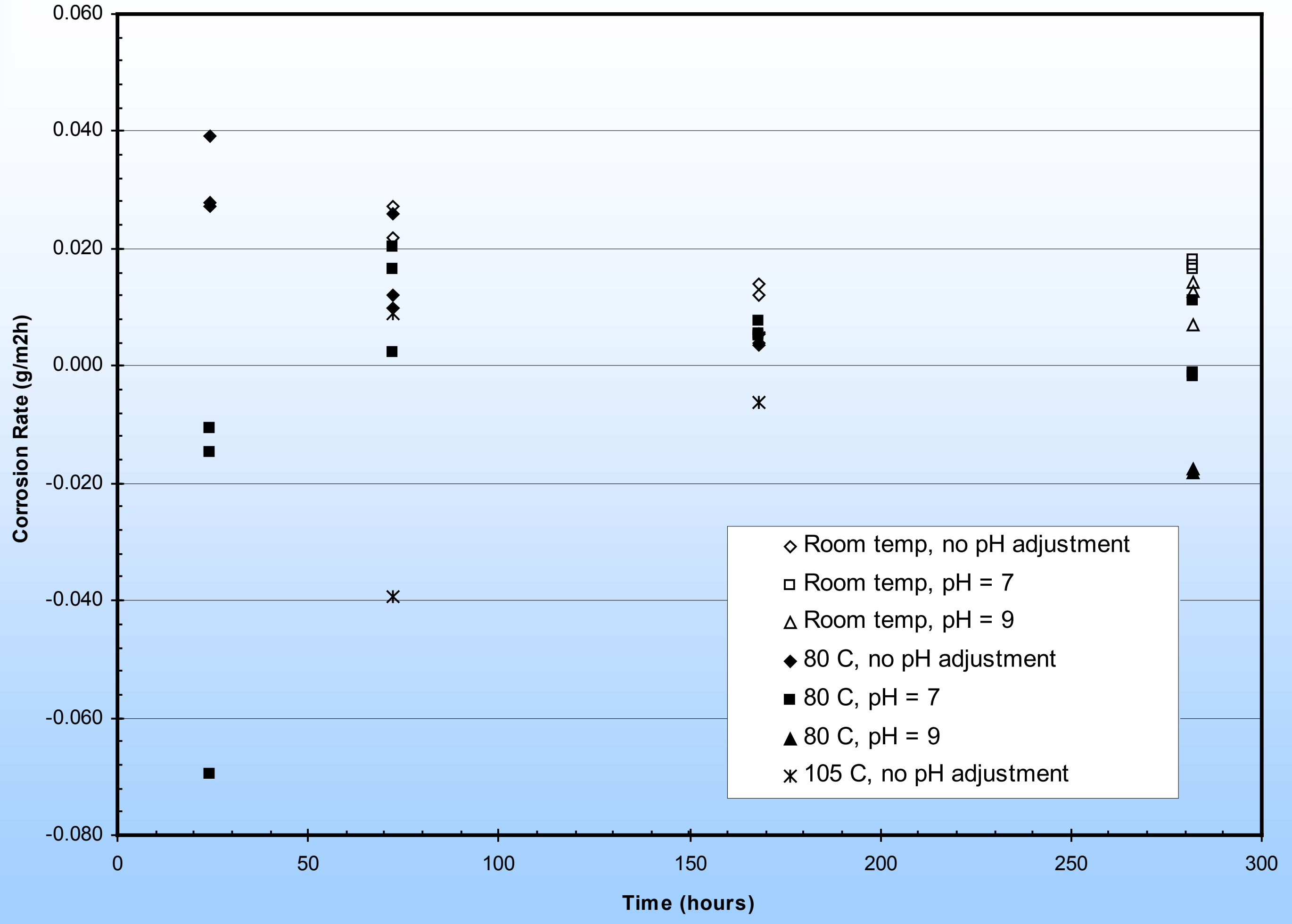


Clean Zinc Granule

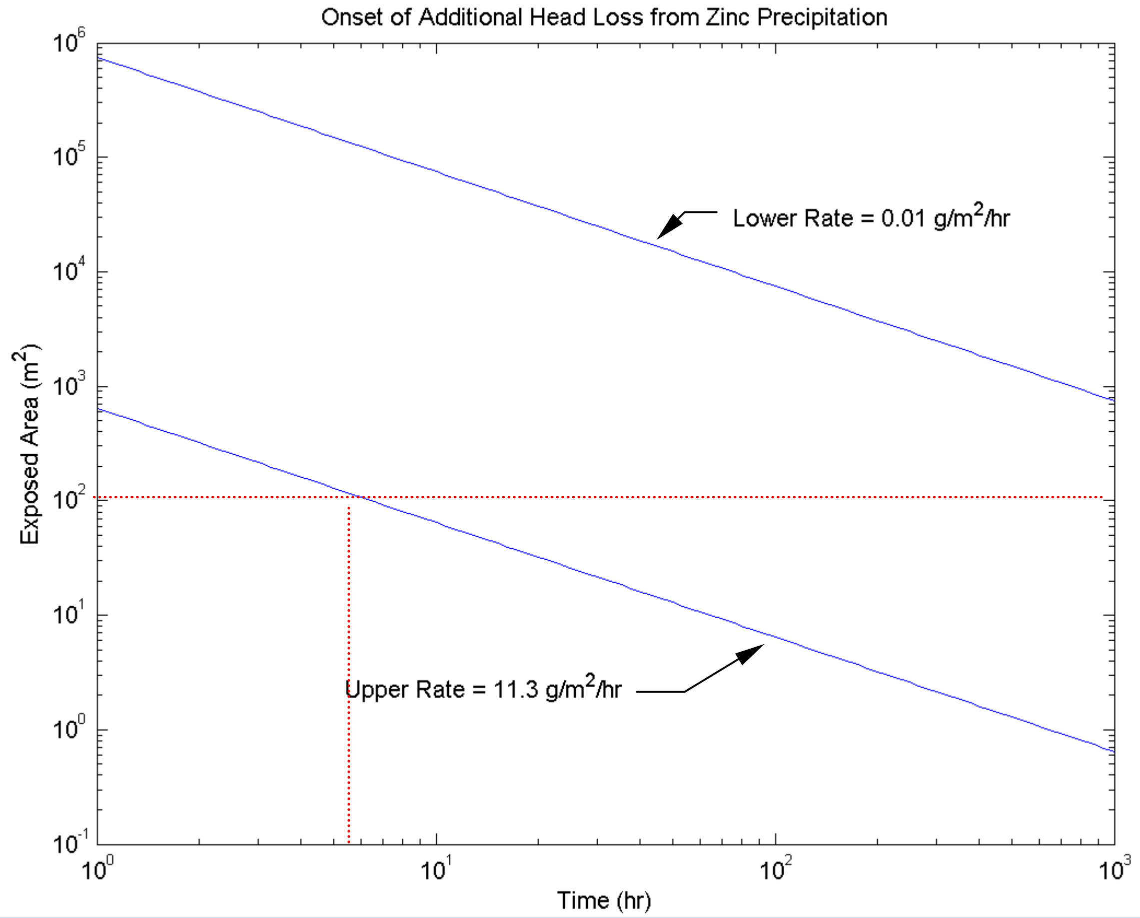


Corroded Zinc Granule

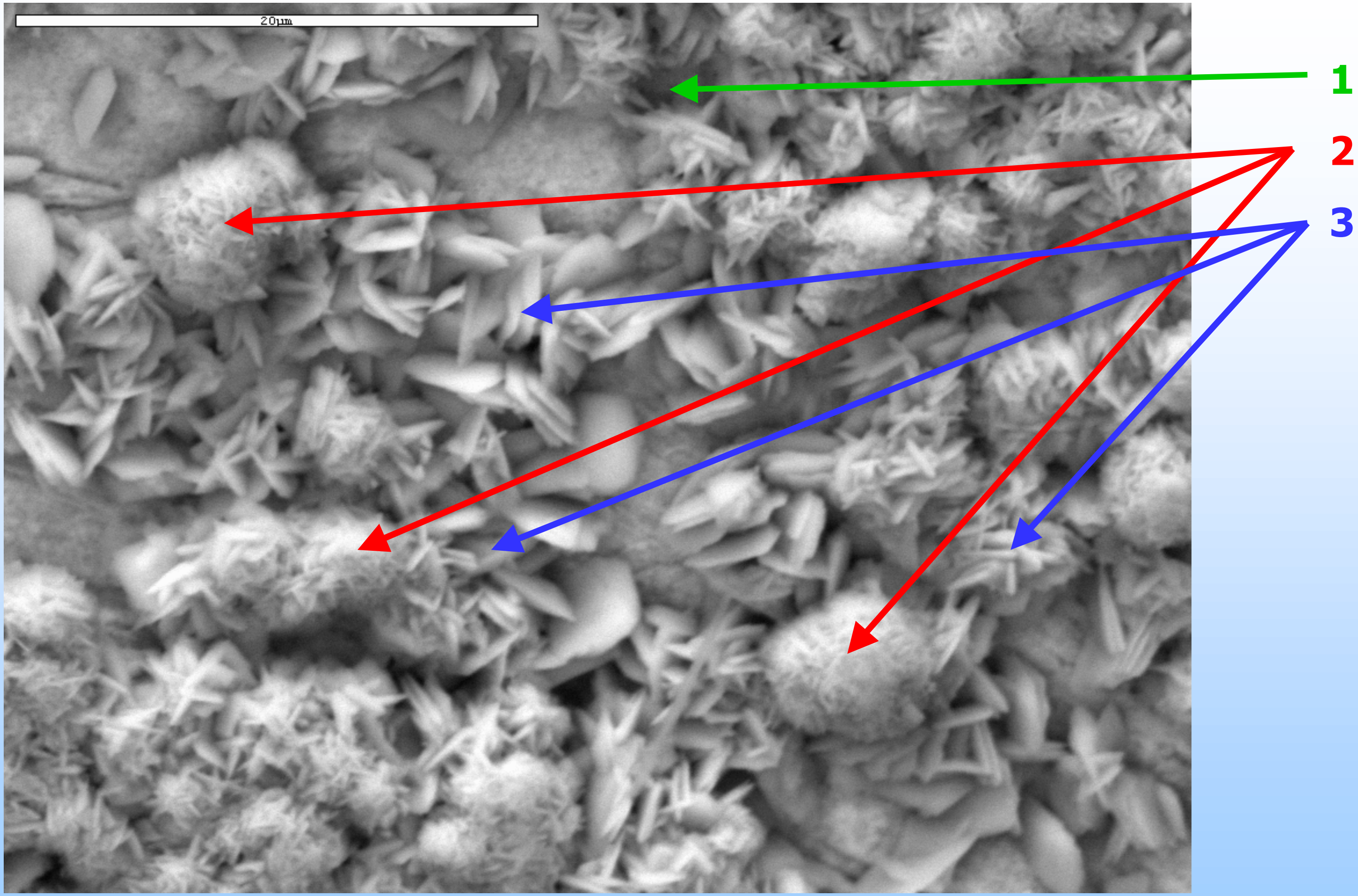
Corrosion Rate Data
(Defined by Mass Change Averaging)



Preliminary Vulnerability Ranges for Zinc Corrosion

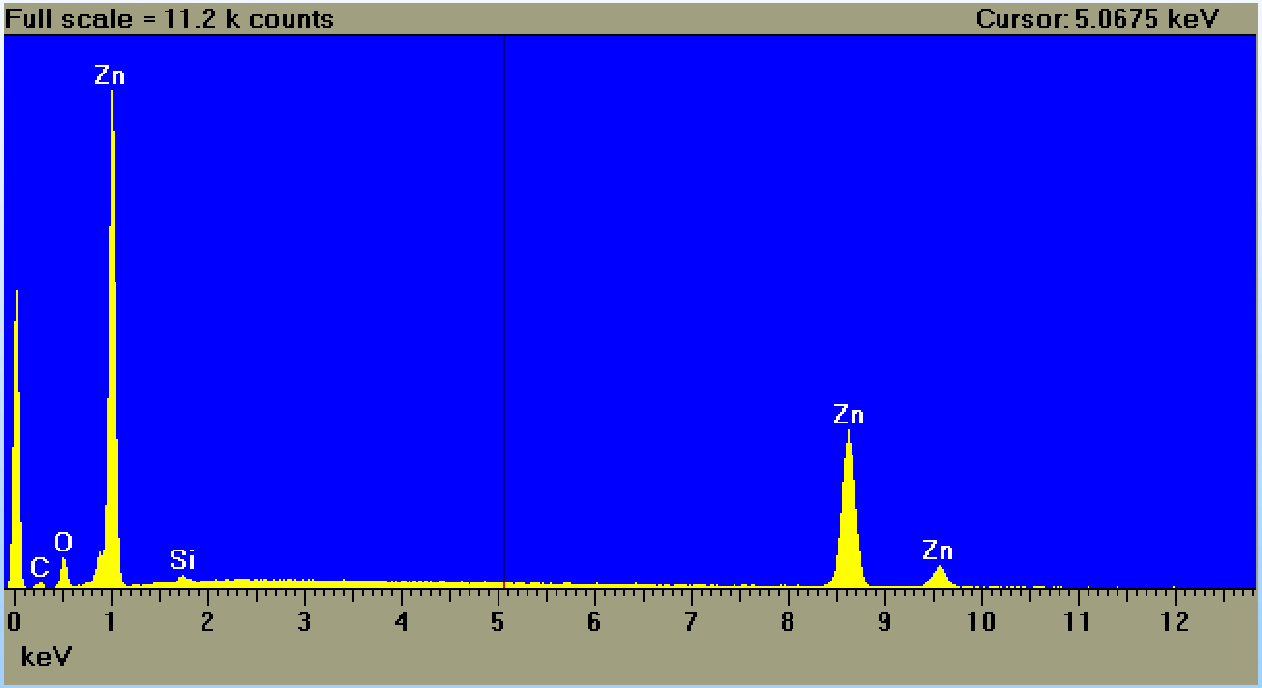


Surface Corrosion Features



Surface Corrosion Composition (1)

- Environmental Scanning Electron Microscopy (ESEM) collects reflected beam to image the surface
- Electron beam also excites nuclear transition states that decay by x-ray emission at characteristic wavelengths



Location 1

Carbon = 3.1%

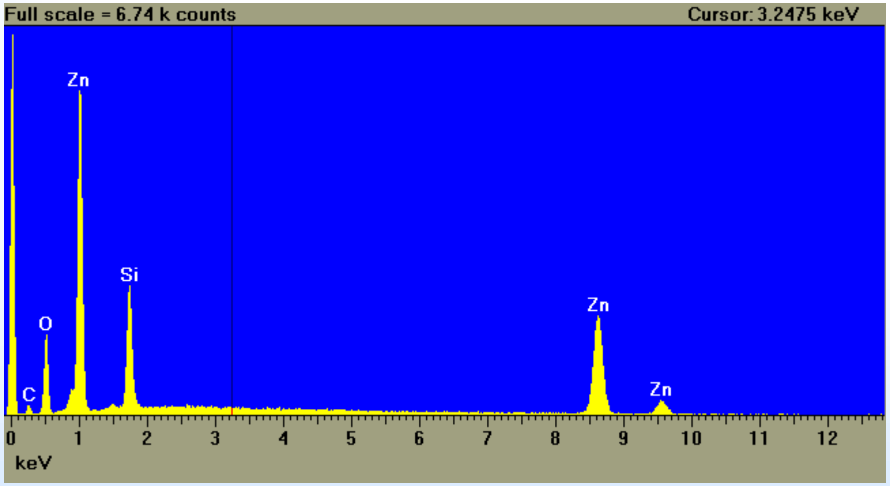
Oxygen = 6.03%

Aluminum=0.23%

Silicon= 0.76%

Zinc= 89.88%

Surface Corrosion Composition (2)



Location 2

Carbon = 9.85%

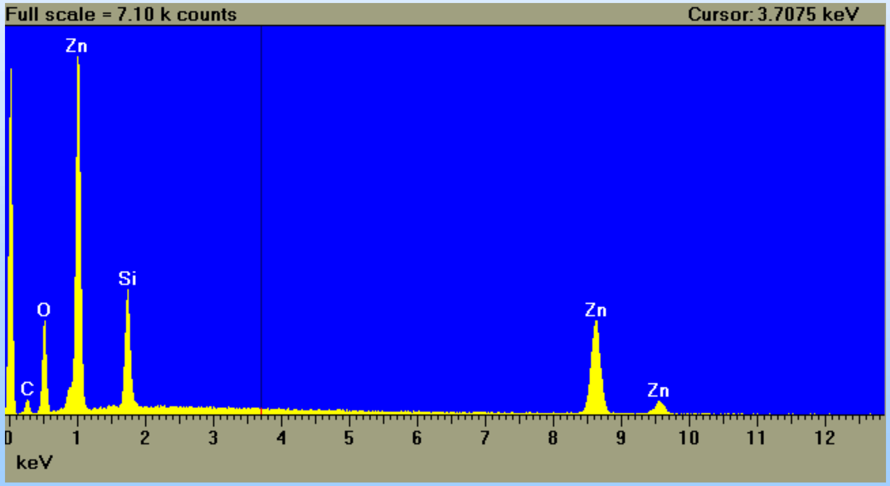
Oxygen = 20.77%

Aluminum=0.24%

Silicon= 10.59%

Zinc= 58.55%

Similar composition of ‘puffs’ and ‘platelets’ suggests alternate crystallization



Location 3

Carbon = 5.93%

Oxygen = 17.74%

Aluminum=0.49%

Silicon= 11.85%

Zinc= 63.99%

Remaining Work on Chem Effects

- **Experimentation essentially complete**
- **Further study of corrosion composition and mechanism**
  - Two hypotheses:
    - Dissolution quickly reaches saturation and deposits as crystals
      - Implies very high corrosion rate
      - Quiescent beaker samples atypical of pool immersion?
    - Heterogeneous surface reaction
      - Mass balance corrosion rates are misleading
      - Metal in solution may reach saturation more slowly
      - Large quantities of additional particulate formed
- **Practical correlation of head loss to debris-bed mass**
- **Documentation of findings in forthcoming NUREG**
- **Forthcoming peer review**