Summary of Recent Chemical Effects Testing

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Test Objectives

- Scope chem/temp induced degradation mechanisms contributing to debris generation and head loss
- Motivated by ACRS concern regarding "gelatinous" material reported in TMI at the time of reentry
  - 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
  - Degradation/dissolution of nonqualified coatings present in containment

Summary of Results

- Metal corrosion credible for exposure to borated cooling water
  - UNM tests confirm literature reports at low temp
  - Follow on studies in progress for high temp
- Low solubility leads to precipitation at low concentrations
- Significant head-loss observed in combination with fiber debris beds
- Plant vulnerability depends on surface area of exposed metal and exposure time

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 ^{o}C (^{o}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
Pressure Mpa (bar)	0.1 (1)	0.38 (3.8)	0.47 (4.7)	0.36 (3.6)	0.14 (1.4)	0.13 (1.3)

Radiolytic decomposition products *not* considered as precursor to sump failure

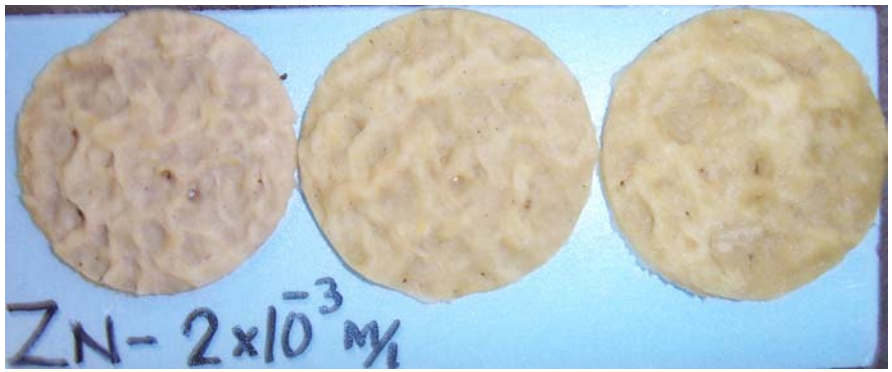
Head-loss Test Apparatus

- 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

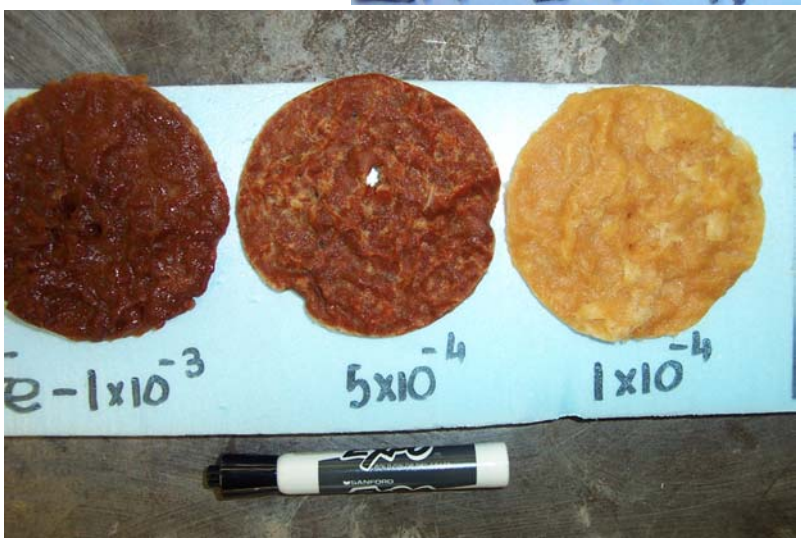
Head Loss in Different Chemical Environments

- Tests done in deionized water supplemented by strong buffer solution of boric acid and lithium hydroxide (Calcium hydroxide [$Ca(OH)_2$] added to simulate concrete ablation)
- Fiber bed established
- Metallic salts (representative concentrations) used to 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

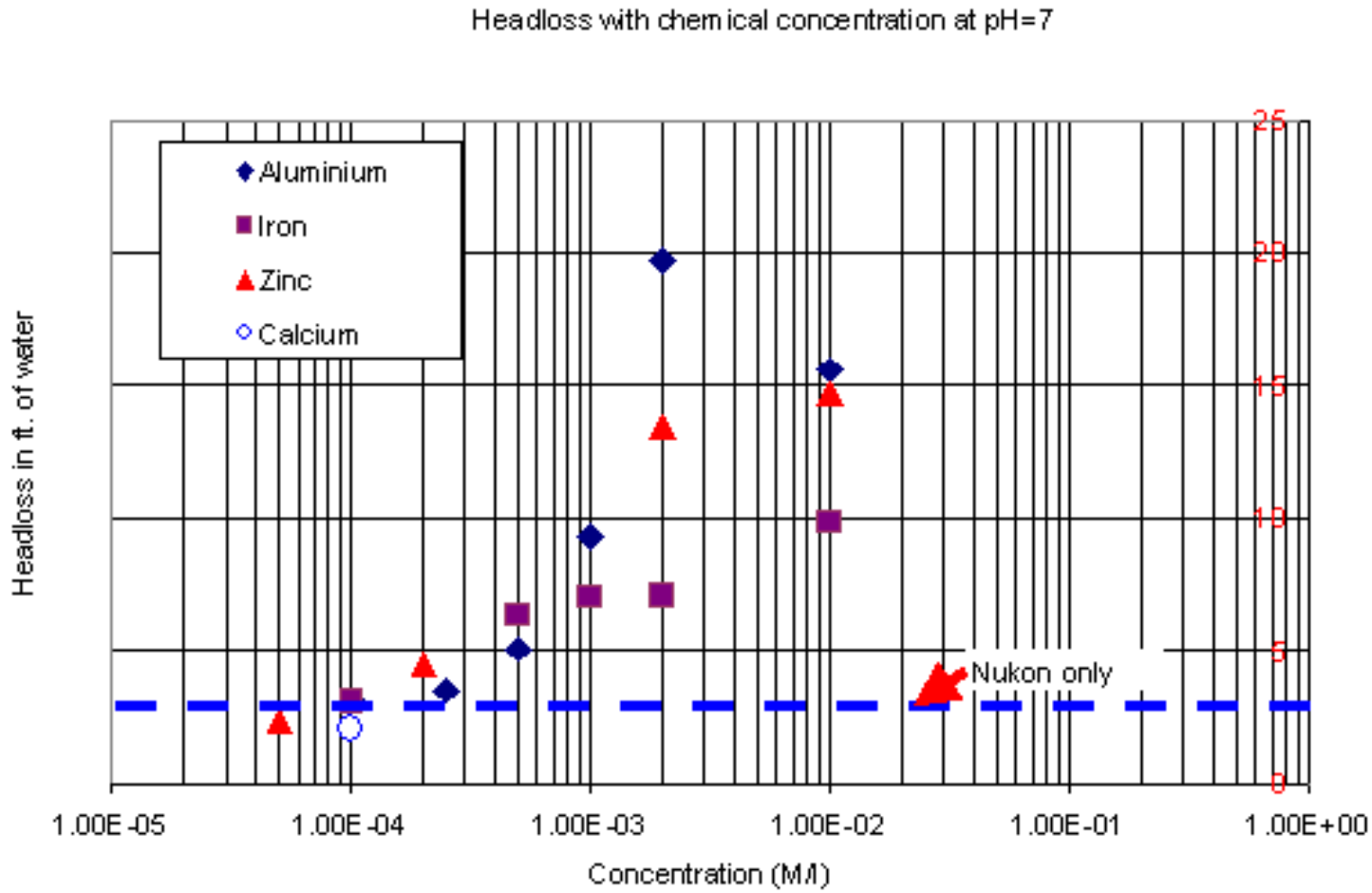


Iron



Iron
Close up

Head-Loss Observations

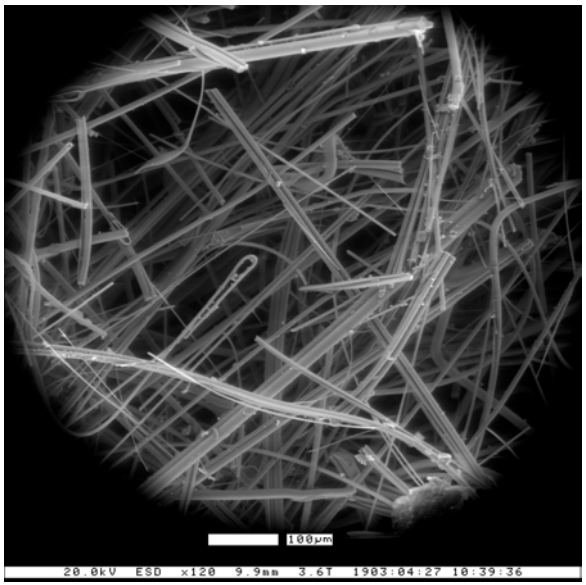


Engineering Chemistry Facts

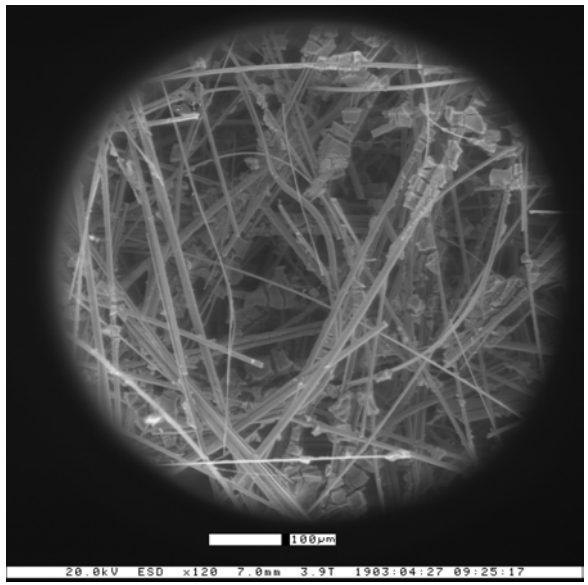
- Atomic Weights:
  - Al = 27 g/mole
  - Fe = 56 g/mole
  - Zn = 65 g/mole
- 10^{-4} M (moles/liter)
  - Al = 23 lb/10^6 gal
  - Fe = 47 lb/10^6 gal
  - Zn = 55 lb/10^6 gal
- Threshold of measurable ΔP increase at 10^{-4} M
- 7 to 10 ft of additional head loss at 10^{-3} M
- 10^{-3} M (moles/liter)
  - Al = 0.27 g/10 liter
  - Fe = 0.56 g/10 liter
  - Zn = 0.65 g/10 liter

- 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

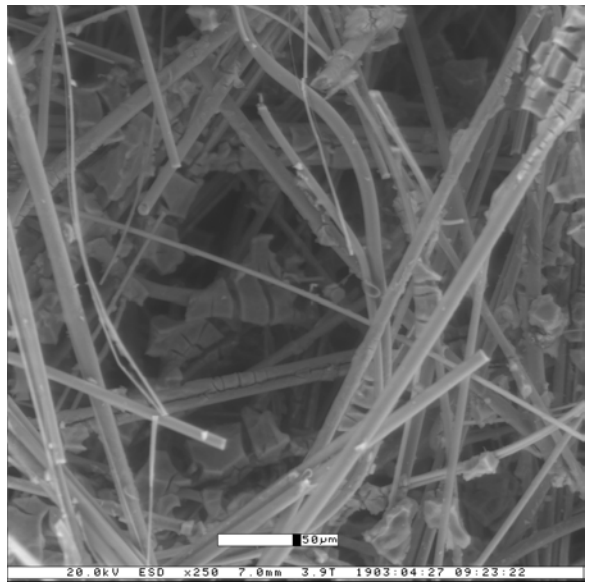
ESEM Images of Dry Samples



Pure Fiber



Iron Bed



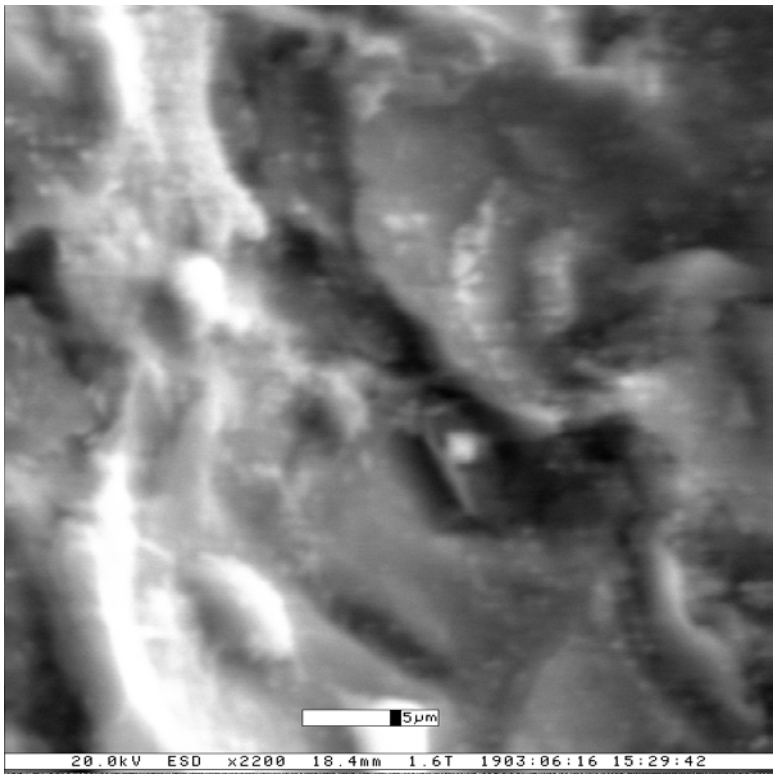
Iron-bed Close Up

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

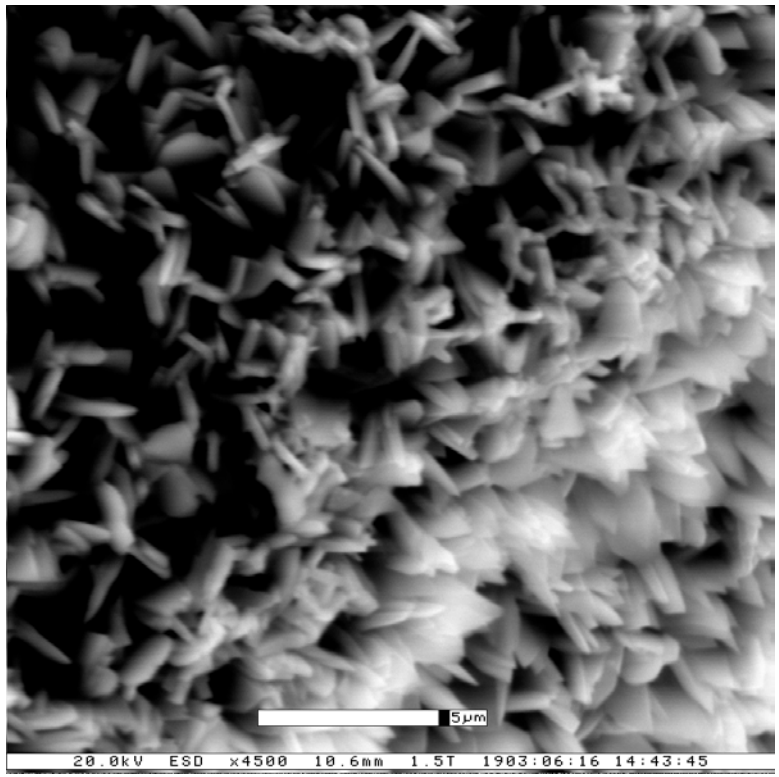
Dissolved Metal Source Terms (Leaching Tests)

- 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
  - Analytic concentration measurement of solution
  - Never reached saturation limit
  - Repeating for chips/granules of inorganic zinc primer
- UNM 11-day immersion tests of zinc granules at 80°C, pH 7 presently inconclusive
  - All samples turn black and gain mass
  - Rapid dissolution suspected to reach solubility limit
  - Secondary reaction products different from precipitation?
  - Hard crystalline particulate formed on surfaces
  - Daily test intervals now used to isolate corrosion rate

ESEM of Secondary High Temp Surface Reaction

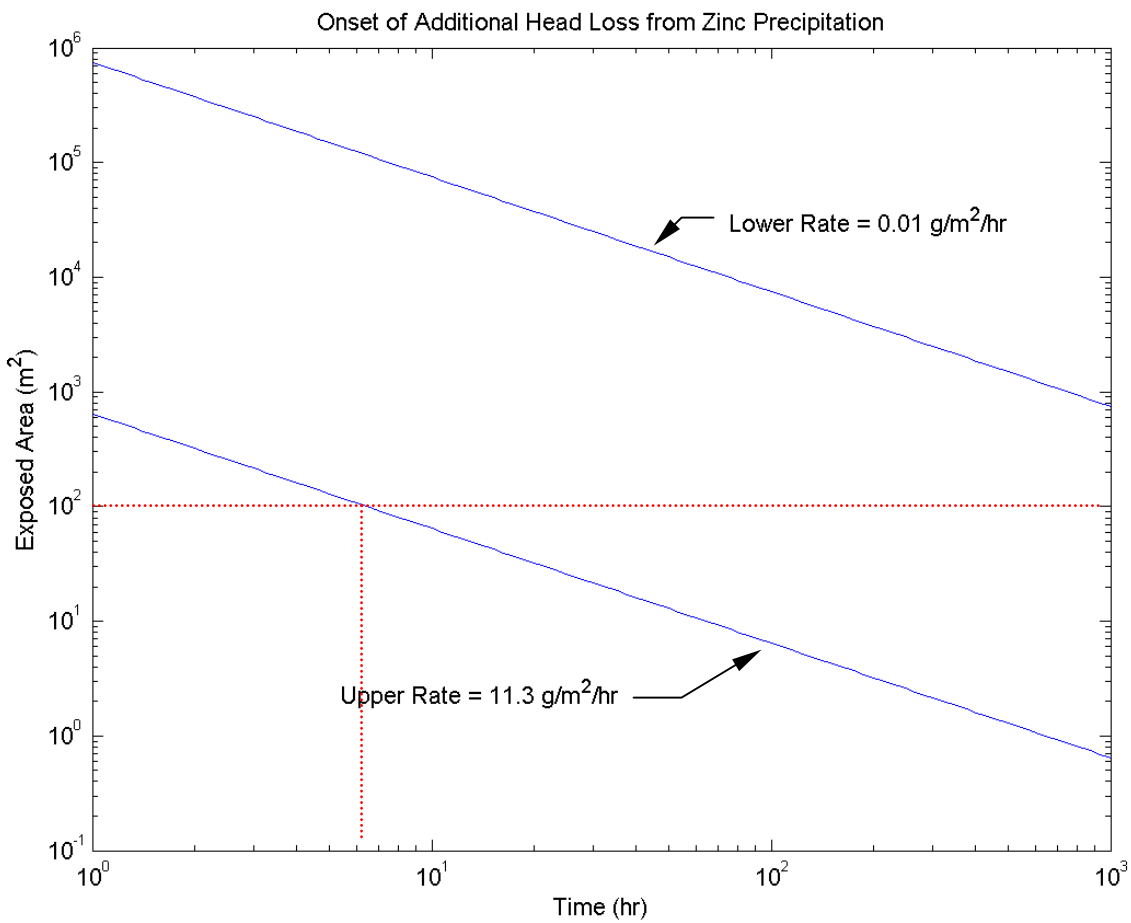


Clean Zinc Granule



Corroded Zinc Granule

Preliminary Vulnerability Ranges for Zinc Corrosion



Remaining Work

- Incremental leaching cycle to measure high-temp corrosion rate
- Immersion of consumer grade alkyd coating samples to monitor for qualitative degradation mechanisms
- Long-term (24 to 36 hr) small loop head-loss tests to monitor for chemical degradation effects
- Practical correlation of head loss to debris-bed mass
- Documentation of findings in forthcoming NUREG
- Conduct of peer review