Zinc and Aluminum Corrosion Product Release During a PWR LOCA Event

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Objectives

- Measure corrosion, corrosion product release from zinc and aluminum alloys under representative post-LOCA conditions
- Characterize corrosion product debris
- Measure time dependent collection of corrosion product debris
- Measure the effects of the most important chemical variables on corrosion product release and collection

Test Considerations

- Simulate containment operation after a LOCA
    - Variables representative of post-accident
        - Chemistry
        - Temperature
        - Flow to levels representative of containment post-accident
    - Values selected to span range of conditions for a LOCA
- Generate corrosion products, characterize debris
    - Corrosion rate
    - Corrosion product release rate
    - Form of the corrosion products from different sources
    - Emphasize species affecting filter bed performance

Test Simulation Assumptions

- No attempt made to model containment chemistry within the first few minutes of a LOCA
    - Large variation of chemistry depending on break size and location
    - However, relative to total corrosion, little corrosion will take place during this short time period
    - Elimination of this time period is reasonable
- Iron not considered a corrosion product source
    - Structural steel in containment coated
    - Other exposed surfaces are limited
    - Corrosion rates in range of pH tested small

Independent Test Parameters

Initial proposed list of parameters

Variable	Maximum Values	Minimum Values
Simulated Sump Temperature (T_{sump})	138°C to 73°C	118°C to 53°C
Containment Surface Temperature	$T_{sump} + 20°C$	$T_{sump} - 20°C$
Submersion of Corroding Surface	Intermittent Submersion	Continuous Submersion
Trisodium Phosphate	1.6 E-1 M	2E-03 M
HCl·	100 ppm	0
Aeration	Air Saturated	Deaerated
Flow/Agitation	0.5 feet per second	0.1 feet per second

Test Matrix Design

- Major considerations in developing test matrix
  - Corrosion chemistry product formation, release, and precipitation reactions are complex
  - Experimental design selected to allow for significant effects of each variable to be determined efficiently
  - Approach allows test matrix to be easily expanded to provide additional information
    - Variable interactions of constituents
    - Reproducibility of results

Initial Test Matrix

Initial proposed test matrix

| Run	Sump Temperature	Containment Temperature	Submersion	Trisodium Phosphate	HCl	Aeration	Agitation / Flow
1	Min Values	Min Values	Min Values	Max Values	Max Values	Max Values	Min Values
2	Max Values	Min Values	Min Values	Min Values	Min Values	Max Values	Max Values
3	Min Values	Max Values	Min Values	Min Values	Max Values	Min Values	Max Values
4	Max Values	Max Values	Min Values	Max Values	Min Values	Min Values	Min Values
5	Min Values	Min Values	Max Values	Max Values	Min Values	Min Values	Max Values
6	Max Values	Min Values	Max Values	Min Values	Max Values	Min Values	Min Values
7	Min Values	Max Values	Max Values	Min Values	Min Values	Max Values	Min Values
8	Max Values	Max Values	Max Values	Max Values	Max Values	Max Values	Max Values

Proposed Test Materials

- Test coupons representative of containment material
  - Galvanized steel   : hot dipped and electroplated
  - Aluminum alloys   : 6061-T6 and 5052
  - Steel with zinc primers
  - Concrete
- Representative coupon surface areas used to obtain meaningful data

Proposed Test Setup

- Exposure of test coupons:
  - Totally submerged
  - Alternately submerged and removed from solution
    - *Dunking approach proposed to simulate spray is expected to give results comparable to spray*
    - *Speed varied simulate different fluid flow conditions within containment*
    - *Corroding surface experiences both liquid and gas phases and liquid coverage over time*

Schematic of Test Facility
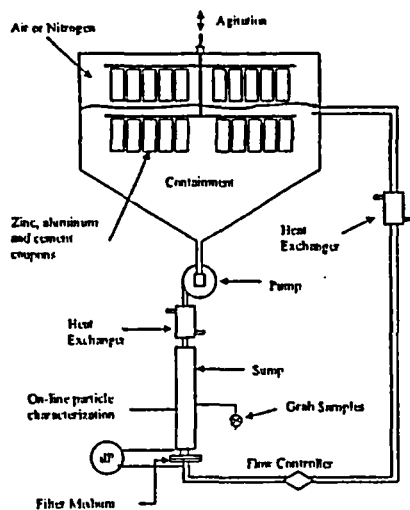
- Closed loop design
- Heat exchangers
  - cool exiting fluid
  - heat returning fluid
- May be modified to:
  - Use spray instead of dunking
  - Use multiple filters in parallel

Proposed Test Operation

- New coupons weighted and installed for each run
- A fraction of coupons removed after 20 hours
  - Coupons will be weighed
  - Oxidized fraction will be determined
- After run is complete
  - Remaining coupons will be weighed
  - Fraction of oxide and metal will be determined
- Supports calculating corrosion product release for materials as a function of temperature and time

Proposed Test Operation

- Test atmosphere
  - Air
  - Hydrogen not included
    - Negligible effect on redox potential and corrosion at test conditions
- Solution volume
  - Representative zinc surface area to volume ratio used to obtain meaningful corrosion data
- Solution chemistry (typical of sump)
  - 2500 ppm boron from boric acid
  - 0.1 ppm Lithium from lithium hydroxide

Solution pH Control

- pH control agents
  - Trisodium phosphate (TSP) selected
    - Similar pH behavior with TSP and NaOH
    - TSP a user friendly chemical
    - Two tests with NaOH to be run to confirm
  - Hydrochloric acid (HCl), formed from degradation of cable insulation material
  - pH range, bounding long term sump pH
    - pH = 9.5, corrected to 25°C
    - pH = 6.5, corrected to 25°C

Other Species in Solution

- Calcium, magnesium and silicon will be present from concrete dissolution
- Levels will not be controlled directly
  - They will be allowed to evolve as dictated by the variables that effect concrete dissolution
- Similarly, corrosion products will be added to solution from the corroding aluminum, zinc coatings and underlying exposed steel
  - Concentrations will be measured but controlled only by chemical and physical conditions that effect corrosion and dissolution

Sump Fluid Temperature

- Sump solution temperature approximates time history for a large break LOCA
  - Maximum initial temperature: 128°C (262°F)
  - Hold for 20 hours
  - Within 24 hours, decreases to: 68°C (155°F)
  - By 48 hours, steady state value: 63°C (145°F)
  - Maintain temperature for an additional 48 hours
  - Each test run until either:
    - Steady state conditions reached, or,
    - Test duration reaches 96 hours

Monitoring Corrosion Effects

- Grab samples taken daily
  - Analyzed for particulate and dissolved material
    - At a minimum, Zn, Al, Si, Fe, Ca, Mg, Sn, Pb, Na, P, and Cl will be looked for
    - Rationale for looking for these elements
      - They are related to the corrosion process
      - They directly affect corrosion product solubility and crystallization / nucleation
      - They may potentially initiate coagulation
  - pH will be measured.

Monitoring Particulates

- On-line measurement of particulate content may be made
  - Turbidity may be measured
  - If the concentration of particulates is high enough, on-line particle size distribution measurement may be performed

Recirculating Sump Fluid

- Recirculating flow
  - Constant linear flow rate of 0.3 ft/sec
  - Fine filters used to collect particulates
- Pressure drop measurements
  - Initial measurements across clean filter
  - Pressure drop across filters monitored continuously throughout test
 - Test will be terminated if pressure drop becomes excessive for test facility

Data Evaluation

- Effects of the independent variables (e.g. submersion) on the dependent variables (e.g. rate of corrosion product release) determined by simple averaging
- Investigate effect of derived variables such as pH
- Filters analyzed for entrained particle composition
  - Use Scanning Electron Microscopy (SEM) combined with elemental analysis using Energy Dispersive X-Ray Emission Spectroscopy (EDS)
  - Weight gain from filtered material is to also be measured
  - X-ray diffraction may also be performed if sufficient material is collected for analysis (approximately 1 mg)

Discussion

- Proposed experiment will determine the main effects of seven dominant variables on zinc and aluminum corrosion and corrosion product release
  - Results will be used to assess potential for sump screen plugging
  - Corrosion product release information will also be used in more detailed time/temperature/position modeling
- Output from experimental program will be an equation for corrosion product release for each alloy
  - Temperature, pH, aeration and flow will be the inputs
  - Output will be predicted corrosion rate and corrosion product release

Candidate Facility #1
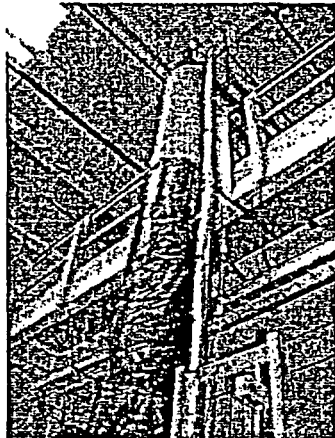
- Existing facility
  - Existing autoclave in a high bay area
  - Total system volume of <5 gallons is planned
  - Small containment simulation
  - Suitable for parametric studies
- Concerns
  - Small volume
  - May be limited with respect to sprays and coupon submergence

Candidate Facility #2
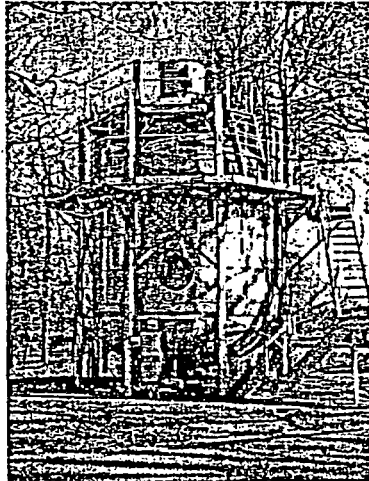
- Existing facility
  - Used for AP600 containment heat transfer tests
  - Large scale and volume
  - May be modified to:
    - Add recirculating loop
    - Add sprays
- Concerns
  - More suitable for integrated tests, not parameter studies
  - Costly to refurbish, modify, operate and clean up

Summary

- Test plan to determine corrosion product release following a postulated LOCA has been defined
  - Variables effecting corrosion are varied to span expected conditions
  - Corrosion rates and corrosion product release rates are measured for concrete and pertinent zinc and aluminum materials
  - The mass of corrosion products is collected and measured
  - The pressure across the filter will also be measured.
- Data gathered from the tests will be used to develop a corrosion release model
  - Model inputs include temperature, flow, submersion, pH and aeration
  - Model outputs are corrosion product release rates
- Candidate facilities identified