CONTINUING INVESTIGATIONS OF LOCAL ENVIRONMENTS ON WASTE CONTAINER SURFACES

Presented by the State of Nevada

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Presented at

Nuclear Waste Technical Review Board Meeting
Las Vegas, Nevada
January 28, 2003
ENVIRONMENTAL CONSIDERATION FOR ASSESSING INTEGRITY OF CONTAINER FOR RADIOACTIVE WASTE

- Should determine the local surface environments before designing and choosing material.

- Corrosion processes are dominated by the local environments that are directly on the surface of containers.

- Local environments on surfaces are products of all surroundings and of multiple interactions, and can change over time.

- Local environments on the surface are affected primarily by:
  - Multiple aqueous chemistries that arrive at the surface from both local and wide ranging sources.
  - Decay heat from inside the container.
  - Presence and composition of insulating deposits.
  - Location and time.

- Surface environments cannot be predicted readily, not can they be simply bounded based on the relatively narrow ranges of conditions in which corrosion occurs on specific alloys. For example, although bulk environments of nuclear PWR steam generators are well defined, the local environments within heat transfer crevices have not been quantified, and can vary widely.
Factors Producing Corrosive Environment

- Ground water
- Dehydration and shrinkage
- Water flow due to impinging thermal gradients
- Fractures as preferred paths (change in fractures and porosity during heating)
- Pore water and its chemistry
- Chemistry of the mountain
- Radiolytic products ($H_2O_2, NO_3^-$)
- Precipitation of solids including retrograde effects
- Separated electrochemical cells—anodic and cathodic sites
- Evaporation of volatile chemical species
- Boiling point elevation and concentration of chemistry
- Superheated surface
- Complex chemistry on fracture surfaces (Mn, Pb, …)
- Metabolic products from microbes and fungi (e.g., $H^+$, $S^=)$
- Human intrusion (drilling, construction materials, waste, flaws in engineered barrier)
- Deposits (top surfaces, supports and general coverage by debris)
- Heat inside container
Superheated Processes at Waste Package

1. Superheat, superheat concentrates chemicals
2. Deposits build up from dust, rockfall, condensation/evaporation, and biological species (including human)
3. Superheated surface and boiling point elevation
4. $H_2O$ with chemicals from mountain and fracture surface
5. $H_2O$ with chemicals from mountain and fracture surface

Cooler

Hot, Decay, Heat
Surface Processes at Superheated Deposits

Deposit forms from interaction of dust, water, mountain and other chemicals

Water evaporation

Radiolytic products ($H_2O_2, NO_3^-$)

Relatively volatile species

Metabolic products from microbial and fungal species (e.g., $H^+, S^-$)

Capillaries

Cathodic (alkaline)

Similar debris and superheat at other locations, such as supports, including piled up debris

Boiling point elevation

Heat

Formation of precipitates and retrograde reactions

Concentrated chemistry

Surface environment changes with time

Note:
Can’t clean

H$_2$O and mountain chemicals (average mountain, pore water, fracture surfaces)
Hot Surfaces Concentrate Chemicals: Similarities

Yucca Mountain

Commercial Steam Generators

- Hot surface
- Accumulating deposit
- Corroding surface
- Tube wall
- Tube support
- Chemicals concentrate and boiling point elevation
- Heat
- Heat
- Heat
EXPERIMENTAL APPROACH

1. Characterize possible local environments as they develop with time on a hot surface of the container.

2. Emphasize a subset of aqueous environments that results from water originating from or passing through the unsaturated zone above the container.

3. Assess both the evaporated environment and the residual environments after evaporation occurs.

4. Start with concentrated solution that had been identified by LLNL (Rosenberg, Gdowski, and Knauss in 2001) from the unsaturated zone and continue concentration by boiling.

5. Measure instantaneous pH of condensed vapor during evaporation.

6. Measure corrosion rate in condensed solutions and in residual solutions by immersed coupon tests.
## STARTING CONCENTRATIONS FOR DISTILLATIONS*

<table>
<thead>
<tr>
<th>ppm ion</th>
<th>Saturated Zone Water (J-13)</th>
<th></th>
<th>Unsaturated Zone water (UZ)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1x</td>
<td>150x</td>
<td>1x</td>
<td>62x</td>
<td>1243x</td>
</tr>
<tr>
<td>Na⁺</td>
<td>45.2</td>
<td>162.2</td>
<td>8.56</td>
<td>476.8</td>
<td>6223</td>
</tr>
<tr>
<td>K⁺</td>
<td>5.2</td>
<td>592.8</td>
<td>4</td>
<td>268.4</td>
<td>2644</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>2.1</td>
<td>1.12</td>
<td>11.8</td>
<td>550</td>
<td>5546</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>5.8</td>
<td>0.06</td>
<td>57.3</td>
<td>1713</td>
<td>15643</td>
</tr>
<tr>
<td>SiO₂</td>
<td>10.4</td>
<td>1040</td>
<td>10.4</td>
<td>503.36</td>
<td>540.8</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>105.0</td>
<td>4410</td>
<td>20.3</td>
<td>9.95</td>
<td>44.66</td>
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<tr>
<td>SO₄²⁻</td>
<td>18.5</td>
<td>2109</td>
<td>83.9</td>
<td>1543</td>
<td>2097.5</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>7.2</td>
<td>813.6</td>
<td>76.6</td>
<td>4259</td>
<td>52165</td>
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<tr>
<td>NO₃⁻</td>
<td>7.9</td>
<td>1034.9</td>
<td>10.7</td>
<td>591.7</td>
<td>2578.7</td>
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<tr>
<td>F⁻</td>
<td>2.3</td>
<td>236</td>
<td>2.16</td>
<td>38.2</td>
<td>432</td>
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<tr>
<td>pH</td>
<td>8.07</td>
<td>10.18</td>
<td>7.55</td>
<td>7.65</td>
<td>6-6.5</td>
</tr>
</tbody>
</table>

*from Rosenberg, Gdowski, and Knauss in 2001
DISTILLATION EXPERIMENTS

Reflux Condenser

Measure Instantaneous pH

Simulates canister with superheat

Boiling Solution

Deposit

Mantle
DISTILLATION OF J-13

![Graph showing condensate pH vs. volume fraction distilled for EJ-13x1 and J-13x150 samples.](image)
DISTILLATION OF UZ PORE WATER

Condensate pH

Volume Fraction Distilled

- 1xUZ in Glass
- 62xUZ in Glass
- 62xUZ in PTFE (1)
- 62xUZ in PTFE (2)
- 1243xUZ in Glass
DISTILLATION OF COMPONENTS OF PORE WATER

![Graph showing pH of condensate vs. volume fraction distilled for different solutions: CaCl₂+KNO₃, MgSO₄, MgSO₄+KNO₃, Ca(NO₃)₂, Mg(NO₃)₂, 62xUZ no Si.](image-url)
CHEMISTRY OF THE CONDENSATES

In flask:
\[
\text{Mg(NO}_3\text{)}_2\cdot x\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{Mg(OH)}_2\cdot n\text{Mg(NO}_3\text{)}_2_{(s)} + \text{H}^+ + \text{NO}_3^{-}_{(aq)}
\]

In condenser:
\[
\text{NO}_3^{-}_{(aq)} \quad \text{HNO}_3_{(g)} \quad \text{HNO}_3_{(aq)}
\]
\[
\text{H}^+_{(aq)} + \text{Cl}^-_{(aq)} \quad \text{HCl}_{(g)} \quad \text{HCl}_{(aq)}
\]
\[
\text{F}^-_{(aq)} \quad \text{HF}_{(g)} \quad \text{HF}_{(aq)}
\]

- \(\text{H}_2\text{SO}_4\) is not volatile, and therefore \(\text{SO}_4^{2-}\) does not appear in condensed vapor.

- \(\text{Ca(NO}_3\text{)}_2\cdot x\text{H}_2\text{O}_{(l)}, \text{CaCl}_2\cdot x\text{H}_2\text{O}_{(l)},\) and \(\text{MgCl}_2\cdot x\text{H}_2\text{O}_{(l)}\) decompose to give acid, but to a lesser extent at these temperatures.
## CORROSION TESTING OF ALLOY 22 IN CONDENSATES*

<table>
<thead>
<tr>
<th>Original Solution</th>
<th>Condensate type</th>
<th>Measured pH</th>
<th>Test temp °C</th>
<th>Corrosion rate †</th>
</tr>
</thead>
<tbody>
<tr>
<td>62xPore</td>
<td>Next-to-last 30 mL</td>
<td>1.62</td>
<td>130</td>
<td>15</td>
</tr>
<tr>
<td>62xPore</td>
<td>Final 30 mL</td>
<td>0.59</td>
<td>130</td>
<td>406</td>
</tr>
<tr>
<td>1243xPore</td>
<td>Next-to-last 30 mL</td>
<td>0.02</td>
<td>90</td>
<td>52</td>
</tr>
<tr>
<td>1243xPore</td>
<td>Final 30 mL</td>
<td>-0.54</td>
<td>90</td>
<td>603</td>
</tr>
</tbody>
</table>

*30 day immersion test
†Based on weight loss, in μm/year
DISTILLATION / REFLUX EXPERIMENTS

(a) (b)

Reflux Condenser

Measure Instantaneous pH

Simulates canister with superheat

Boiling Solution

Change configuration when pH = 1.5 and volume of boiling solution is 40-250 ml

(b)

Reflux Condenser

Cup with midget thermometer and C-22 rectangular piece

Soxhlet Extractor (simulates cool part where condensate forms)

Distillation flask with C-22 or Ti rectangle or disk (simulates solution of constant temperature)

Constant Temperature Solution
## DISTILLATION / REFLUX EXPERIMENTS*

<table>
<thead>
<tr>
<th>Metal</th>
<th>Original Solution</th>
<th>Sample environment</th>
<th>pH</th>
<th>Temp °C</th>
<th>Corrosion rate†</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-22</td>
<td>62xPore</td>
<td>Residual Paste</td>
<td>2.63</td>
<td>144</td>
<td>134</td>
</tr>
<tr>
<td>C-22 (#21)</td>
<td>1243xPore</td>
<td>Clear residual solution</td>
<td>0.22</td>
<td>144</td>
<td>10943</td>
</tr>
<tr>
<td>C-22 (#21)</td>
<td>1243xPore</td>
<td>Soxhlet cup</td>
<td>0.18</td>
<td>78</td>
<td>14</td>
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<tr>
<td>C-22 (#34)</td>
<td>1243xPore</td>
<td>Residual Paste</td>
<td>2.21</td>
<td>144</td>
<td>678</td>
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<tr>
<td>C-22 (#34)</td>
<td>1243xPore</td>
<td>Embedded in Residual solid</td>
<td>2.21</td>
<td>144</td>
<td>30</td>
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<tr>
<td>C-22 (#34)</td>
<td>1243xPore</td>
<td>Soxhlet cup</td>
<td>-0.48</td>
<td>77</td>
<td>938</td>
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</tbody>
</table>

*22-29 day test
†Based on weight loss, in μm/year
DISTILLATION / REFLUX EXPERIMENTS

C-22 #34 IN SOXHLET CUP (78°C, 29 DAYS)
DISTILLATION / REFLUX EXPERIMENTS

C-22 #21 IN CLEAR RESIDUAL SOLUTION (144°C, 28 DAYS)
### DISTILLATION / REFLUX EXPERIMENTS

<table>
<thead>
<tr>
<th>Metal</th>
<th>Original Solution</th>
<th>Sample environment</th>
<th>pH</th>
<th>Temp °C</th>
<th>Corrosion rate †</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-7</td>
<td>1243xPore</td>
<td>Residual Solution</td>
<td>1.60</td>
<td>144</td>
<td>969</td>
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<tr>
<td>Ti-7</td>
<td>1243xPore</td>
<td>Residual Solid</td>
<td>1.6</td>
<td>144</td>
<td>36</td>
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<tr>
<td>T-7</td>
<td>1243xPore</td>
<td>Soxhlet cup</td>
<td>-0.88</td>
<td>78</td>
<td>114</td>
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</tbody>
</table>

Ti-7 in Residual solution
DISTILLATIONS – IMPORTANCE OF THE SOLIDS

The solids that precipitate during distillations, including halite (NaCl), tachyhydrite (CaMg$_2$Cl$_6$·12H$_2$O), and basic Mg oxy salts, are porous and heterogeneous. When allowed to deliquesce as a paste, may become aggressive as well.

A sample of C-22 embedded in a moist paste of residual solids from an distillation of 1243xPore water showd signs of tarnishing after 8 weeks at room temperature.
Corrosion of Hastelloy C, Alloys 600 and 690 in Concentrated Sodium Silicate Solutions

(From the literature)

It is of note that the Hastelloy C wire (0.8 mm diameter) used to support the U-bends was observed to have broken in solution No. 4. After a solution No. 6 run that was aborted after 76 hrs., SCC was noted in several places in the Hastelloy C wire. No conclusion can be drawn as to whether solution No. 6 is as aggressive toward Alloy C276 as it is toward Alloy 600. This is due to an undefined increase in concentration (caused by a leak) as well as the unknown stress in the wire. Ref. C.R. Bergin Corrosion Journal, p. 85, 1985
CONCLUSIONS

1. Continued evaporation of concentrated aqueous UZ pore water solutions produce significant acidity in both residual and condensed environments. Similar evaporations of J-13 well water produce generally alkaline environments.

2. The acidity of the evaporated UZ environments relative to that of the J-13 results from the relatively higher combined concentrations of Mg^{2+}, NO_3^-, and Cl^-.

3. Residual and evaporated environments are significantly corrosive to both C-22 and Ti-7. Corrosion rates in the range of 0.1 to 1.0 mm/year were observed, with rates as high as 10 mm/year.

4. The environments studied represent a small subset of many that can result from water passing through the UZ, reaching the containers, evaporating, and interacting with the heated surface and other deposits.

5. Future work will consider the chemistry of the precipitated solids, and the possibility of stress corrosion cracking.

6. The combination of a wide range of chemistries in the surroundings, the surfaced heated by radioactive decay, and the formation of surface deposits over time will produce a range of corrosive conditions on the surfaces of container that cannot be readily quantified nor their effect on corrosion predicted.