U.S. DEPARTMENT OF ENERGY
OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

PRESENTATION TO
THE NUCLEAR WASTE TECHNICAL REVIEW BOARD

SUBJECT: CORROSION MODELING AND TESTING

PRESENTER: DR. JOSEPH C. FARMER

PRESENTER'S TITLE: CHEMICAL ENGINEER
AND ORGANIZATION: LAWRENCE LIVERMORE NATIONAL LABORATORY
LIVERMORE, CALIFORNIA 94550

PRESENTER'S TELEPHONE NUMBER: (415) 423-9777

JANUARY 18-19, 1990
Outline of presentation

- Conditions outside one specific spent-fuel container
- Documentation of existing models
- Modeling and testing for vapor-phase environment
  - Rates of uniform oxidation
- Modeling and testing for aqueous environment
  - Pit initiation and propagation
  - Crack initiation and propagation
- Status of corrosion research at LLNL
  - Corrosion and pitting potential measurements
  - Identification of corrosion products
  - Monitoring of crack initiation and propagation
Conditions expected outside one specific spent-fuel container

- Time immediately following emplacement
  - Temperature *expected* to remain above boiling point
  - Radiolytic formation of NO₂ in *dry* air
  - Radiolytic formation of HNO₃ and *some* NH₃ in *moist* air
  - Possible formation of salt crust on container surface

- After very long periods of time
  - Temperature *expected* to drop below boiling point
  - Possible formation of concentrated electrolyte
  - Radiolytic formation of H₂O₂ in aqueous phase
  - Radiolytic formation of HNO₃ in vapor phase
Documentation of existing models and data


Containers exposed to vapor-phase environments

**Environment**
- Temperature
- Partial Pressures
  - Water Vapor
  - Radiolysis Products
- Microbial Growth

**Materials Properties**
- Mechanical
- Metallurgical
- Chemical

**Mechanical Forces**
- Residual Stress
- Lithostatic Stress
- Internal Pressure
- Structural Load

**Uniform Oxidation**
- Linear
- Parabolic

**Stress Corrosion Cracking**
- Sensitization
- Initiation
- Propagation

**Mechanical Failure**

Time Required for Complete Penetration of Wall
Models and testing for vapor-phase oxidation

- Models for vapor-phase oxidation
  - Parabolic growth law: adherent protective oxide film
  - Linear growth law: spalling non-protective oxide film

- Testing to support models
  - Coupons exposed to steam and water
  - Periodic measurement of weight gain
  - Experiments at temperatures ranging from 50 to 150°C
  - Determination of the effects of $\gamma$ irradiation
  - Identification of corrosion products by X-ray diffraction
Container life is not limited by uniform corrosion and oxidation of the austenitic alloys

From McCright et al., UCID-21044, December 1987 (Table 2)
Container life may be limited by uniform corrosion of the copper-based alloys in saturated steam at 95°C

From McCright et al., UCID-21044, December 1987 (Table 13)
X-Ray diffractometry of corrosion product on copper from target cave of 100-MeV electron LINAC

<table>
<thead>
<tr>
<th>Observed</th>
<th>Known Spectrum of Cu₂NO₃(OH)₃</th>
<th>Known Spectrum of Cu₂NO₃(OH)₃</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>d(Å)</strong></td>
<td><strong>Peak Area</strong></td>
<td><strong>d(Å)</strong></td>
</tr>
<tr>
<td>7.90</td>
<td>0.2</td>
<td>6.91</td>
</tr>
<tr>
<td>6.85</td>
<td>100.0</td>
<td>5.597</td>
</tr>
<tr>
<td>5.606</td>
<td>0.3</td>
<td>5.398</td>
</tr>
<tr>
<td>5.510</td>
<td>0.2</td>
<td>4.554</td>
</tr>
<tr>
<td>5.398</td>
<td>0.2</td>
<td>4.188</td>
</tr>
<tr>
<td>4.554</td>
<td>0.5</td>
<td>4.121</td>
</tr>
<tr>
<td>4.096</td>
<td>4.0</td>
<td>3.631</td>
</tr>
<tr>
<td>3.610</td>
<td>2.5</td>
<td>3.454</td>
</tr>
<tr>
<td>3.440</td>
<td>58.9</td>
<td>3.047</td>
</tr>
<tr>
<td>3.184</td>
<td>0.3</td>
<td>3.006</td>
</tr>
<tr>
<td>3.027</td>
<td>1.6</td>
<td>2.927</td>
</tr>
<tr>
<td>3.000</td>
<td>3.4</td>
<td>2.842</td>
</tr>
<tr>
<td>2.927</td>
<td>0.3</td>
<td>2.843</td>
</tr>
<tr>
<td>2.842</td>
<td>0.2</td>
<td>2.795</td>
</tr>
<tr>
<td>2.781</td>
<td>9.6</td>
<td>1.937</td>
</tr>
</tbody>
</table>

Van Konynenenburg, 1989
Containers exposed to aqueous environments

**Environment**
- Temperature
- Microbial Growth
- Concentrations
  - Ground Water Ions
  - Radiolysis Products

**Materials Properties**
- Mechanical
- Metallurgical
- Chemical

**Mechanical Forces**
- Residual Stress
- Lithostatic Stress
- Internal Pressure
- Structural Load

**Uniform Corrosion**
- Passivation
- Dissolution

**Localized Attack**
- Crevice Corrosion
  - Initiation
  - Propagation

**Stress Corrosion Cracking**
- Sensitization
- Initiation
- Propagation

**Mechanical Failure**

**Time Required for Complete Penetration of Wall**
Pitting models

• Initiation on passive surfaces of austenitic alloys
  1. Halide nuclei theory (Okada, 1984)
  2. Point defect model (Chao et al., 1981)
  3. Critical suppression of pH (Galvele, 1976)
  4. Electrostriction model (Sato, 1971)
  5. Inclusion model (Manning et al., 1980)
  6. Stochastic theory (Shibata and Takeyama, 1977)

• Propagation of pits in austenitic alloys
  1. Quasi-steady-state mass-transport model assuming active surface at base of pit (Pickering and Frankenthal, 1972; Galvele, 1976)
  2. Transient mass-transport model assuming highly resistive salt film at base of pit (Beck and Alkire, 1978)

• Predictive models for pitting of copper-based alloys do not exist

• Time will be required for the development of such models
Halide nuclei theory of pit initiation (Okada, 1984)

- Two independent approaches were used to derive the same expressions for the critical pitting potential ($E_c$) and the incubation time ($\tau$)
  - General evolution criterion proposed by Glansdorff and Prigogine for irreversible thermodynamics
  - Application of perturbation theory

- The expressions relating $E_c$ and $\tau$ to chloride concentration and temperature are simple linear functions

$$E_c = \text{constant} - \frac{RT}{F}\ln[\text{Cl}^-]$$

$$\ln(\tau) = \text{constant} - 2n \ln[\text{Cl}^-] - \frac{2FE}{RT}$$
The linear relationship existing between $E_c$ and $\ln[\text{Cl}^-]$ is well established

- Equations deduced from the point defect model (Chao et al., 1981) have the same functional forms as those deduced from the halide nuclei theory (Okada, 1984)

- Similar results have been derived from a model based upon pH suppression inside cracks in the passive film (Galvele, 1976)

- The following relationship between chloride concentration, temperature and pH has been observed (Matamala, 1987)

  $$Ec = 2570 - 5.81 \cdot T + 0.07 \cdot T \cdot pH - 0.49 \cdot T \cdot \log[\text{Cl}^-]$$

- This type of functionality has also been observed experimentally in cases involving pit initiation at sulfide inclusions (Manning, 1980)
Experiments supporting predictive models for the initiation of pits

- Critical pitting potential ($E_c$)
  - Potentiodynamic linear-sweep polarization
- Incubation time ($\tau$)
  - Potentiostatic polarization
- Application of statistics
  - Factorial designs to determine the dependence of $E_c$ and $\tau$ on chloride, pH and temperature
  - Stochastic theory to determine probability density functions for $E_c$ and $\tau$ (Shibata and Takeyama, 1977)
Pitting potentials were determined by linear sweep anodic polarization

Scan rate: $5 \times 10^4$ mV/hr
pH = 8.2, T = 80°C

Alloy 625
Alloy 825
Type 316
Type 304

Factorial designs minimize the number of experiments required to determine the coefficients in linear equations.

- Most general form of the equation for pitting potential

\[ Ec = a_0 + a_1 \cdot \ln[\text{Cl}^-] + a_2 \cdot \text{pH} + a_3 \cdot T + a_{12} \cdot \ln[\text{Cl}^-] \cdot \text{pH} + a_{13} \cdot \ln[\text{Cl}^-] \cdot T + a_{23} \cdot \text{pH} \cdot T + a_{123} \cdot \ln[\text{Cl}^-] \cdot \text{pH} \cdot T \]

- Important two- and three-factor interactions are included

- Only eight experiments are required to determine eight parameters

- A similar approach can be used to determine parameters in the equation for the incubation time
Factorial design for determining parameters in the pitting potential equation

<table>
<thead>
<tr>
<th>Expt.</th>
<th>ln[Cl\textsuperscript{-}]</th>
<th>pH</th>
<th>T</th>
<th>ln[Cl\textsuperscript{-}].pH</th>
<th>ln[Cl\textsuperscript{-}].T</th>
<th>pH.T</th>
<th>ln[Cl\textsuperscript{-}].pH.T</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>#2</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>#3</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>#4</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>#5</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>#6</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>#7</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>#8</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

Note: (+) high level of variable; (-) low level of variable.
Experiments supporting predictive models for the propagation of pits

- Determination of pit depth ($x$ or $a_p$) as a function of time ($t$)
  - Exposure of specimens to environment
  - Optical microscopy to measure focal distance at base of pit
  - Optical microscopy of metallographic cross-section
- Fractional coverage of surface by pits
  - Optical microscopy with video camera
  - Use of digital image processing for quantification
- Overall loss of material due to pitting
  - Weight loss measurements
Lucey has proposed a mechanism for the pitting of copper which involves a porous cuprous oxide membrane.

Reaction occurring within the mound above a pit:

\[ 4\text{CuCl} + \text{Ca} (\text{HCO}_3)_2 + \text{O}_2 \rightarrow \text{CuCO}_3 \text{Cu(OH)}_2 + \text{CaCO}_3 + 2\text{CuCl}_2. \]

Stress corrosion cracking models

- Initiation of cracks
  1. Linear-elastic fracture mechanics model for initiation of fatigue crack at pit (Hagn, 1983)
  2. Crack-tip-opening displacement model for initiation of stress corrosion crack at pit (Buck and Ranjan, 1984)
  3. Spontaneous initiation (Andresen and Ford, 1985)

- Propagation of cracks
  1. Anodic dissolution of active crack tip (Turnbull and Thomas, 1982)
  3. Film-induced cleavage of base metal (Paskin et al., 1980-83)
Buck and Ranjan (1984) developed the CTOD model for SCC initiation

- Assumptions of the CTOD (crack-tip-opening displacement) model
  - Stress corrosion cracking (SCC) initiates at pits
  - Corrosion at base of pit obeys Butler-Volmer kinetics
    
    Active surface at base of pit

    Pit depth varies linearly with time

  - Displacement at mouth of pit ($\delta$) sufficient to prevent blunting of base by corrosion

    Due to applied stress ($s$)

    Elastic and plastic contributions

  - Propagation rate of microcrack at base of pit ($da_m/dt$) proportional to displacement
The CTOD model predicts the **conditions** and **time** required for the initiation of SCC at a pit

- **Criteria for initiation**

  \[ \delta - (\delta_o + \delta_c) > 0 \quad \text{and} \quad (\sigma^2 - \sigma_o^2) a_p - (K_{ISCC})^2/\pi > 0 \]

- **Incubation time** \( t_{inc} \) is the time required for initiation

  \[ t_{inc} = \frac{1}{\pi} \frac{(K_{ISCC})^2}{(\sigma^2 - \sigma_o^2)} \exp\left(-\frac{\beta FE}{RT}\frac{V_{M_i corr}}{zF}\right) \]

  - mechanical stress -
  - electrochemical corrosion -

- **Mechanical effects** (residual stress) are taken into account by the first factor

- **Environmental effects** are taken into account by the second factor
Experiments supporting predictive models for initiation of SCC

- Threshold stress intensity factor for SCC ($K_{ISC}$)
  - Modified Wedge-Opening-Loading (WOL) fracture specimen (Novak and Rolfe, 1969)

- Effects of environment on incubation time ($t_{inc}$)
  - Load specimen in screw-driven tensile machine (Buck and Ranjan, 1984)

  - Vary chemistry of environment, electrochemical polarization and temperature

  - Measure time required for reduction in stress at constant displacement

  - Monitor stress with load cell
The model developed by Andresen and Ford (1982-1988) involves film fracture at the crack tip

- The crack propagation rate is proportional to the charge density associated with repassivation and the crack tip strain rate

\[ \frac{da}{dt} = \left[ \frac{MQ_t}{zF} \right] \left( \frac{d\varepsilon_{ct}/dt}{\varepsilon_t} \right) \]

- The charge density can be calculated from the current transient immediately following film fracture

\[ i = m t^{-n} \]

- Effects of environment and material chemistry on propagation rate can be represented by the single parameter (n)

\[ \frac{da}{dt} = f(n) \left( \frac{d\varepsilon_{ct}/dt}{\varepsilon_t} \right)^n \]
Andresen-Ford model (cont.)

- An empirical relationship between the crack tip strain rate and stress intensity has been established for the case of constant load

\[ \frac{d\varepsilon_{ct}}{dt} = 6 \times 10^{-14} K^4 \]

- This model has been used to successfully predict rates of crack propagation in Type 304 stainless steel used in boiling water reactors (BWR’s)
Schematic of electrochemical apparatus for gamma irradiation studies
Effect of gamma irradiation on the corrosion potential of 316L in J-13 well water

From Glass et al., Corrosion Science, Vol. 26, No. 8, 1986, pp. 577-590
Effect of gamma irradiation on corrosion potential of CDA 102

From Glass et al., Paper No. 258, Corrosion 86, NACE, Houston, Texas, March 17-21, 1986
Effect of gamma irradiation on the pitting potential of 316L in NaCl solution

From Glass et al., Corrosion Science, Vol. 26, No. 8, 1986, pp. 577-590
Effect of chloride on pitting potential of 316L determined by potentiodynamic polarization

\[ E_{\text{corr}} \]

\[ E_c \]

ASTM G5 Procedure. Farmer, 1989
## Implementation of QAP (quality assurance plan)

<table>
<thead>
<tr>
<th>Sub-Activity Description</th>
<th>Identification Number of Plan</th>
<th>Planning Document</th>
<th>Status of Lab Work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion Modeling</td>
<td>E-20-16a</td>
<td>Approved</td>
<td>Planned</td>
</tr>
<tr>
<td>Linear Polarization</td>
<td>E-20-18a</td>
<td>Approved</td>
<td>In Progress</td>
</tr>
<tr>
<td>Long-Term Tests</td>
<td>E-20-18b</td>
<td>Approved</td>
<td>Planned</td>
</tr>
<tr>
<td>Measurement of $K_i$</td>
<td>E-20-18c</td>
<td>Approved</td>
<td>Planned</td>
</tr>
<tr>
<td>Measurement of $K_{isc}$</td>
<td>E-20-18d</td>
<td>Approved</td>
<td>Planned</td>
</tr>
<tr>
<td>SEM and STEM</td>
<td>E-20-18e</td>
<td>Approved</td>
<td>Planned</td>
</tr>
<tr>
<td>Radiation Effects</td>
<td>E-20-18f</td>
<td>Approved</td>
<td>In Progress</td>
</tr>
<tr>
<td>SCC in J-13 Water</td>
<td>E-20-18g</td>
<td>Approved</td>
<td>Planned</td>
</tr>
<tr>
<td>CERT Testing</td>
<td>E-20-18h</td>
<td>Approved</td>
<td>Planned</td>
</tr>
</tbody>
</table>
Summary

- Description of conditions outside one specific container
  - Predicted temperature profile
  - Chemical species formed by $\gamma$ radiolysis and their effects on container materials
  - Role of ions found in ground water on localized attack of container materials
- Review of models and testing for vapor-phase and aqueous corrosion
  - Uniform oxidation
  - Pit initiation and propagation ($E_{corr}$, $E_c$, $\tau$)
  - Crack initiation and propagation ($t_{inc}$, $K_{ISCC}$, $da/dt$)