Development & Validation of Realistic Degradation Mode Models for the Waste Package and Drip Shield

Presentation to:
Nuclear Waste Technical Review Board (NWTRB)

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Alexandria, VA
September 14-15, 1999
Waste Package Concept

Environment

Corrosion Resistant Outer Barrier (Alloy 22)

Support

Drip Shield (Ti Gr 7)

Structural Support & Radiation Shielding (316 NG)
Abstracted Model for Waste Package Degradation

Drift Environment → Waste Package Surface Environment

Threshold Relative Humidity

No Dripping

Dry Oxidation Rates → Humid Air Corrosion Rates

Localized Corrosion Rates → General Corrosion Rates

Corrosion & Threshold Potentials

Minimum Possible Crevice pH

Heat Generation in Waste Package

Dripping

Phase Stability Model

TTT Diagrams & Precipitation Kinetics

Manufacturing Data

Residual Weld Stress

Laser Peening Effects

Flaw Size Distribution

Stress Corrosion Cracking Model A

Threshold Stress Intensity Factor

Stress Corrosion Cracking Model B

Film Rupture Model

Overall Rate of Wall Penetration
Examples of Model Validation

- Validation is an essential part of model development
  - Corroboration with independent measurements
  - Bounding analyses

- Examples will be given relevant to the overall process model
  - General & Localized Corrosion
    - Weight loss measurements indicated very low corrosion rates
    - Cyclic polarization indicates very high thresholds potentials
    - Atomic Force Microscopy used for confirmation (validation)
  - Minimum Possible Crevice pH
    - Transport model used to predict low pH in crevice
    - Measurements and published data used to confirm predictions
    - Investigation of hydrogen absorption in titanium crevices
  - Stress Corrosion Cracking Models
    - Elimination of need through mitigation of weld stress
  - Aging & Phase Stability Model
    - Experimental validation with TEM & related techniques
Establishment of New WP Surface Environment by Evaporative Concentration

Basis of Near-Saturation Test Media (BP ~ 112°C and pH ~ 12)

Starting Solution ~ 5000X J-13

Since oxygen solubility (and corrosion rate) decreases with increasing salt concentration, the electrolyte formed by removing 90% of the water may be more severe than a fully saturated solution.
Dissolved Oxygen Measurements in LTCTF Validated by Comparison to Published Data for Synthetic Geothermal Brine

![Graph showing dissolved oxygen measurements vs. temperature for different pressures and brine types.](image)
General Corrosion of DS & WP Materials

General Corrosion of Ti Gr 16:
Crevice Samples from LTCTF

General Corrosion of Alloy 22:
Weight Loss Samples from LTCTF

General corrosion rates fall below the limit due to measurement error

Such low corrosion rates will not be life limiting
Low General Corrosion Rates Confirmed with AFM: Alloy 22 in LTCTF SAW at 90°C for 1 Year

- **Control Sample**
- **Vapor-Phase Exposure**
- **Silica Deposit**
- **Liquid-Phase Exposure**
DS & WP Resistant to Localized Corrosion

The DS & WP materials appear to have exceptional resistance to localized corrosion.

Stainless steel is to serve primarily as a structural material.
Anodic Oxidation Peak with Alloy 22 in SCW

Anodic oxidation peaks observed in CP scans for Alloy 22 in SCW electrolytes

CP scans with Pt blank show that anodic peak due to surface phenomena

Stability of Passive Film on Alloy C-22
Gamma Radiolysis Effects:
Insignificant Impact on Corrosion Potential & Breakdown of Passive Film

- Gamma radiolysis could promote localized corrosion
  - Production of hydrogen peroxide
  - Anodic shift of the corrosion potential, closer to the threshold for breakdown of passive film

- A strategy has been formulated for addressing any enhanced radiolysis effects in the EDA II design
  - Re-examination stainless steel corrosion data from gamma pit that was produced by Yucca Mountain Project in the mid 1980’s
  - Discussions with investigators at General Electric Corporation
  - Measurement of corrosion & threshold potentials of Alloy 22 and other WP materials as functions of H₂O₂ concentration

- Based upon such measurements, gamma radiolysis is being screened out as a significant detrimental process
Simulated Gamma Radiolysis Experiments with Alloy 22 in SCW and SAW

Effect of H$_2$O$_2$ on Corrosion Potential of Alloy 22 in SCW at 25 Centigrade

Effect of H$_2$O$_2$ on Corrosion Potential of Alloy 22 in SAW at 25 Centigrade

Hydrogen peroxide does not drive corrosion potential into anodic oxidation or regions of passive film destabilization in SAW or SCW
Minimum Possible Crevise pH

- Crevices will be formed
  - Beneath mineral precipitates, corrosion products, dust, rocks, cement and biofilms
  - Between waste package and supports
  - Between outer barrier (Alloy 22) and inner barrier (316 NG)

- The crevice environment will be more severe than the NFE
  - Suppression of pH due to the accumulation of H⁺ from the hydrolysis of dissolved metal
  - Field-driven electromigration of Cl⁻ (and other anions) into crevice must occur to balance cationic charge associated with H⁺

- The crevice environment sets the stage for other modes of attack
  - General corrosion
  - Pitting (initiation & propagation)
  - Stress corrosion cracking (initiation & propagation)

- Successful defense of the Waste Package (WP) design requires adequate understanding of such phenomena
Predicted Crevice Environment Confirmed with In Situ Measurements

Stainless Steel 316L: 4M NaCl, 200 mV & 23 Centigrade

Alloy C-22 in 4M NaCl at 23 Centigrade

Alloy C-22 in SCW at 23 Centigrade

Alloy C-22 in 4M NaCl at 23 Centigrade

Sensors return to original values at end of experiment

Sample returns to corrosion potential

Predicted Crevice Environment Confirmed with In Situ Measurements
Determination of Crevice pH for WP Materials

- **Expected Case for Alloy 22 & 316L (Ground Water with Buffer)**
- **Bounding Case for Alloy 22 (High Chloride and No Buffer)**
- **Bounding Case for Alloy 22 (High Chloride and No Buffer)**

**Graph Details:**
- **X-axis:** Potential at Crevice Mouth (mV vs. Ag/AgCl)
- **Y-axis:** Crevice pH
- **Data Points:**
  - Alloy 22 in SCW
  - Alloy 22 in 4M NaCl
  - 316L in SCW
  - 316L in Satd. KCl
  - 316L in 4M NaCl

**Legend:**
- Red squares for 316L
- Black triangles for Alloy 22
- Blue diamonds for Ground Water with Buffer
- Green triangles for High Chloride and No Buffer

**Notes:**
- The graph illustrates the crevice pH values for different materials under various conditions.
- The expected case shows the pH behavior in ground water with buffer, while the bounding cases demonstrate the pH in high chloride environments with and without buffer.
Hydrogen absorption by titanium is exacerbated by crevice. Additional work is needed to fully understand this phenomena. However, at the present time, it is not believed that the threshold hydrogen concentration for HIC will be exceeded.
Validation of Stress Corrosion Cracking Models

- Slow strain rate testing
  - Experimental determination of stress-strain curves
  - Used for screening environment for other SCC tests

- Initiation based upon threshold stress intensity factor
  - Method employed by Yucca Mountain Project
  - Double Cantilever Beam Method (Ajit Roy)
  - Data have been obtained for Alloy 22 in NaCl solutions

- Finite propagation rate based upon film-rupture model
  - Method employed by General Electric Corporation
  - Reverse DC Method (Peter Andresen)
  - No data have been generated for Alloy 22

- Microbes may pose unique threats
  - Sulfate reducing bacteria (sulfide)
  - Iron oxidizing bacteria (ferric ion)
The Need for SCC Models Eliminated with Validated Technique for Stress Mitigation

Weight Stress

Weld Stress

Laser Peening Process

Tensile Stress (Shrink Fit)

Residual Weld Stress in a Closure Weld of Waste Package

Double-Pass Laser Peening (4340 Steel)

The Ring Core Method was used to measure the stresses 0.2 inches from the edge of the fusion line

Residual Stress (ksi)

Depth (mils)
Mitigation of Weld Stress in Alloy 22 with Laser Peening

0.2 Inches from Fusion Line

- As Welded - Minimum
- As Welded - Maximum
- Laser Peened - Maximum
- Laser Peened - Minimum

Centerline

- As Welded - Minimum
- As Welded - Maximum
- Laser Peened - Maximum
- Laser Peened - Minimum

Stress (ksi)

Depth (mils)
Theoretical Models for Aging & Phase Stability

- Theoretical tools and expertise are now in place to establish time-temperature-transformation (TTT) diagrams for multicomponent alloys
  - THERMO-CALC
  - DICTRA

- Phenomenological THERMO-CALC and DICTRA codes predict
  - Energetics
  - Regions of stability & metastability
  - Phase transformation rates limited by
    - Kinetics
    - Diffusive transport

- Electronic structure-based approach combined with Monte Carlo simulations used to
  - Supplement the thermodynamic databank
  - Predict solute effects on ordering processes, complex phase formation and evolution
Precipitated Intermetallic Phase Observed in Welded Alloy 22 Aged for 40,000 hr at 427°C

Theoretical models are being validated through detailed scientific research with transmission electron microscopy, electron beam diffraction, and other relevant techniques.
Alloy C-22 Aged at 649 °C for Various Times

10 hr

100 hr

1000 hr
TTT Diagram for Alloy 22

- Complete coverage of GBs with precipitates
- Partial coverage of GBs
- No precipitates on GBs
- LRO

Legend:
- ☺ Partial GB Coverage
- ■ Complete GB Coverage
- ▲ No GB Precipitation
- □ LRO
- ◆ Not Examined

Applicable to Base Metal
Preliminary Precipitation Kinetics for Alloy 22

- Grain Boundary Start
- Grain Boundary Finish
- Bulk Start
- Based on ASTM G28-B

800 Centigrade

Extrapolates to well beyond 10,000 years at 300 degrees Centigrade

593 Centigrade
Summary

- Validation is an essential part of model development
  - There are multiple ways to accomplish this
  - All have to be based upon good scientific investigation

- Examples will be given relevant to the overall process model
  - General & Localized Corrosion
    - Weight loss measurements indicated very low corrosion rates
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    - Atomic Force Microscopy used for confirmation (validation)
  - Minimum Possible Crevice pH
    - Transport model used to predict low pH in crevice
    - Measurements and published data used to confirm predictions
    - Investigation of hydrogen absorption in titanium crevices
  - Need for Stress Corrosion Cracking (SCC) model eliminated
    - Validation of new technique for mitigation of weld stress
  - Validation of Phase Stability Model
Summary

- Preliminary conclusions
  - No significant localized corrosion expected
  - Life not limited by general corrosion
  - Phase stability appears to be acceptable
  - Focus on the mitigation of SCC at final closure weld

- New design has increased the need for additional testing
  - Stainless steel & titanium were not used in TSPA-VA design
  - Tests on these materials have just started
  - Limited availability of qualified data

- Additional R&D must be directed towards fabrication processes
  - Thermally enhanced fit of Alloy 22 outer barrier over 316NG
  - Need to minimize tensile stress in Alloy 22 during cooling
  - SCC threat at unannealed closure welds in Alloy 22
  - Mitigation of through application of laser peening
Valid WP Model Based Upon Contributions of Many

- Definition of Interfacial Waste Package Environment
  - Greg Gdowski & Francis Wang
- Long Term Corrosion Testing
  - Dan McCright, John Estill, Ken King, Steve Gordon & Larry Logotetta
- Electrochemical Studies & Surface Physics
  - John Estill, Ken King, Steve Gordon & Larry Logotetta
  - Peter Bedrossian & David Fix
- Phase Stability
  - Tammy Summers, Patrice Turchi & Larry Kaufman
- Stress Corrosion Cracking Studies
  - Ajit Roy, John Estill, Maura Spragge, Dennis Fleming & Beverly Lum
- Microbial Influenced Corrosion
  - JoAnn Horn, Denny Jones & Tiangan Lian
- Welding Processes, Residual Stress Analysis & Laser Peening
  - Don Stevens, Lloyd Hackel, Fritz Harris (MIC) & Al Lingenfelter
- Waste Package Modeling
  - Patrice Turchi, Stephen Lu, & Jia-Song Huang