



# ***Summary of NRC Work and Waste Package Corrosion Risk Insights***

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Alloy 22 in Yucca Mountain Environments*

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# OUTLINE

- **UNCERTAINTIES IN PERSISTENCY OF PASSIVE FILM**
- **RESTRICTED OPENING OF WASTE PACKAGE (WP) SURFACE**
  - **Observation in Crevice Corrosion**
  - **Sensitivity Analyses**
  - **Hypothetical Dose Calculations**
- **SUMMARY OF NRC WORK**
- **RISK INSIGHTS**
- **PATH FORWARD**

# ***UNCERTAINTIES IN PERSISTENCY OF PASSIVE FILM***

- **Accelerated corrosion by passivity breakdown related to localized corrosion, assurance of extremely low general corrosion rates.**
  - **Structural change – micro-structure (crystalline or amorphous), various defects, compact/porous, void**
  - **Change of chemical compositions**
  - **Thickness change with time**
  - **Examples:**
    - (i) anodic sulfur segregation**
    - (ii) development of porous structure**
    - (iii) mechanical spallation by void formation at film interface**
    - (iv) development of large cathodic surface area**
    - (v) anion selective sorption**

Ahn, T., T. Shinohara and S. Fujimoto, Long-Term Effects in the Initiation of Non-passive Corrosion of Corrosion-resistant Passive Waste Package under Geological Repository Conditions, presented at Materials Research Society, San Francisco, CA, 2004, NRC ADAMS 041110309 - partly presented

# UNCERTAINTIES OF PERSISTENCY OF PASSIVE FILM *(cont'd.)* - Anodic Sulfur Segregation

**- Formation of sulfur monolayer may increase general corrosion rate.**

Penetration Depth (Amount Corroded) =  
 $\sum[(CR_p * Ct_p) + (CR_f * Ct_f)]$

$CR_p$  : slow corrosion rate  
 (from passive current density of Alloy 22)

$Ct_p$  : time period of slow corrosion  
 (sulfur segregation time)

$CR_f$  : fast corrosion rate (from potentiostatic current  
 transient of Alloy 22)

$Ct_f$  : time period of fast corrosion (from  
 potentiostatic current transient of Alloy 22)

**Premises: Cyclic Mo-S removal, breakdown of  
 passivity with monolayer S, more updated  
 information by Jones et. al., 2006**

Passarelli, A. and D. Dunn, O. Pensado, T. Bloomer and  
 T. Ahn, Risk Assessment of Uniform and Localized Corrosion, Met. Mat.  
 Trans. A, Vol. 36A, p. 1121 – 1127, 2005 – Equation here  
 Jones, R., D. R. Baer, C. F. Windisch, Jr., and R. B. Rebak, Corrosion Enhanced  
 Enrichment of Sulfur and Implications for Alloy 22, Paper 06621, 2006 –  
 recent test results

- At  $CR_p = 10^{-6}$  cm/yr,  $Ct_p = 500$  yrs

- $CR_f = 10^{-4}$  cm/yr

- $Ct_f = 0.0119$  yr

- Penetration time:  $2.0 \times 10^6$  yrs  
 (for 2 cm thick WP)

- $CR_f = 10^{-2}$  cm/yr

- $Ct_f = 0.0119$  yr

- Penetration time:  $1.6 \times 10^6$  yrs

- $CR_f = 10^{-2}$  cm/yr

- $Ct_f = 1.19$  yr

- Penetration time:  $7.8 \times 10^4$  yrs

- At  $CR_p = 10^{-4}$  cm/yr,  $Ct_p = 5$  yrs

- $CR_f = 10^{-2}$  cm/yr

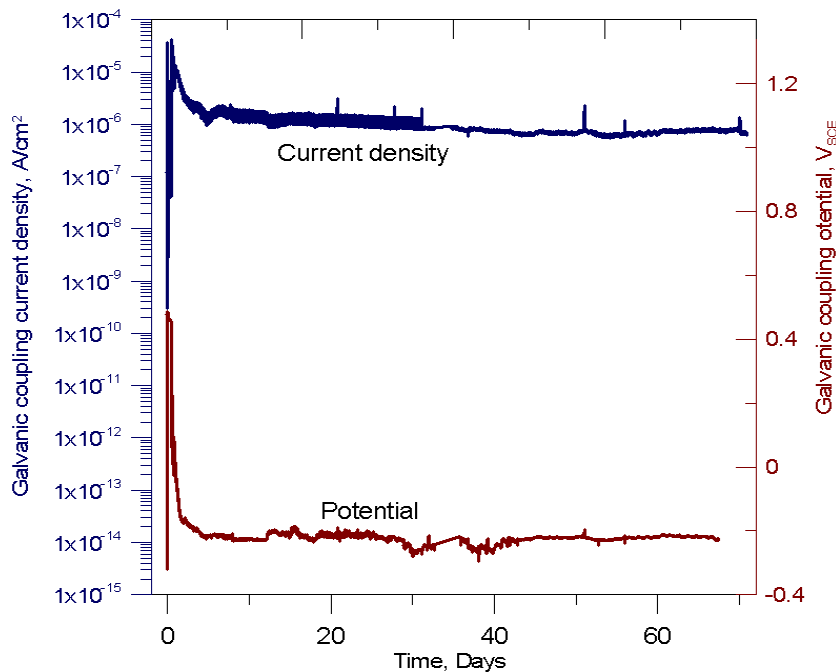
- $Ct_f = 1.19$  yr

- Penetration time:  $\sim 10^3$  yrs

# RESTRICTED OPENING OF WP SURFACE

## – Observation in Crevice Corrosion

- Crevice corrosion initiates, but quickly stops except for limited number of pits.



Measured current density and potential using the single crevice assembly for an Alloy 22 cylindrical specimen galvanically coupled to a large Alloy 22 plate in 5 M NaCl solution with the addition of  $2 \times 10^{-4}$  M  $\text{CuCl}_2$  at 95 °C [203 °F]

- **Observations:**
  - (i) the initiation of crevice corrosion over a wide crevice area
  - (ii) the current density decayed significantly as a result of the potential drop
- a single corroded site persisted and grew to a greater depth than the area
- This could happen at  $E_{\text{corr}} < E_{\text{breakdown}}$
- **Other Restrictions:**
  - (i) uncertainties in  $E_{\text{Eoorr}}$ ,  $E_{\text{crev,rep}}$  and  $E_{\text{breakdown}}$ ,
  - (ii) potential distribution,
  - (iii) limited groundwater volume,
  - (iv) restricted crevice area, and
  - (v) weld area

# *RESTRICTED OPENING OF WP SURFACE*

*(Cont'd.)*

## *– Sensitivity Analyses*

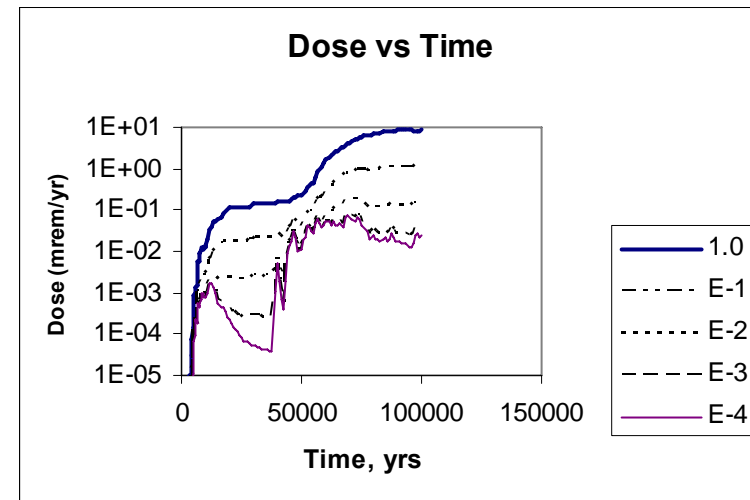
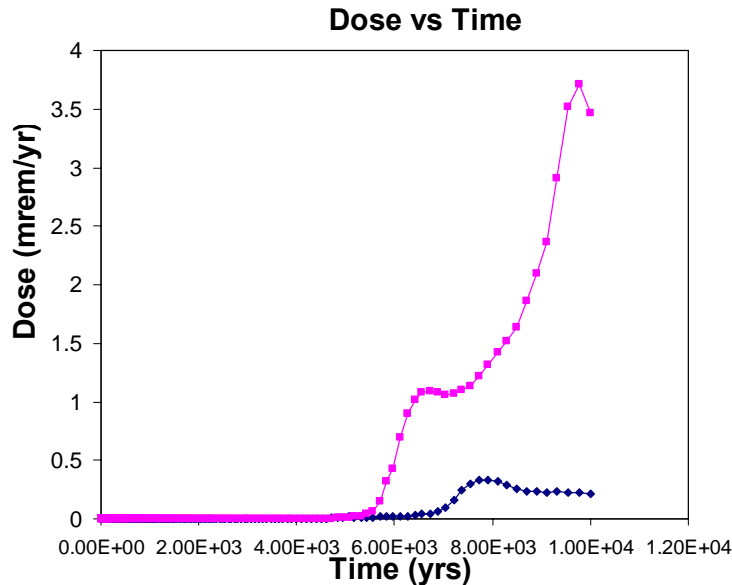
- Sensitivity study performed using NRC performance assessment code, TPA4.
- Sensitivity study of restricted opening shows clear relationship to dose.
- Analysis assumes log-uniform distribution to simulate the restricted opening of waste package (e.g., pinholes or hairline cracks).
- Sensitivity study simulates a range of pit sizes from the literature, but specific data for Alloy 22 were not available.

TPA4: Mohanty, S., T. McCartin and D. Esh, Total-system Performance Assessment (TPA): Version 4.0 Code: Module Description and User's Manual, Center for Nuclear Waste Regulatory Analyses, San Antonio, TX, 2000

# RESTRICTED OPENING OF WP SURFACE

(Cont'd.)

## - Hypothetical Dose Calculation Results



Estimated dose vs. time (yrs) by giving credit (lower curve) in the radionuclide release to the remaining WP surface area after localized corrosion in comparison with no credit (radom values, upper curve) with about 87 % WP failure in NaCl solution

Estimated dose by giving credit in the radionuclide release to the remaining WP surface area after localized corrosion in comparison with no credit (mean values); no credit to pit plugging

Passarelli, A. and D. Dunn, O. Pensado, T. Bloomer and T. Ahn, Risk Assessment of Uniform and Localized Corrosion, Met. Mat. Trans. A, Vol. 36A, p. 1121 – 1127, 2005

# *SUMMARY OF NRC WORK*

- Brines formed from salt mixtures (Na-K-Cl-NO<sub>3</sub>) at elevated temperatures will more likely result in general corrosion than localized corrosion (L. Yang, this workshop) .
  - CNWRA experiments indicate high general corrosion rates on the order of 1 μm/yr, which may lead to potential reductions in wall thickness of the Alloy 22 waste package.
  - Mechanical interaction analyses may need to take this wall thickness reduction into account.
  - Longer-term tests are ongoing to evaluate uncertainties in general corrosion rates and localized corrosion susceptibility.



## *SUMMARY OF NRC WORK (Cont'd.)*

- Brines that form by evaporation of seepage waters are mostly benign to Alloy 22, but some compositions could initiate localized corrosion of the waste package material (R. Pabalan, this workshop).
  - Contact of seepage water may be prevented by drip shield.
  - The localized corrosion susceptibility decreases with decreasing temperature.
  - If seepage water contacts waste packages at temperatures close to 100°C [212°F], localized corrosion should be considered in performance assessments.

## *SUMMARY OF NRC WORK (Cont'd.)*

- Soluble salts have significant concentrations of corrosion inhibitors nitrate and sulfate (based on limited data on dust samples) (R. Pabalan, this workshop).
- Crevice corrosion of Alloy 22 shows a strong tendency of stifling and repassivation near boiling (X. He, this workshop).

# *RISK INSIGHTS*

- General corrosion appears to be more significant process than localized corrosion.
- Uncertain effects from long-term chemical or structural changes in passive film stability warrant additional consideration.
- Crevice corrosion showed a strong tendency of stifling and repassivation in a simulated crevice corrosion environment of Alloy 22 near boiling.
- Crevice corrosion of WP could result in a small opening area, which limits potential for the radionuclide release.
- Brines that form by evaporation of seepage waters are mostly benign to Alloy 22, but some compositions could initiate crevice corrosion of the waste package material.

# *PATH FORWARD*

Understand and better constrain conditions and mechanism of localized and general corrosion

To reduce data and model uncertainties, additional model support and data will be continued in:

- Effects of long-term chemical or structural changes in passive film stability
- Elevated temperature effects on corrosion rate
  - Chemical evolution and stability of salt mixtures
  - Longer-term tests to measure general corrosion rates and monitor localized corrosion susceptibility

# *PATH FORWARD* (Cont'd.)

- Chemistry of water contacting engineered barrier
  - Updated thermodynamic analyses
  - Effect of drift degradation
  - Further sampling and characterization of Yucca Mountain dust
- Crevice corrosion initiation and propagation tests
  - Corrosion supported by dust deliquescent salts and thin water films
  - Tests to monitor stifling and repassivation
  - Measurements of opening area from crevice corrosion
- Corrosion model to support independent total system performance assessments
  - Long-term stability of passive film as bases for general corrosion rates
  - Stifling and repassivation
  - Extent of surface damage
- Integrated confirmatory tests on corrosion and evolution of near-field chemistry

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## *Disclaimer*

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