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Corrosion of Waste Package and Drip Shield Materials in Potential Repository Conditions

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- Dust Deliquescence Corrosion
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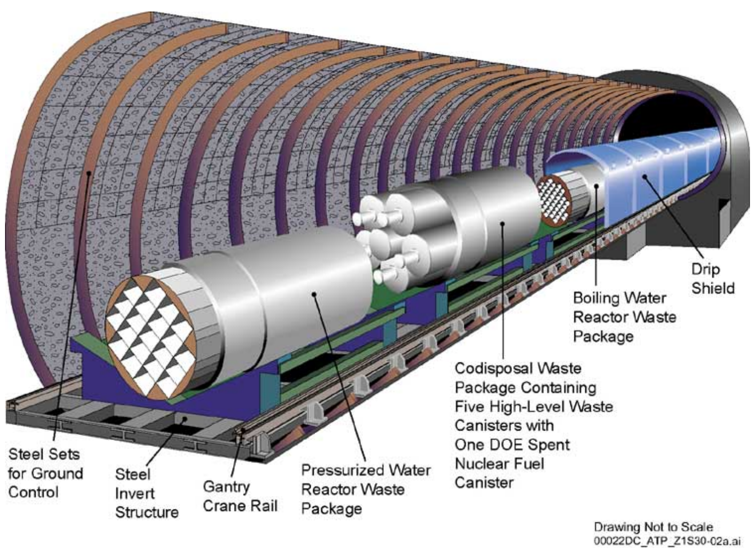
Purpose

- **Summarize key processes affecting corrosion in the waste package (WP) and the drip shield (DS) at the potential Yucca Mountain (YM) repository**

- **Discuss current understanding of potentially significant uncertainties in corrosion processes for Alloy 22 and titanium alloys**

Engineered Barrier System

(DOE, 2002)

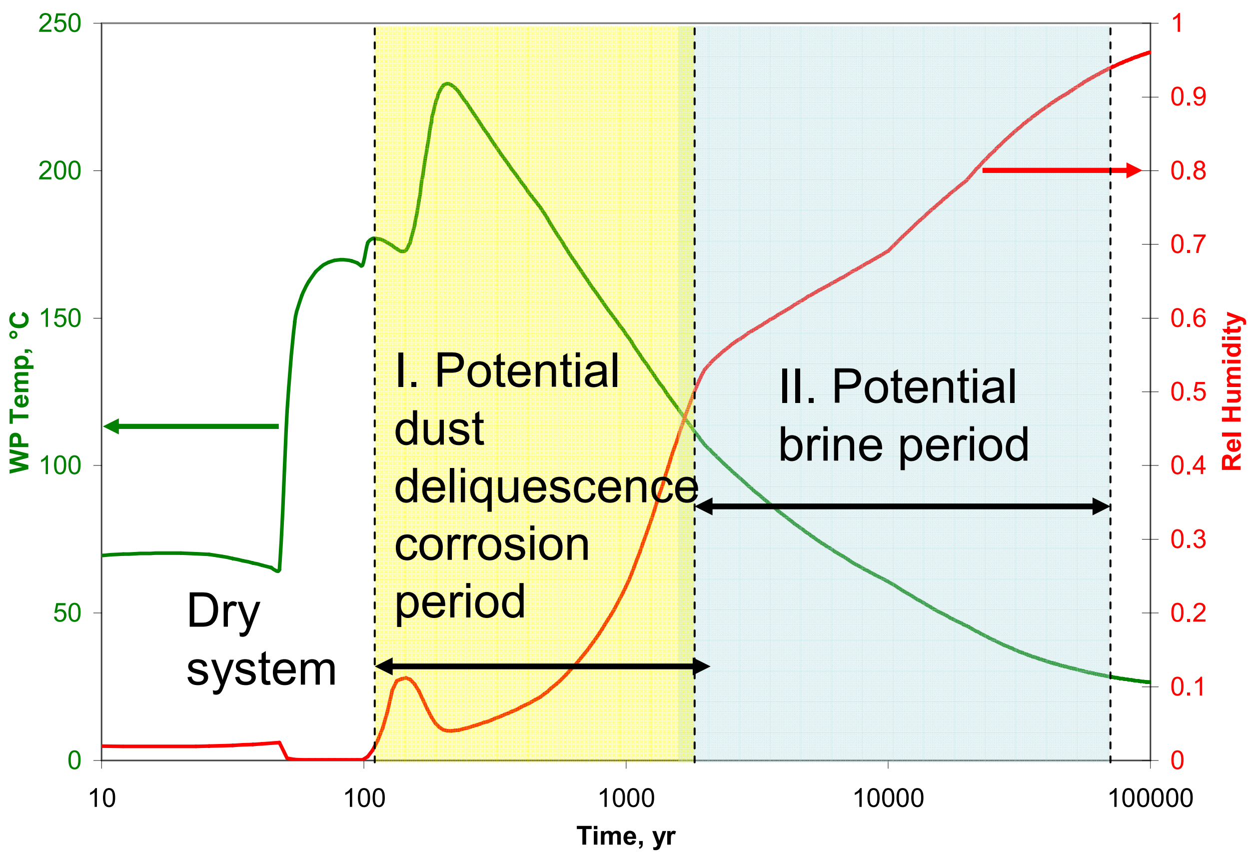


- **Drip Shield – Titanium Alloys (Grades 7 and 29)**
  (i) prevents contact of seepage water with WP
  (ii) prevents rockfall impact on WP

- **Waste Package – Alloy 22 (Ni-22Cr-13Mo-3W-4Fe)**
  (i) prevents water contact with waste form
  (ii) controls radionuclide release

- **Good understanding of potential corrosion mechanisms, with residual uncertainties**

WP Environment and Corrosion Modes



(After Pensado, 2006)

- Persistence of long-term passive film in general corrosion (I, II, and longer period)
- Dust deliquescence corrosion (I)
- Seepage water brines - crevice corrosion (II)
- Microbially influenced corrosion (II, and longer period)
- Hydrogen effects on Titanium (II, and longer period)

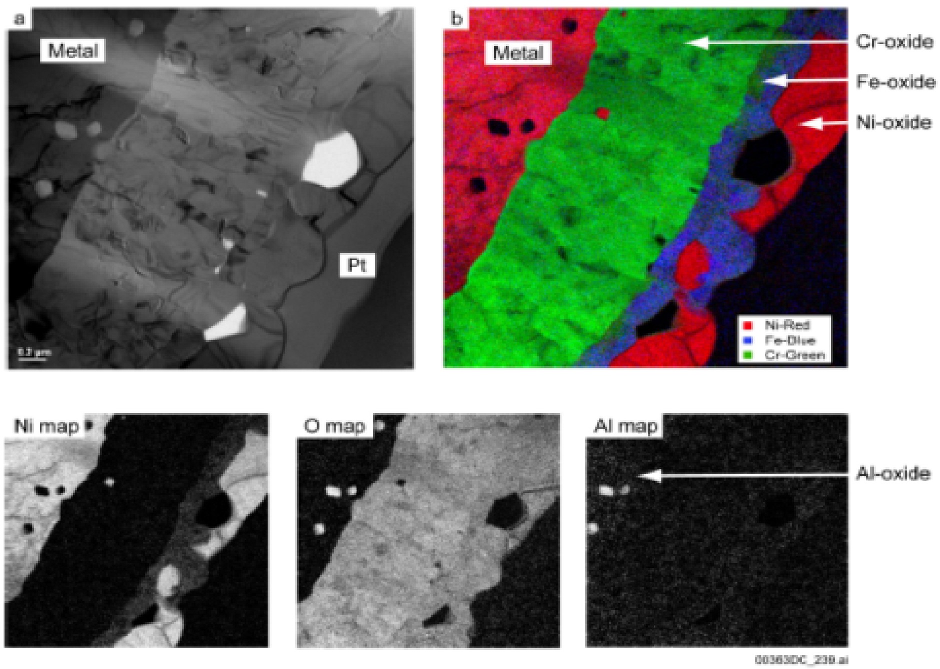
WP Environment and Corrosion Modes *(Contd.)*

Corrosion Modes Not Seen As Risk Significant

- **Alloy 22:**
  stress corrosion cracking, hydrogen embrittlement, galvanic corrosion, and dry oxidation

- **Titanium alloys:**
  localized corrosion (pitting and crevice corrosion), stress corrosion cracking, microbially influenced corrosion, galvanic corrosion, and dry oxidation

General Corrosion: Persistence of Passive Film



A Cross-Sectional View of a Solution Annealed Alloy 22 Substrate (Orme, 2005)

- **Uncertainties of passive film stability affect long-term general corrosion rates**
- **Passive film stability is primarily affected by changes in**

  - chemical composition
  - microstructure
  - thickness

General Corrosion: Persistence of Passive Film *(Condt.)* *Chemical Composition, Microstructure, and Thickness – Conformance of Chromium Oxide*

Models, analogue information, and limited laboratory data suggest that a chromium-rich oxide layer is responsible for the persistence of passive film (i.e., conformance).

- **Models: conformance by point defect model (PDM, Macdonald et al., 2004; Chao et al. and Lin et al., 1981; Urquidi-Macdonald and Macdonald, 1987); finite thickness of passive film (Urquidi-Macdonald and Macdonald, 2003), and minimal effects of potential void formation (Pensado et al., 2002)**

  - uncertainties: long-term changes in chemical compositions and microstructure

- **Long lifetime of natural analogue, nickel-iron meteorites (Sridhar and Cragnolino, 2002)**

  - uncertainties: applicability to Alloy 22 in the YM environment (e.g., role of chromium)

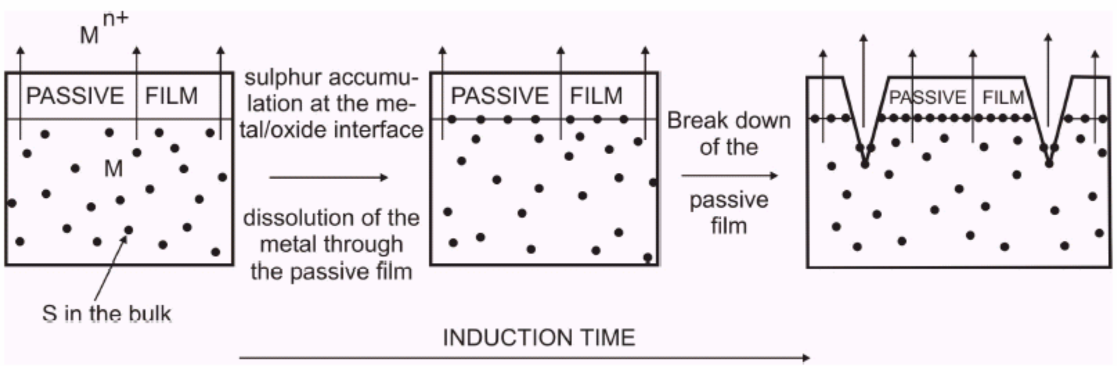
- **Limited laboratory data: decrease of general corrosion rates of Alloy 22 with time**

  - example uncertainties: properties of passive film under deliquescence conditions (Yang et al., 2007); effects of foreign deposits such as silica

General Corrosion: Persistence of Passive Film

(Contd.) Chemical Composition - Anodic Sulfur Segregation

Mechanism of the breakdown of the passive film induced by enrichment of sulfur at the metal-passive film interface (Marcus, 1995)



(Reprinted from "Sulfur-Assisted Corrosion Mechanisms and the Role of Alloyed elements" by P. Marcus in *Corrosion Mechanisms in Theory and Practice* edited by P. Marcus and J. Oudar, Marcel Dekker, Copyright (1995), with permission from Marcel Dekker)

Uncertainties

- Dissolution rate of segregated sulfur with molybdenum

- Repassivation rate in chloride solution with chromium and oxyanions

(Ahn, et al., 2007; Passarelli et al., 2005)

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Dust Deliquescence Corrosion

- **Dust deliquescence corrosion is potentially important for approximately first 2000 years after closure.**

- **Dust on WP may form brines from deliquescent at elevated temperatures. Some deliquescent brines can induce general and crevice corrosion of Alloy 22.**

- **Brines formed from very corrosive salt mixtures (Na-K-Cl-NO_3) at elevated temperatures will more likely result in general corrosion rather than crevice corrosion:**

  - **CNWRA experiments indicate high general corrosion rates at elevated temperatures, on the order of 1μm/yr [0.04 mil/yr], only during an approximately 2000-year thermal period; and**

  - **Extent of corrosion depends on distribution of dust and duration of corrosive brine formation.**

- **Current uncertainties in deliquescence-induced corrosion rates result from extrapolating short-term experimental results to repository time scales.**

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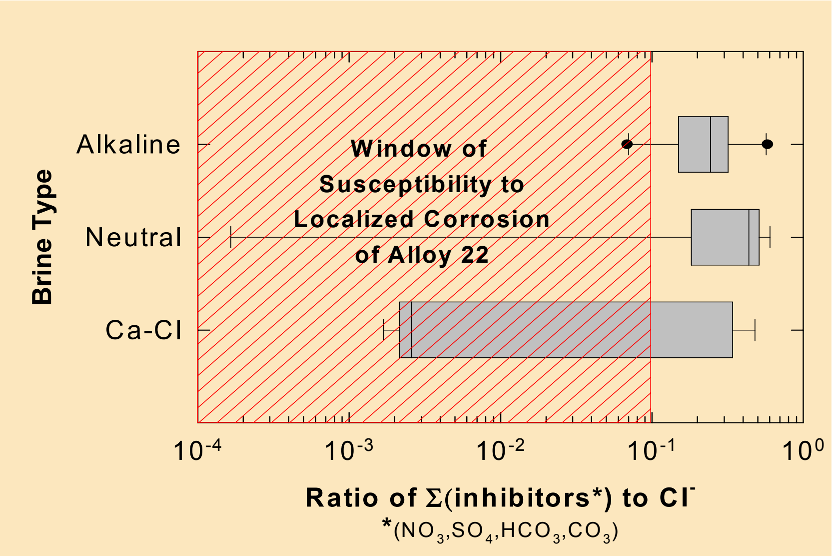
Seepage Water Brines: Crevice Corrosion

- **Brines that form by evaporation of seepage waters are mostly benign to Alloy 22, but some compositions (less than approximately 10 percent) could initiate crevice corrosion for approximately 2,000 to several ten thousand year post closure.**

  - **Contact of seepage water may be prevented by DS.**
  - **The susceptibility of crevice corrosion decreases with decreasing temperature below approximately 110 ºC.**



Pabalan (2006); localize corrosion is crevice corrosion

- **Uncertainties associated with likelihood of seepage-water brines to initiate crevice corrosion**

Seepage Water Brines: Crevice Corrosion *(Contd.)*

- **In addition to temperature and water chemistry, tight contact environment is necessary to initiate crevice corrosion.**

- **Crevice area – tight area of buckled DS and WP under applied stress by rock falls and earthquakes**
  - uncertainties in timing and extent of mechanical effects

- **Weld area – more susceptible for crevice corrosion than base metal**
  - uncertainties in weld characteristics from fabrication processes

- **Crevice corrosion propagation was limited to some deep sites, after initial transient period, due to repassivation effects (He and Dunn, 2005)**
  - uncertainties in long-term repassivation rate and under possible wide range of environment

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Additional Corrosion Processes

- **Microbially Influenced Corrosion (MIC)**

  - Models and limited laboratory data indicate low potential for MIC.

  - Uncertainties: Some MIC is difficult to detect (e.g., MIC-induced long-term pitting or crevice corrosion)

- **Hydrogen Effects in Titanium Alloys**

  - Preliminary analyses suggest some minor effects on long-term integrity of DS.

  - Uncertainties:
  (i) hydrogen sorption rates during titanium alloy corrosion; and
  (ii) hydrogen diffusion rates between dissimilar titanium metals (e.g., base metal and welds)

Summary

- Long-term chemical or structural changes in passive film stability strongly affect uncertainties in Alloy 22 general corrosion rates.
- Current information indicates that crevice corrosion by dust deliquescence does not affect WP performance significantly.
- Crevice corrosion from seepage water (less than approximately 110 ºC) requires tight crevices and aggressive brines (less than approximately 10 percent of expected seepage water compositions). Susceptibility decreases with decreasing temperature.
- Microbially influenced corrosion appears unlikely because of short induction time and no evidence of long-term pitting and crevice corrosion.
- Hydrogen effects on titanium alloy integrity appear to be low significance.
- Uncertainties in persistence of passive film appear more significant than uncertainties in other corrosion processes.
- Information from laboratory investigation, numerical models, and analog materials is available to support staffs review of corrosion processes.

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Disclaimer

The NRC staff views expressed herein are preliminary and do not constitute a final judgment or determination of the matters addressed or of the acceptability of a license application for a geological repository at Yucca Mountain. This presentation describes work performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA) for the NRC under contract number NRC-02-02-012. The activities reported here were performed on behalf of the NRC office of Nuclear Material Safety and Safeguards, Division of High Level Waste Repository Safety. This presentation is an independent product of the CNWRA and does not necessarily reflect the view or regulatory position of the NRC.

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