



# **LONG-TERM EFFECTS IN THE INITIATION OF NON-PASSIVE CORROSION OF CORROSION-RESISTANT PASSIVE WASTE PACKAGE UNDER GEOLOGICAL REPOSITORY CONDITIONS**

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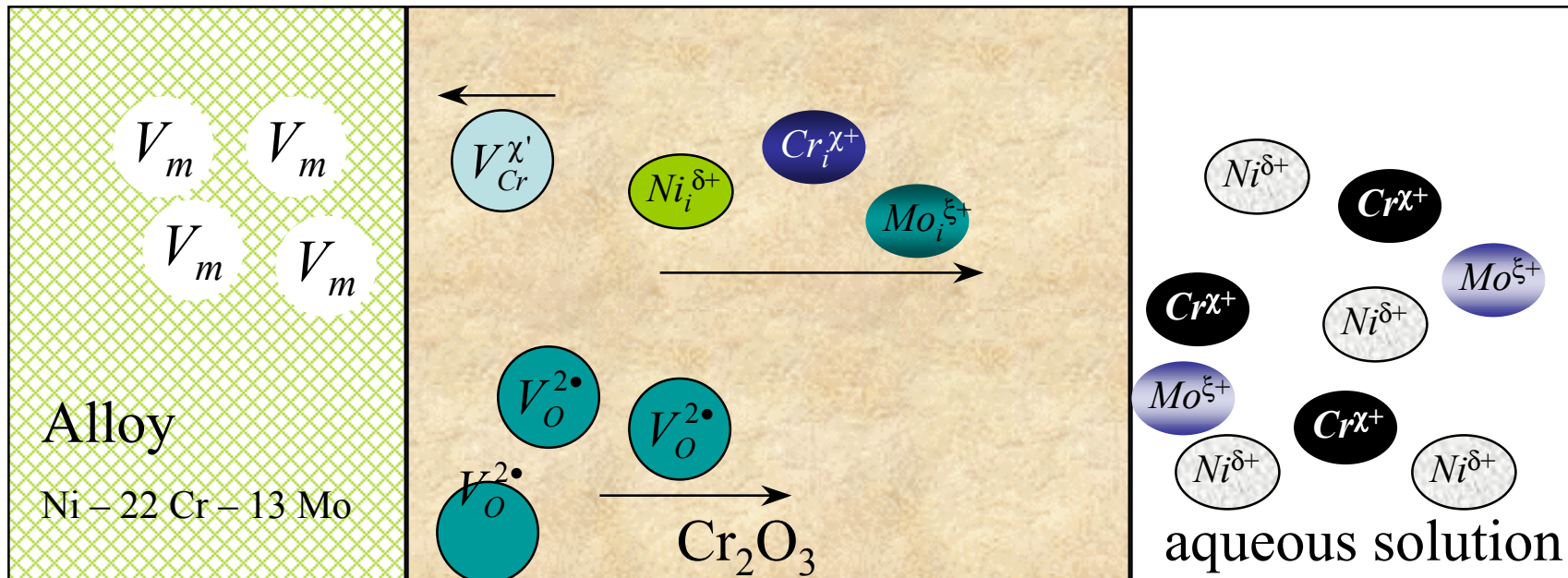
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## **OBJECTIVES**

- **Improve confidence in the long-term projection of potential waste package (WP) lifetime**
- **Evaluate how existing and new models for the initiation of the non-passive corrosion behavior of potential WP materials in the long-term regulatory compliance period**
  - (1) uniform passivity breakdown:**
    - **void formation leading to mechanical spallation of passive film**
    - **accelerated anodic dissolution – ion selectivity through the corrosion products to alter the aqueous chemistry, development of large surface area cathodic corrosion products, anodic sulfur segregation**
  - (2) localized corrosion: long-term behavior of critical electrochemical potential, critical chemistry**
  - (3) stress corrosion cracking (SCC): long-term behavior of critical stress (or stress intensity factor), critical chemistry, critical electrochemical potential**

## UNIFORM PASSIVITY BREAKDOWN – VOID FORMATION (Pensado et al., 2002)



- Cation interstitials were identified as charge carriers and the interstitials during the alloy dissolution causes the creation of vacancies in the alloy.
- The vacancy injection implies the oxide film could become unstable over an extended period.
- Periodic spalling of the film may lead to the evolution of the surface into rough morphology, resulting in the increase of the effective uniform corrosion rate.
- The increase most likely within the uncertainty range of the values in performance assessment.

## **UNIFORM PASSIVITY BREAKDOWN – *ANION SELECTIVE SORPTION***

- **In the crevice of limited aqueous volume, chlorides, nitrates, sulfates, carbonates, fluorides, or silicates may be sorbed selectively on the accumulated corrosion products in the very long-term period of time. The resulting altered chemistry may lead to localized corrosion or more benign conditions.**
- **On hydrous ferric oxide,  $10^{-5}$ M sulfates showed sorption greater than 20 % at pH lower than 6 at ambient temperature (Dzombak and Morel, 1990)**
- **Anion-selective action with the iron rust membrane stabilized pitting 304L stainless steel (Suleiman et al., 1994)**
- **National Institute for Materials Science in Japan observed this phenomenon in the atmospheric corrosion of steels.**
- **In U. S., the Long Term Corrosion Test Facility (LTCTF) in various simulated solutions for about five years, no indication of long-term localized corrosion in the crevice were observed at up to 90 °C (194 °F).**

## **UNIFORM PASSIVITY BREAKDOWN – *ANODIC SULFUR SEGREGATION***

- **Observations:** It would take approximately 180 years to form a mono-layer of sulfur at the metal-oxide interface in nickel-based alloys containing 100 appm sulfur, assuming a uniform corrosion rate of  $10^{-2}$   $\mu\text{m}/\text{year}$  [ $3.9 \times 10^{-7}$  inch/year] (Jones, 2002).
- **Postulates:** A protective oxide film should eventually form after the sporadic occurrence of enhanced transient non-passive corrosion rates (Pensado, 2002)– with soluble molybdenum-sulfur compounds (Marcus, 1995) and repassivation with chromium oxide.
- **This will lead to the cyclic behavior of the transient non-passive corrosion and following slow corrosion from repassivation.**

## UNIFORM PASSIVITY BREAKDOWN – *ANODIC SULFUR SEGREGATION*

Penetration Depth (Amount Corroded) =

$$" [CR_p * Ct_p + CR_f * Ct_f]$$

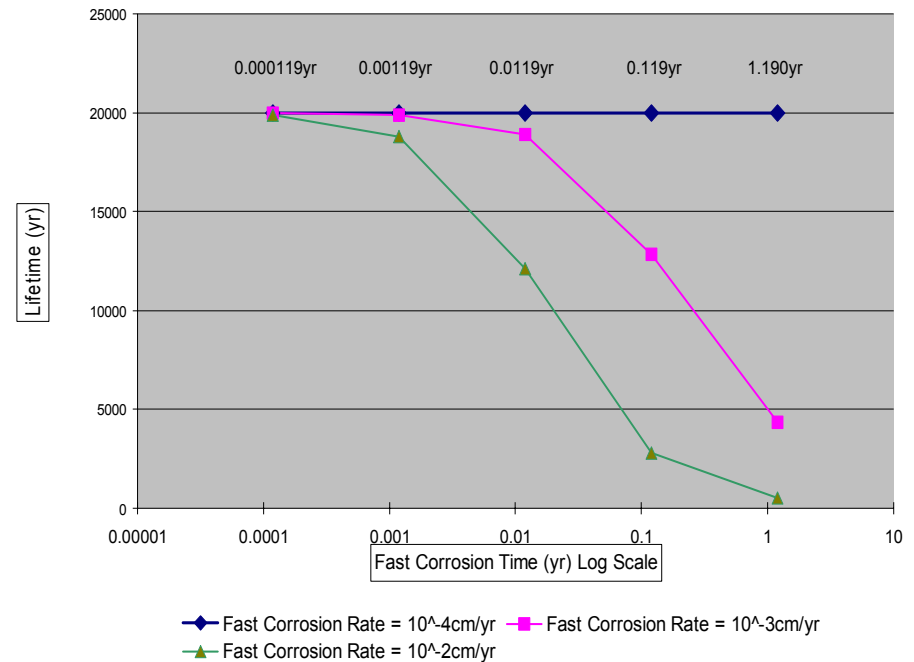
$CR_p$  : slow corrosion rate,  $10^{-4}$  cm/yr (from passive current density of Alloy 22)

$Ct_p$  : time period of slow corrosion, 1.8 yrs (sulfur segregation time)

$CR_f$  : fast corrosion rate,  $\sim 1.04 \times 10^{-4}$  cm/yr [ $4.09 \times 10^{-5}$  inch/yr] (from current transient)

$Ct_f$  : time period of fast corrosion, 0.0119 yr (from current transient)

Fast Corrosion Time vs Lifetime for 3 Different Fast Corrosion Rates



**Potential Waste Package Lifetime Involving Cyclic Processes of Slow and Fast Corrosion from Sulfur Segregation**

**UNIFORM PASSIVITY BREAKDOWN –  
*LARGE CATHODIC SURFACE AREA OF SEMICONDUCTING  
CORROSION PRODUCTS***

- **Further Acceleration of Penetration Depth**

**by Increased Fast Current Transient during Passive Film Spallation  
Associated with Void Formation and Anodic Sulfur Segregation**

**in the Presence of Large Cathodic Surface Area of Semiconducting  
Corrosion Products**

- **Ni-Cr-Mo alloys: while the inner compact passive layer is  
semiconducting and its thickness is kept constant, the accumulating  
outer porous hydroxides are insulators.**

## LOCALIZED CORROSION – *INDUCTION TIME*

- $$t_{ind} = \frac{\epsilon}{\zeta} \left[ \exp\left\{ \frac{\chi F \alpha \Delta V}{2 R T} \right\} - 1 \right]^{-1}$$

$\Delta V$ : applied potential minus the critical potential  
(i.e., pitting potential or breakdown potential)

$\chi$ : charge on a cation

F: Faraday constant

R: gas constant

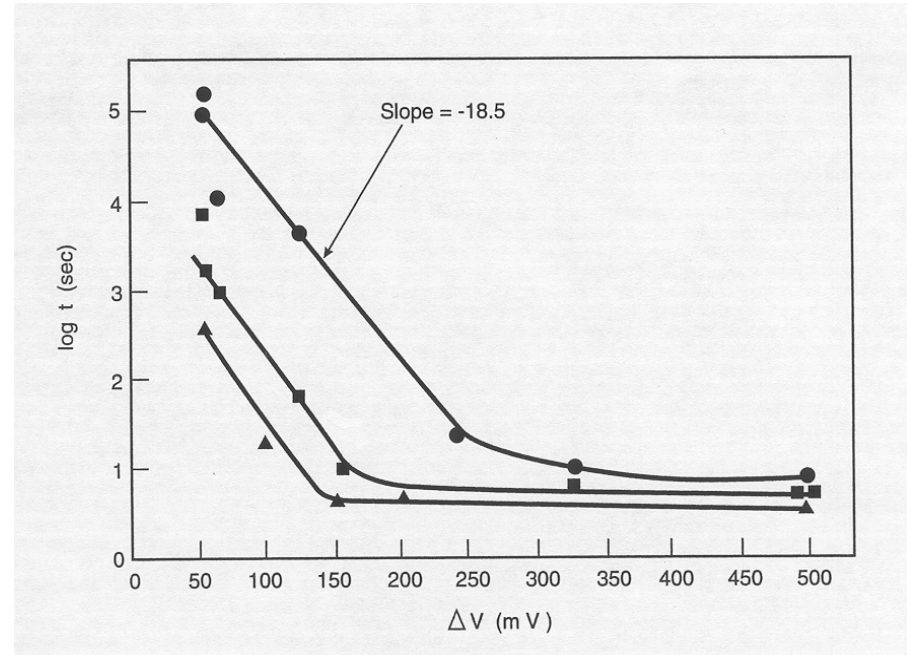
T: temperature

$\zeta$ : transient aqueous diffusion time

$\alpha$ : a constant relating the potential drop at the film/solution interface and applied potential, and

$\epsilon$ : a function of chloride activity, critical potential, diffusivity of cation vacancy, and a critical amount of metal holes.

(Lin et al., 1981; Urquidi-Macdonald and Macdonald, 1987)



### Induction Time vs. $\Delta V$

Data for Pitting of Passive Iron in Borate Buffer Solution at 25 °C (77 °F)

Triangle: pH 7.3 0.1M NaCl, Rectangle: pH 7.3 0.01M NaCl, Circle: pH 8.3 0.01M NaCl  
(Lin et al., 1981)



**LOCALIZED CORROSION –  
*DISTRIBUTION,*  
*REPASSIVATION POTENTIAL***

- **Distribution:**

**with respect to Critical Potential and Averaged Induction Time from Inhomogeneities of Alloys (Lin et al., 1981; Urquidi-Macdonald and Macdonald, 1987)**

- **Increasing the distributed induction time from the averaged induction time of 100s seconds to ~ 1 year, the frequency decreased drastically**
- **Stifling could occur under free open-circuit conditions**

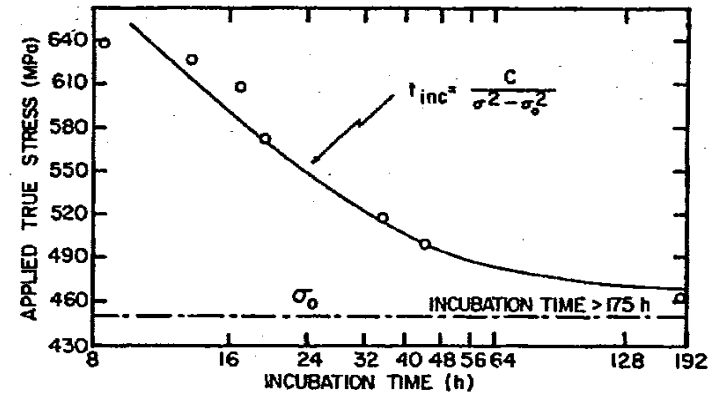
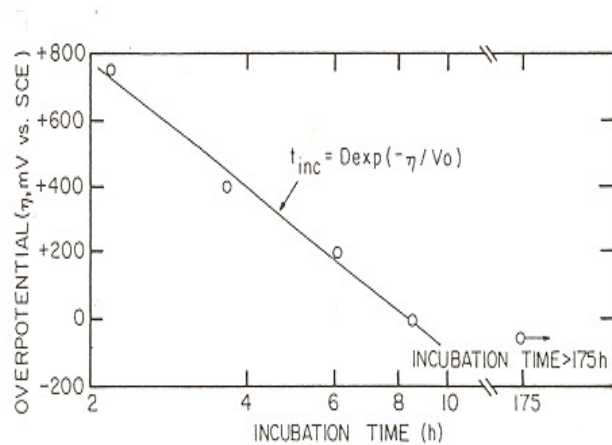
- **Repassivation Potential: behavior similarly in induction time (Dunn et al., 1996). It involves nucleation process (e.g., oxide reformation, Okada, 1984) for the behavior.**

**LOCALIZED CORROSION –  
*CRITICAL CHEMISTRY,  
EXTERNAL TEMPERATURE***

- **Times to Reach the Critical Chemistry**
  - **Constant potentials and pH arrive as a function of position from the crevice mouth and laboratory test times.**  
**(Combrade, 2001; Shinohara et al., 1997; Walton et al., 1996)**
  
- **External Temperature in the U.S. System**
  - **(170 - 280) °C (338-536 °F) during the early 100 years**
  - **(130 - 170) °C (266-338 °F) for 100s years**
  - **60 °C (140 °F) in 10,000 years**
  
  - **drift collapse considered (Manepally et al., 2003)**

# STRESS CORROSION CRACKING (SCC) – *INDUCTION TIME*

**Effects of Applied Stress and Applied Potential on Induction (Incubation) Time in SCC of Alpha Brass in Ammoniacal Solution (Buck and Ranjan, 1986)**



$V_0$  and  $\sigma_0$ : constants

$C$ : a function of stress intensity factor and applied potential

$D$ : a function of stress intensity factor and applied stress

- Applied Stress: residual stress and rockfall stress

## CONCLUSIONS

- - The vacancy injection during the passive dissolution of alloys may not destabilize significantly the passive film in Ni-Cr-Mo alloys .
  - Long-term corrosion tests in the U.S. system for more than 5 years at 90 °C (194 °F) did not show any indication of the localized corrosion because of the chemistry alteration with the accumulated corrosion products.
  - All conditions decreasing the potential waste package lifetime from the sulfur segregation are likely to be severe and unrealistically aggressive.
  - The accumulation of large surface area corrosion products may not accelerate the transient anodic dissolution in Ni-Cr-Mo alloys, because the accumulated porous oxides are likely to be insulators.
- - Mass transport models for localized corrosion suggest that the steady state chemistry arrives rapidly in the occluded area.
  - The initiation times for localized corrosion and SCC are approaching very long times near the critical potential or stress.
  - These suggest that the measured critical potential or stress in the laboratory time scale may be sufficiently close to the real long-term value in a given external environmental condition.
- Better confidence may be obtained as to the long-term stability of passive film in Ni-Cr-Mo alloys in the U.S. system. Supporting studies of this hypothesis are conducted for void formation, anion sorption in corrosion products, anodic sulfur segregation, and large surface area corrosion products. Although more theoretical investigation is needed, it is suggested that non-passive corrosion data measured in the laboratory are sufficient in projecting them in the long-term periods of time.

- **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.**

# REFERENCES

- O. Buck and R. Ranjan, Evaluation of a Crack-Tip-Opening Displacement Model under Stress-Corrosion Conditions, in Proceedings of a Symposium on Modeling Environmental Effects on Crack Growth Processes edited by R. Jones and W. Gerberich, The Metallurgical Society of AIME, P. 209, 1986
- P. Combrade, The Crevice Corrosion of Metallic Materials, MC TC R 01-1190, FRAMATOME ANP, 2001, Chapter 11 in *Corrosion Mechanisms in Theory and Practice*, second edition, edited by Ph. Marcus, Marcel Dekker, Inc., NY, 2002, p. 349
- D. A. Dzombak and F. M. M. Morel, Surface Complexation Modeling - Hydrous Ferric Oxide, John Wiley & Sons, New York, 1990
- D. S. Dunn, G. A. Cragolino and N. Sridhar, Long-Term Prediction of Localized Corrosion of Alloy 825 in High-Level Nuclear Waste Repository Environments, *Corrosion*, Vol. 52, p.115, 1996
- R. Jones, Metallurgical Stability and Radiation Effects, Peer Panel on Waste Package Performance, presented to U.S. Department of Energy and Bechtel SAIC Company, Las Vegas, Nevada, 2002
- L. F. Lin, C. Y. Chao and D. D. Macdonald, A Point Defect Model for Anodic Passive Films, II. Chemical Breakdown and Pit Initiation, *J. Electrochemical Society*, Vol.128, p. 1194, 1981
- C. Manepally, R. Fedors, G. Adams, and S. Green, "Effects of Drift Degradation on Environmental Conditions in Drifts," *Eos Transactions*, Vol. 84(46), Fall Meeting Supplement, Abstract H21D-0836, American Geophysical Union 2003 Fall Meeting, San Francisco, CA, December 8–12, 2003
- P. Marcus, Sulfur-Assisted Corrosion Mechanisms and the Role of Alloyed Elements, *Corrosion Mechanisms in Theory and Practice*, P. Marcus and I. Olefjord, edited, New York City, New York: Marcel Dekker, p. 239, 1995
- T. Okada, Halide Nuclei Theory of Pit Initiation in Passive Metals, *J. Electrochemical Society*, Vol. 131, p. 241 - 247, 1984
- O. Pensado, D. S. Dunn, G. A. Cragolino, and V. Jain, Passive Dissolution of Container Materials - Modeling and Experiments, CNWRA 2003-01, Center for Nuclear Waste Regulatory Analyses, San Antonio, Texas, 2002
- T. Shinohara, S. Fujimoto, N. J. Laycock, A. Msallem, H. Ezuber and R. C. Newman, Numerical and Experimental Simulation of Iron Dissolution in a Crevice with a Very Dilute Bulk Solution, *J. Electrochemical Soc.*, Vol. 144, p. 3791 - 3796, 1997
- M. I. Suleiman, I. Ragault and R. C. Newman, The Pitting of Stainless Steel under a Rust Membrane at Very Low Potentials, *Corrosion Science*, Vol. 36, p. 479 - 486, 1994
- M. Urquidi-Macdonald and D. D. Macdonald, Theoretical Distribution Functions for the Breakdown of Passive Films, *J. Electrochemical Society*, Vol. 134, P. 41, 1987
- J. C. Walton, G. Cragolino and S. K. Kalandros, A Numerical Model of Crevice Corrosion for Passive and Active Metals, *Corrosion Science*, Vol. 38, p. 1-18, 1996