Corrosion Performance of Alloy 22 and Ti-7 in the Yucca Mountain Environment

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U.S. NRC

- **The U.S. Nuclear Regulatory Commission (NRC) is an independent agency established by the Energy Reorganization Act of 1974 to regulate civilian use of nuclear materials.**

- **The NRC's mission is to regulate the Nation's civilian use of byproduct, source, and special nuclear materials to ensure adequate protection of public health and safety, to promote the common defense and security, and to protect the environment.**

- **The NRC's regulatory mission covers three main areas:**

  (1) Reactors

  (2) Materials

  (3) Waste

OUTLINE

SCOPE

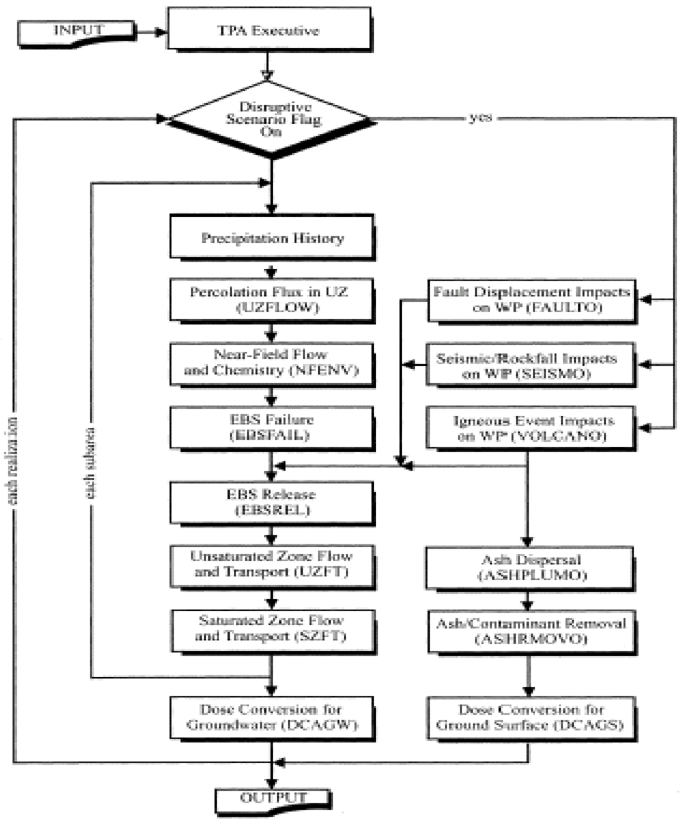
- Knowledge of Current Data
- Long-term Confidence – modeling and analogue studies
- Risk Significance

TOPICS

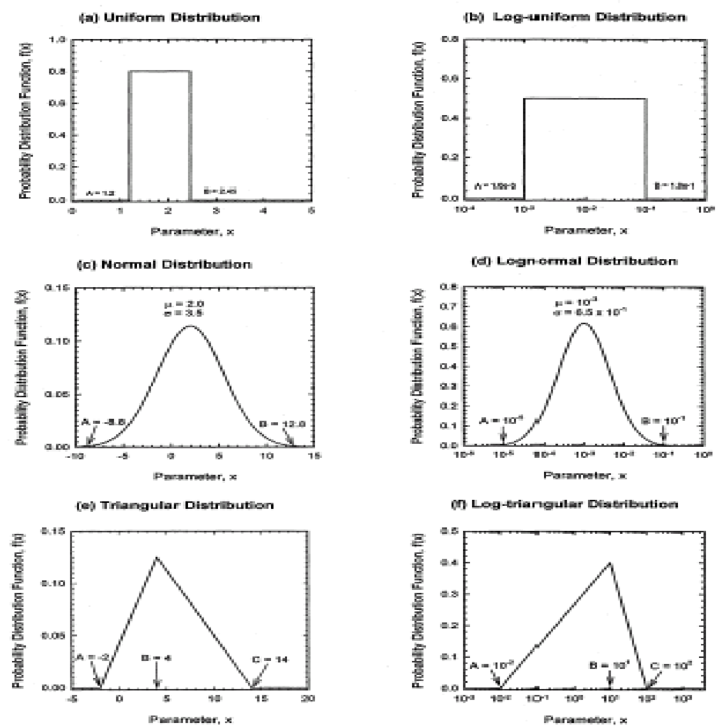
- Uniform Corrosion
- Localized Corrosion
- Stress Corrosion Cracking
- Ti-7 Corrosion
- Uncertainties

Risk Assessment

(1) What can go wrong? (2) how likely is it? (3) what are the consequences?

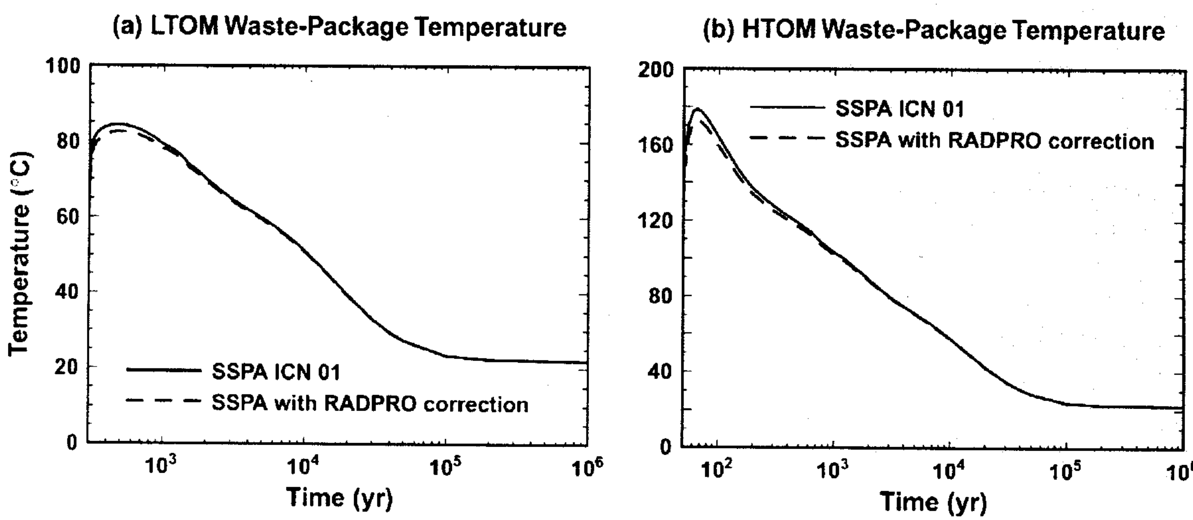


Flow Diagram for TPA Version 4.0 Code (Mohanty et al., 2002)



Examples of various distribution functions for random pick ups. Parameters include critical relative humidity for aqueous corrosion, chloride concentration, repassivation potential, parameters for determining corrosion potentials, passive current density, and etc. (Mohanty et al., 2002)

Environmental Conditions



Temperature calculated by the MSTHM for a design-basis 21-PWR commercial spent nuclear fuel waste package, for the supplemental TSPA model and after corrosion of RADPRO-calculated thermal radiation coefficient in NUFT LDTH submodels (MIS-MGR-RL-000001 REV 00, 2001).

Principal test environments for general and localized corrosion measurements

(Data from J.C. Farmer, "General and Localized Corrosion of Waste Package & Drip Shield Materials", presentation to Waste Package Materials Performance Peer Review Panel, February 28, 2002 and from LLNL Scientific Notebooks)

	*Long Term Corrosion Test Facility (LTCTF) Large tank environments			Other corrosion test bulk environments			Thermo-gravimetric Analyses
	Concentration (mg/L)						Water films
Ion	Simulated Dilute Water (SDW)*	Simulated Concentrated Water (SCW)*	Simulated Acidified Water (SAW)*	Basic Saturated Water (BSW)	Simulated Saturated Water (SSW)	Pure $CaCl_2$ (with and without nitrate)	Pure *$CaCl_2$ (with and without nitrate)
K	34	3,400	3,400	81,480	141,600		
Na	409	40,900	40,900	231,224	487,000		
Mg	1	<1	1,000	---	---		
Ca	0.5	<1	1,000	---	---	1M - 9M	~220,000
F	14	1,400	0	1,616	---		
Cl	67	6,700	24,250	169,204	128,000	2M -18M	~390,000
NO_3	64	6,400	23,000	177,168	1,313,000	0 - 2M	variable
SO_4	167	16,700	38,600	16,907	---		
HCO_3	947	70,000	0	107,171	---		
Si	27 (60°C); 49 (90°C)	27 (60°C); 49 (90°C)	27 (60°C); 49 (90°C)	9,038	---		
Molar Ratio Cl/NO_3+SO_4	0.7	0.7	0.9	1.6	0.2	1- ∞	1- ∞
pH	10.1	10.3	2.8	>12	6.7	5.8-6.4	
Temp. °C	25-90	25-90	25-105	25-105	25-120	30-150	≤ 150°C

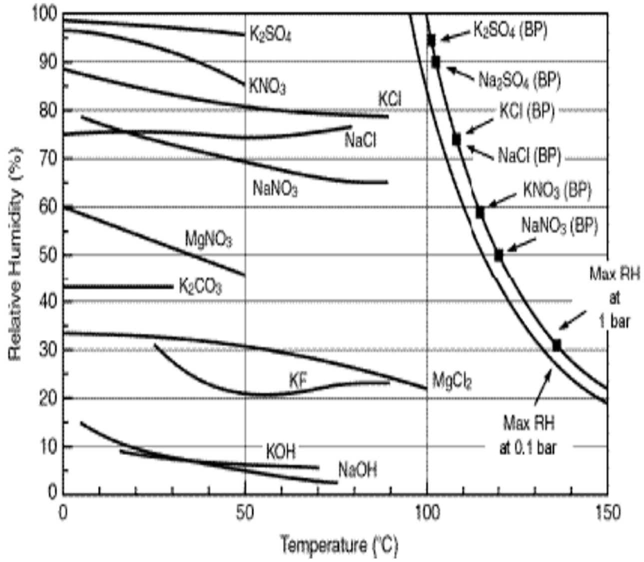
*Thin surface films

Environments evaluated cover range of relevant and accelerated concentrated brines, pH's, Cl^-/NO_3^- ratios and temperatures

YUCCA MOUNTAIN PROJECT

(Gordon, 2003)

Environmental Conditions



Handbook data on equilibrium relative humidity as a function of temperature for saturated solutions of some pure salts. Each curve probably terminates at the boiling curves to the right, but there are gaps in the available handbook data at intermediate temperature. Figure modified from DOE (2000).

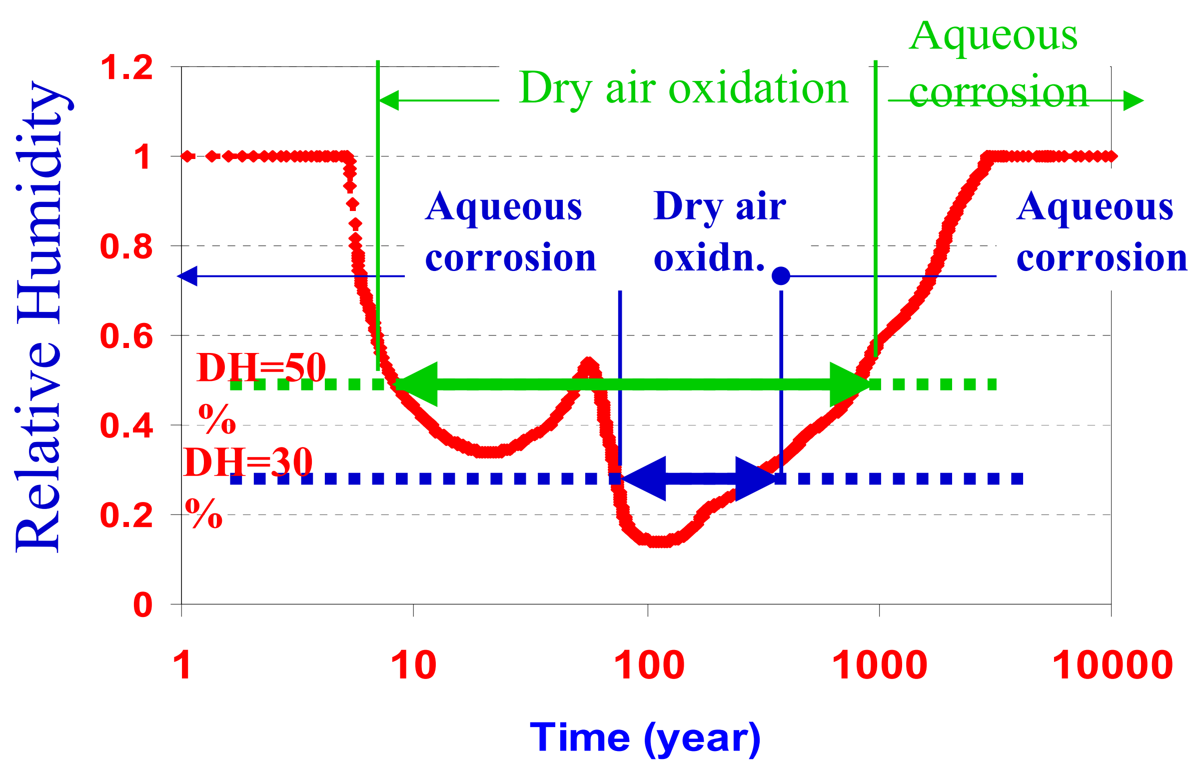
Deliquescent point for salts and salt mixtures at 16.5 °C

Salts	Deliquescence Point (Percent)
NaCl	76*
$NaNO_3$	78*
KNO_3	95
Mixture of above three (with composition corresponding to a saturated solution of the three salts)	30.5†

*Civilian Radioactive Waste Management System Management and Operating Contractor. *Environment on the Surfaces of the Drip Shield and Waste Package Outer Barrier.* ANL–EBS–MD–000001, ICN 01. Revision 00. Las Vegas, NV: Office of Civilian Radioactive Waste Management System Management and Operating Contractor. 2000.

†Weast, R.C., and Astle, M.J., eds. *CRC Handbook of Chemistry and Physics: A Ready Reference Book of Chemical and Physical Data.* 62nd Edition. Boca Raton, FL: CRC Press. 1981.

Environmental Conditions



Deliquescence Humidity and Aqueous or Dry Air Corrosion (Yang, 2001)

Candidate Alloys

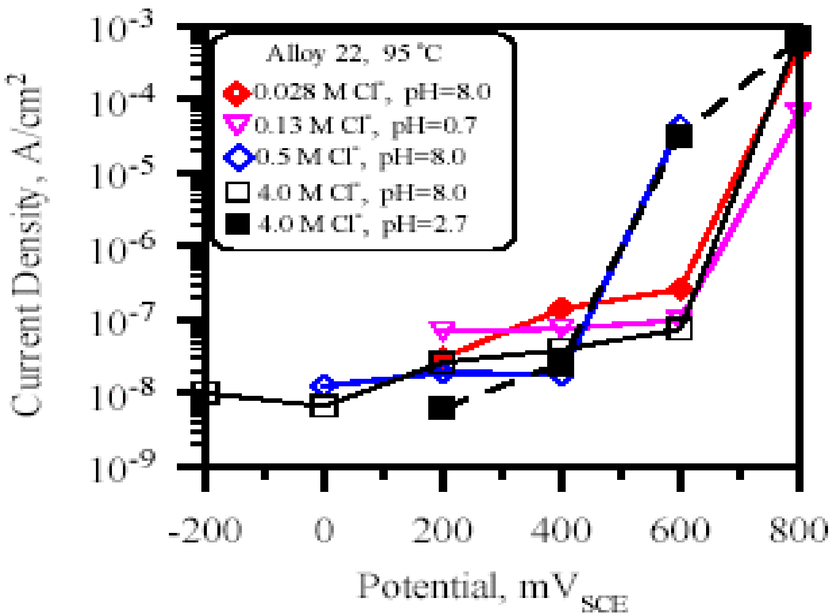
Alloy 22

- Nickel-based Alloy, Chemical Composition (wt %):Fe (3.80), Cr (21.4), Ni(57.8), Mo(13.6), Mn(0.12), Si(0.03), S(0.002), C(0.004), W(3.0), and V(0.15)
- Highly resistant to uniform corrosion, localized corrosion and stress corrosion cracking for a variety of industrial applications
- Excellent phase stability

Ti - 7

- Titanium-based Alloy, Chemical Composition (wt %): Ti (balance), Pd (0.155), C (0.009), N (0.007), Fe (0.115), O (0.140), and H (0.005)
- Alpha Titanium Alloy – similar mechanical properties to commercially pure titanium, but exhibit considerably better corrosion resistance
- Pd was added to improve the resistance to hydride embrittlement and corrosion

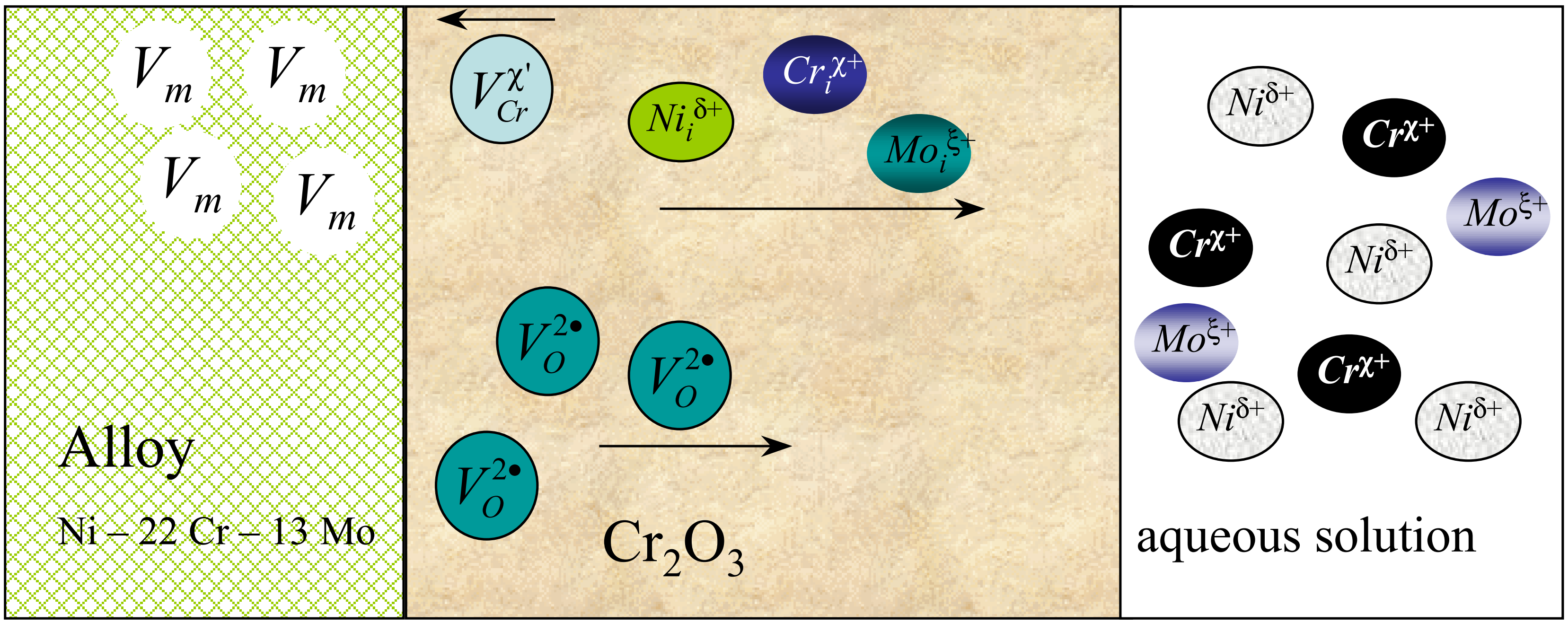
Uniform Corrosion



Uniform corrosion of Alloy 22 (Cragnolino et al., 2003)
[conversion: 10^{-6} A/cm^2 (9.29×10^{-4} A/ft^2), 10^{-4}mm/yr (3.28×10^{-7} ft/yr)]

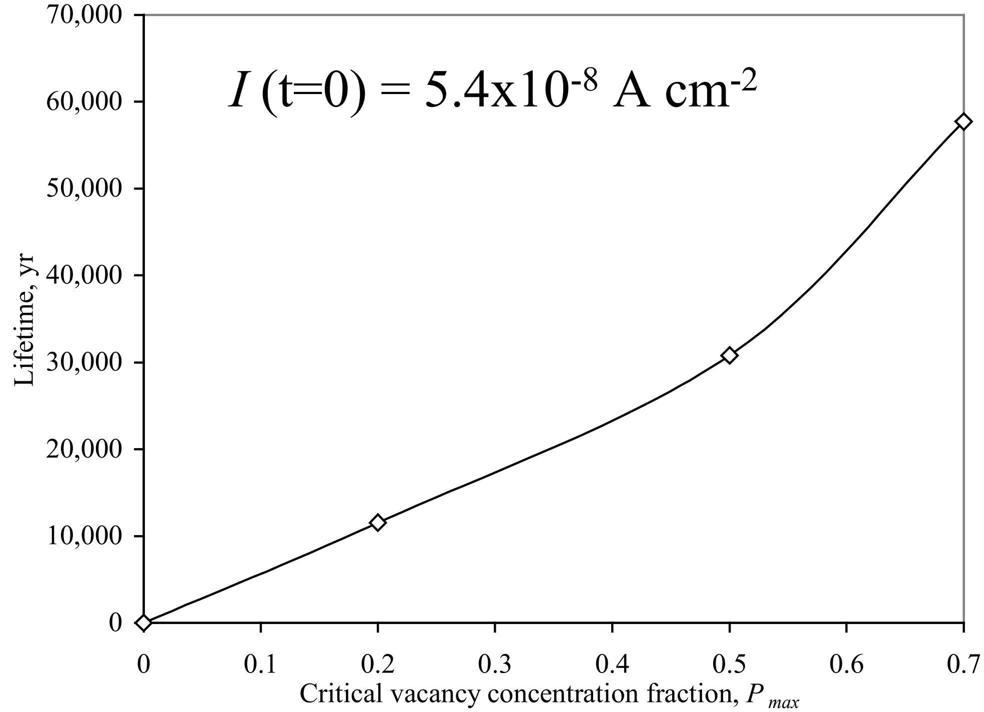
Uniform Corrosion

Point Defect Model (Pensado, 2002)



$$I_{22} \approx F\left[\chi\, a_{Cr}\left(k_1^{Cr} + k_3^{Cr}\right) + \delta\, a_{Ni}\left(k_1^{Ni} + k_3^{Ni}\right) + \xi\, a_{Mo}\, k_1^{Mo}\right]$$

Uniform Corrosion



Life time of Alloy 22 plate versus the critical vacancy fraction (Pensado, 2001)

Uniform Corrosion

- Data from DOE, CNWRA, industries and international community (e.g., long-term German tests in rocksalts) point out similarities of uniform corrosion rates. A container lifetime of greater than 10,000 years can be estimated.

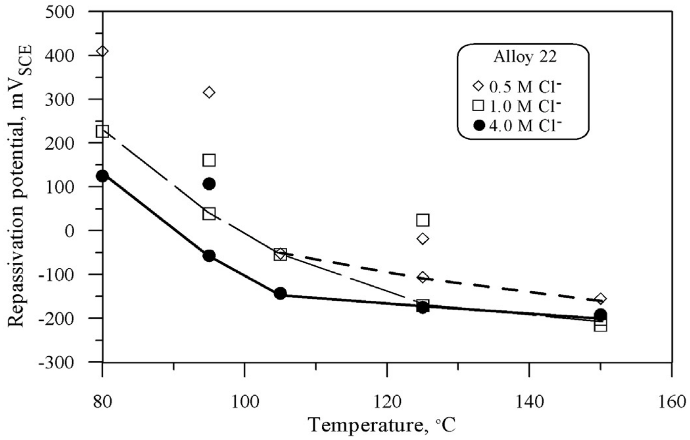
- A point defect model (Pensado, 2002) of passivity suggests a long-term integrity of passive film.

- Analogue studies suggests that modern electrochemical theories for corrosion may explain the analogue observation: void formation, stoichiometric dissolution of meteorites and josephinite, possible passivity of Indian Pillar, and long-term passivity of carbon and stainless steel over half a century (Sridhar and Cragnolino, 2002).

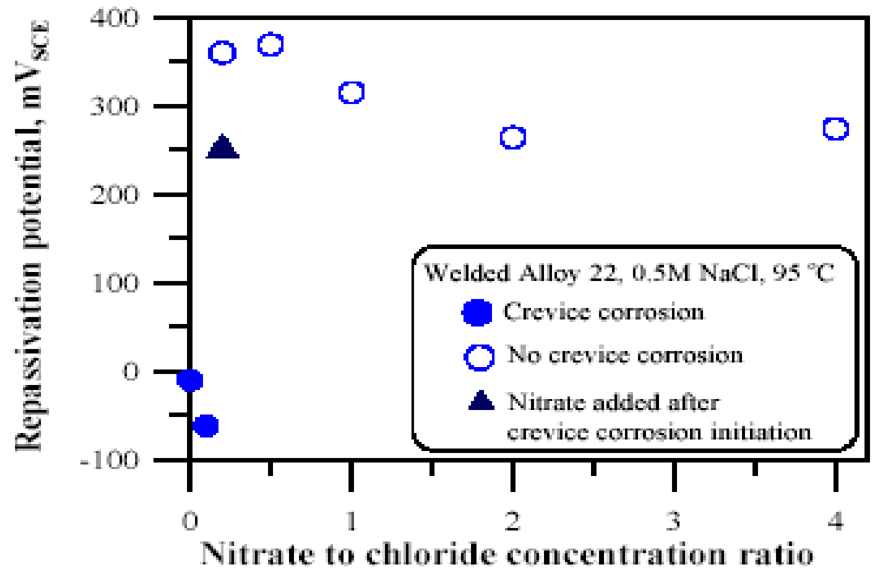
- Need to understand the likelihood and risk significance of the extreme acidic/ halide effects at elevated temperatures (Cragnolino, 2003, Shettel et al., 2003, Walton, 2003 and Pulvirenti et al., 2002)

- Need to understand anodic sulphur segregation and long-tern development of surface roughness

Localized Corrosion

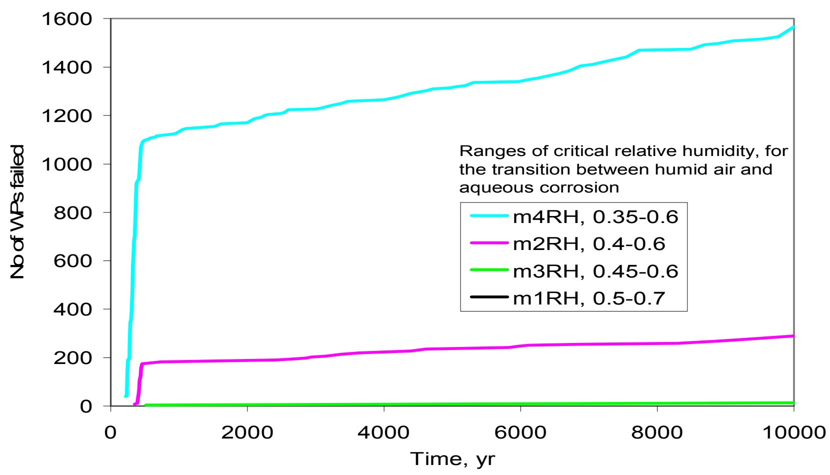


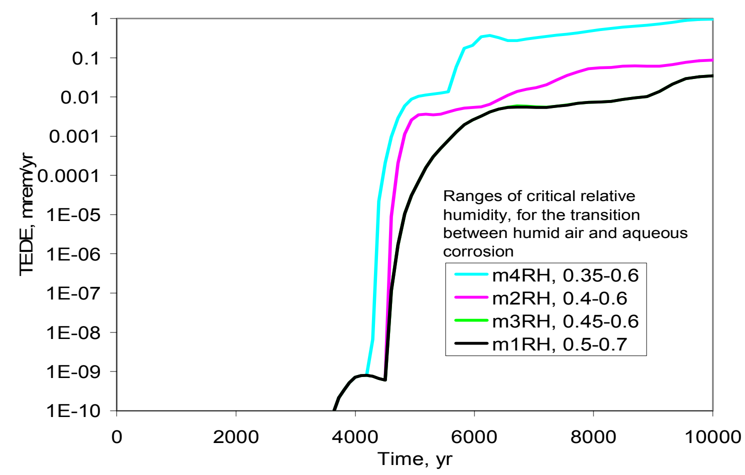
Effect of temperature on the repassivation potential crevice corrosion of Alloy 22 in Cl^- solutions (Brossia et al., 2001)



(Dunn et al., 2003)

Localized Corrosion





Average number of waste packages failed as a function of time for various selection of $(RH)_c$ distribution functions for the onset of aqueous corrosion (Rivera-Feliciano et al., 2002)

Mean annual TEDE as a function of time for various selection of $(RH)_c$ distribution functions for the onset of aqueous corrosion (Rivera-Feliciano et al., 2002)

Localized Corrosion

- German Data of Alloy C 4 in Rock Salt Brine up to 200 C (Smailos, 2003, 1999, 1995, 1992, 1990)

  (1) In NaCl rich brine (25.9NaCl-10.16$MgSO_4$-0. 21$CaSO_4$-0.23K_2SO_4, pH from 6.7 to 7), no pitting/crevice corrosion/ stress corrosion cracking (SCC) to 200 C for about 3 years
  (2) In Q brine containing $MgCl_2$ and $CaCl_2$ (pH= ~4), no pitting/crevice corrosion at 170 C up to 400 days
  (3) After 3 years in Q brine at 90, 170 and 200C, no pitting/SCC but crevice corrosion at 90 and 170, pitting/crevice corrosion at 200 C

- Interpretation of analogue studies: high concentrations of chloride in the solution trapped within pits and crevices of meteorites (Sridhar and Cragnolino, 2002)

- Examining the risk significance of restricted radionuclide releases through corrosion pits: typically the pit size is in the order of micrometer to mm and the pit density is approximately (0.1 to 100)/cm^2 (9.29x10 to 9.29x10^4/ft^2) (Ahn, 1994, Isaacs, 1990, Szklarska-Smialowska, 1986). Sampling the fraction of surface area of spent fuel from 10^{-9} to 1 (log uniform distribution), the release was reduced significantly.

- Need to understand the likelihood and risk significance of the extreme acidic/halide effects (Shettel et al., 2003, Walton, 2003 and Pulvirenti et al., 2002)

- Need to understand the behavior of localized corrosion in relevant environments at temperatures above 100 C

Stress Corrosion Cracking (SCC)

Test conditions and results for the testing of Alloy 22 DCB specimens

Specimen ID (Orientation)	Test Solution and Temperature	Potential (mV_{SCE})	Duration (hr)	Results
22-1(T-L)	0.9 molal Cl^- (5% NaCl), pH 2.7 90 °C, N_2 deaerated	-330 to -310 (OC)	9,264 (386 days)	No SCC
22-2(T-L)	14.0 molal Cl^- (40% $MgCl_2$), 110°C	-280 to -260 (OC)	9,264 (386 days)	No SCC Grain Boundary Attack
22-7(S-L)	14.0 molal Cl^- (40% $MgCl_2$), 110°C	-270 to -250 (OC)	9,264 (386 days)	No SCC Secondary Cracking

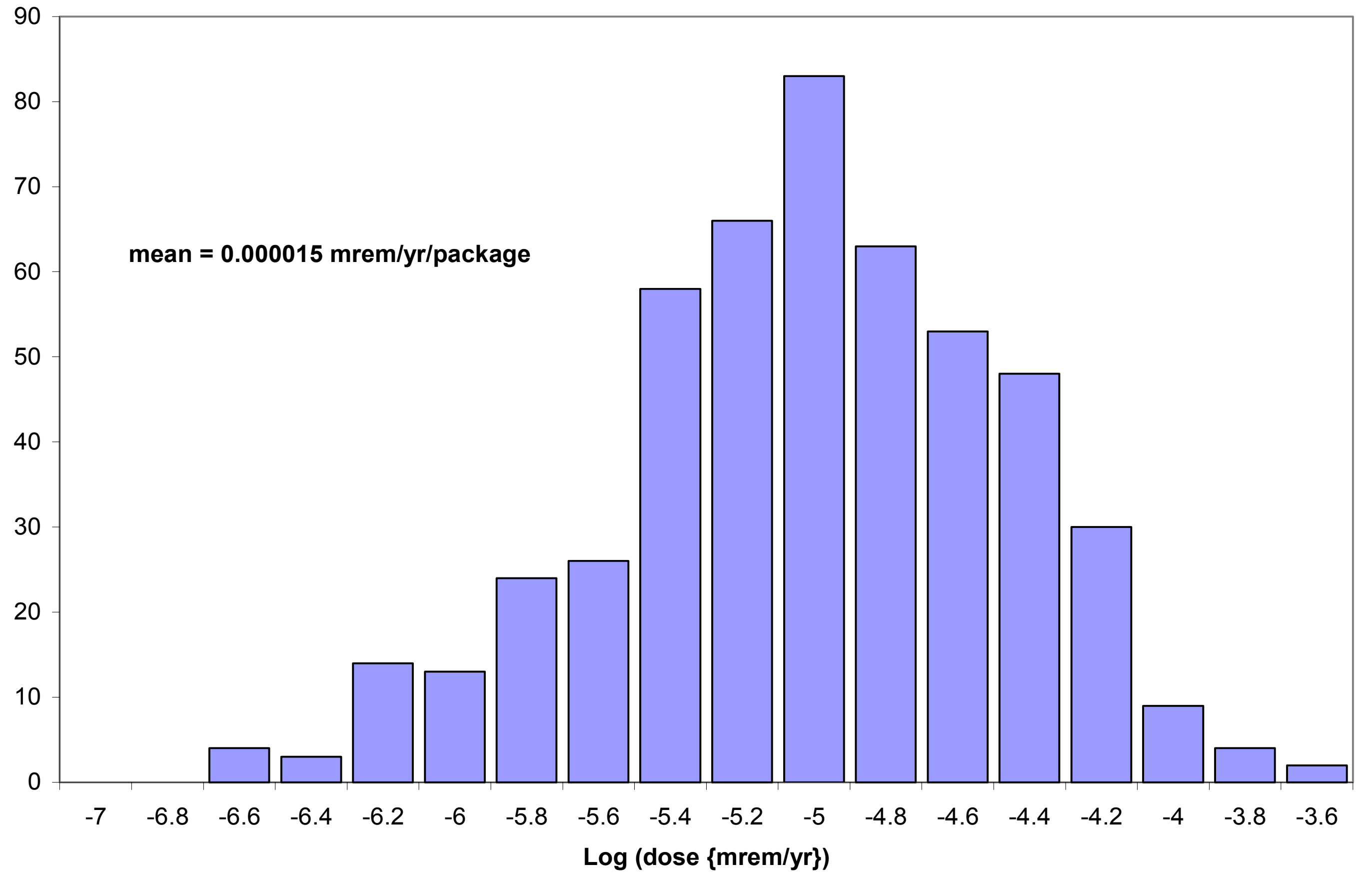
T-L – Transverse-Longitudinal; S-L – Short transverse-Longitudinal;
OC – Open-Circuit

- No crack growth was observed at $K_I = 32.7$ MPa·$m^{1/2}$ after 386 days, implying a detection limit of 3 x10^{-13} m/s
- It appears that $E_{corr} < E_{SCC}$ and/or $K_I < K_{Iscc}$

Conversion: 32.7 MPa $m^{1/2}$ (29.7 ksi $in^{1/2}$), 3x10^{-13}m/s (9.84x10^{-13} ft/s)

(Cragnolino, 2003)

Stress Corrosion Cracking (SCC)



GoldSim model for the release from SCC failed waste package (Esh, 2003)

Stress Corrosion Cracking (SCC)

- NRC confirmatory testing found no SCC in hot concentrated chloride solutions under controlled potentials and dynamic conditions. Lead impurity did not affect the SCC susceptibility (Cragnolino, 2003).

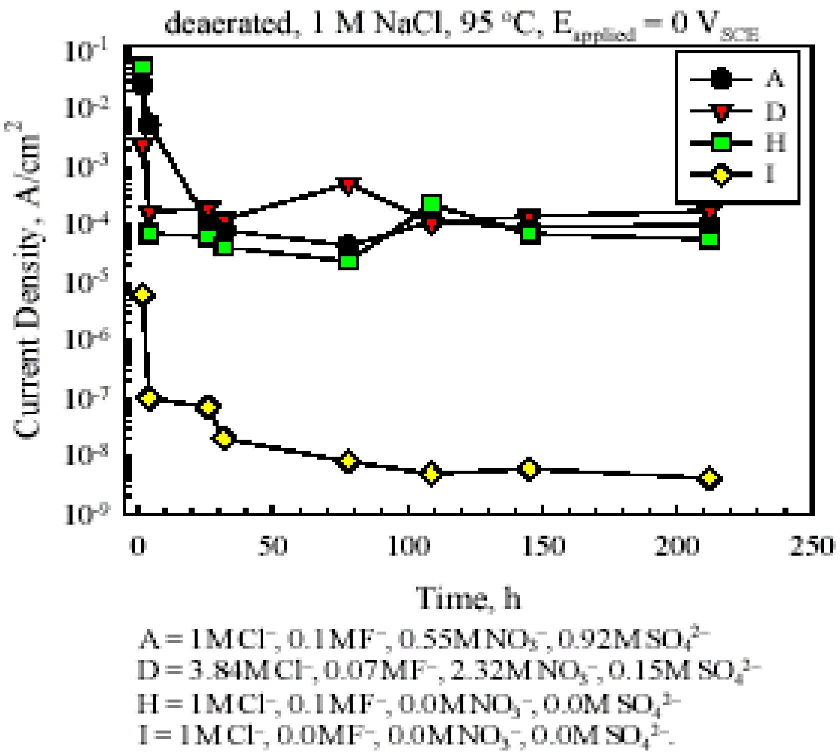
- Assuming SCC, radionuclide releases through cracks appear to be restricted significantly.

- Interpretation of analogue studies: high concentrations of chloride in the solution trapped within cracks of meteorites (Sridhar and Cragnolino, 2002)

- Understand the likelihood and risk significance of the extreme acidic/halide effects and high corrosion potentials (Cragnolino, 2003, Shettel et al., 2003, Walton, 2003 and Pulvirenti et al., 2002)

- Understand the DOE's mitigation process

Ti-7 Corrosion



Effects of groundwater anions on fluoride-induced corrosion of T-7 (Brossia et al., 2001)

- DOE uses weight loss measurements of titanium in fluoride concentrations
  - No fluoride, $[F^-] = 7.37 \times 10^{-4}$ M, and

  $[F^-] = 7.37 \times 10^{-2}$ M

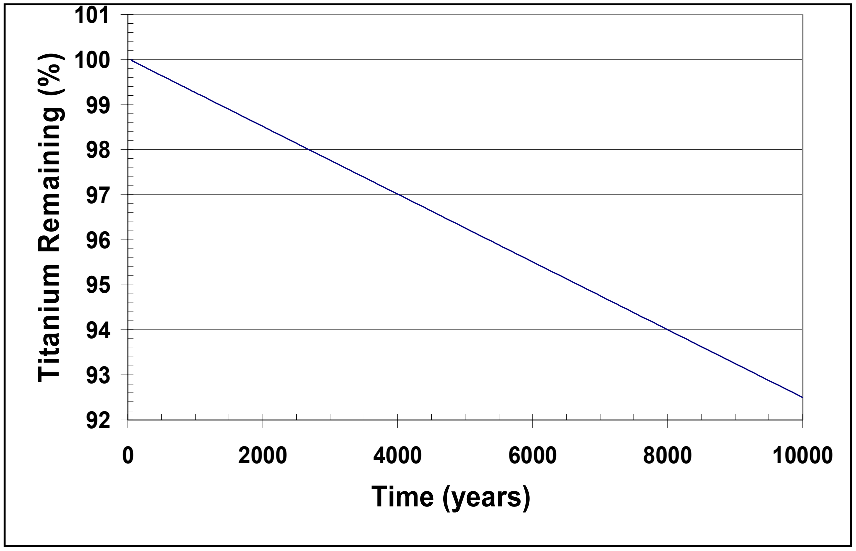
- General corrosion rate determined to be 3.25×10^{-4} mm/yr

- No enhanced corrosion by fluoride observed by DOE tests.

Ti-7 Corrosion

- **Most common products of titanium-fluoride reaction are TiF_6^{2-} and TiF_4**

- **Is there sufficient water for complete corrosion of drip shield?**



Cumulative reduction of drip shield titanium from corrosion by fluoride at average influx (Lin et al., 2003)

Ti-7 CORROSION

- Other factor considered: focused flow, water flow off, diffusion rate across water film, evaporation rate
- Average water influx appears to be too low to cause complete corrosion of drip shield.
- Evaporation may provide sufficient fluoride for corrosion but combination of required factors for complete corrosion appears to be unlikely.

- Need to understand the likelihood and risk significance of the extreme acidic/halide effects (Shettel et al., 2003, and Pulvirenti et al., 2002)
- Need to understand the potential of screening out the hydride embrittlement and SCC

SUMMARY

- **Based on the currently available uniform corrosion rates, a container life time of greater than 10,000 years can be estimated.**

- **The localized corrosion of Alloy 22 needs to be better understood with respect to temperature and nitrate-to chloride concentration ratio. Existing pits are considered to reduce the radionuclide release significantly.**

- **No SCC is expected in hot concentrated chloride solutions under controlled potentials and dynamic conditions. Assuming SCC, radionuclide releases through cracks appear to be restricted significantly.**

- **Average water influx appears to be too low to cause complete corrosion of drip shield.**

SUMMARY

- **To build long-term confidence, modeling and analogue studies are highlighted.**

- **Uncertainties associated with extreme environments and long-term passivity need to be clarified further**