Corrosion-Related Studies at CNWRA

by

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Presented at the

NWTRB Meeting

Washington, D.C.

May 9, 2001

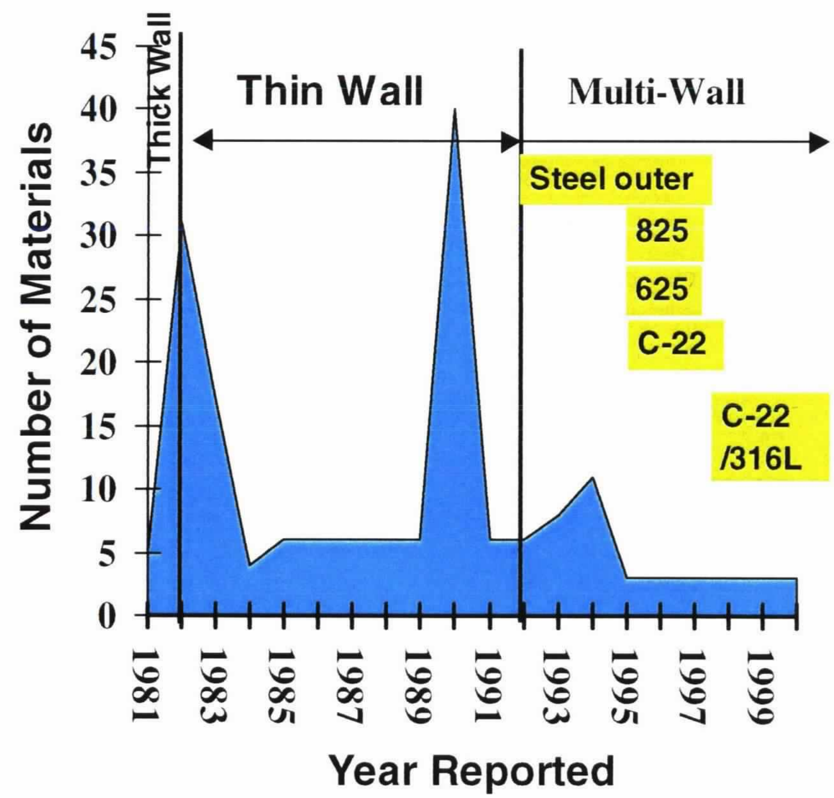
Acknowledgement

T.M. Ahn, C.S. Brossia, G.A. Cragnolino, D.S. Dunn, C. Greene, K.Gruss, V. Jain, O. Moghissi, Y.M. Pan, O. Pensado, and L.T. Yang

This presentation is an independent view of CNWRA and does not necessarily reflect the views or regulatory position of the NRC

Overall Approach

- Identify risk significance
- Provide input to performance assessment
- Increase confidence in models
- Assess the adequacy of DOE data/analyses by evaluating classes of materials



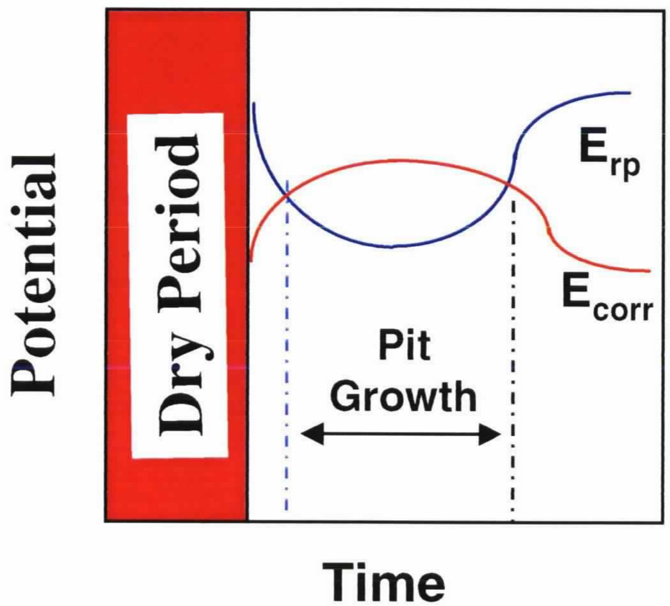
Corrosion-Related Experimental Program

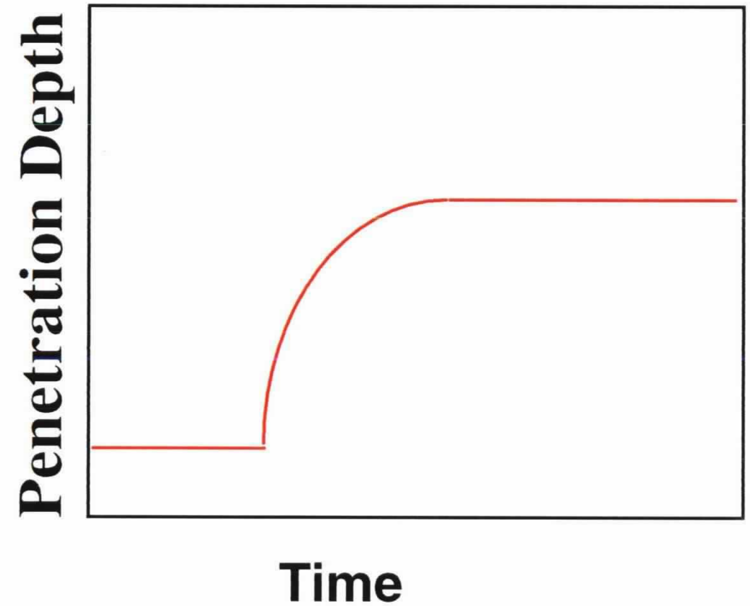
- Evolution of waste package environment
- Container studies
- Cladding studies
- Drip shield studies
- Performance confirmation tools

Near Field Environment

- Deliquescence humidity (DH) of salt mixtures is lower than that of pure salts
  - Confirmatory studies to understand the DH of salt mixtures formed from J-13 and other YM waters
- Simulation of evaporative concentration using OLI speciation software
- MULTIFLO simulation of temperature, RH, and chemistry at drift surface
- Presence of drip shield may influence the effect of deliquescence and chemistry of condensed water

Semi-Empirical Model



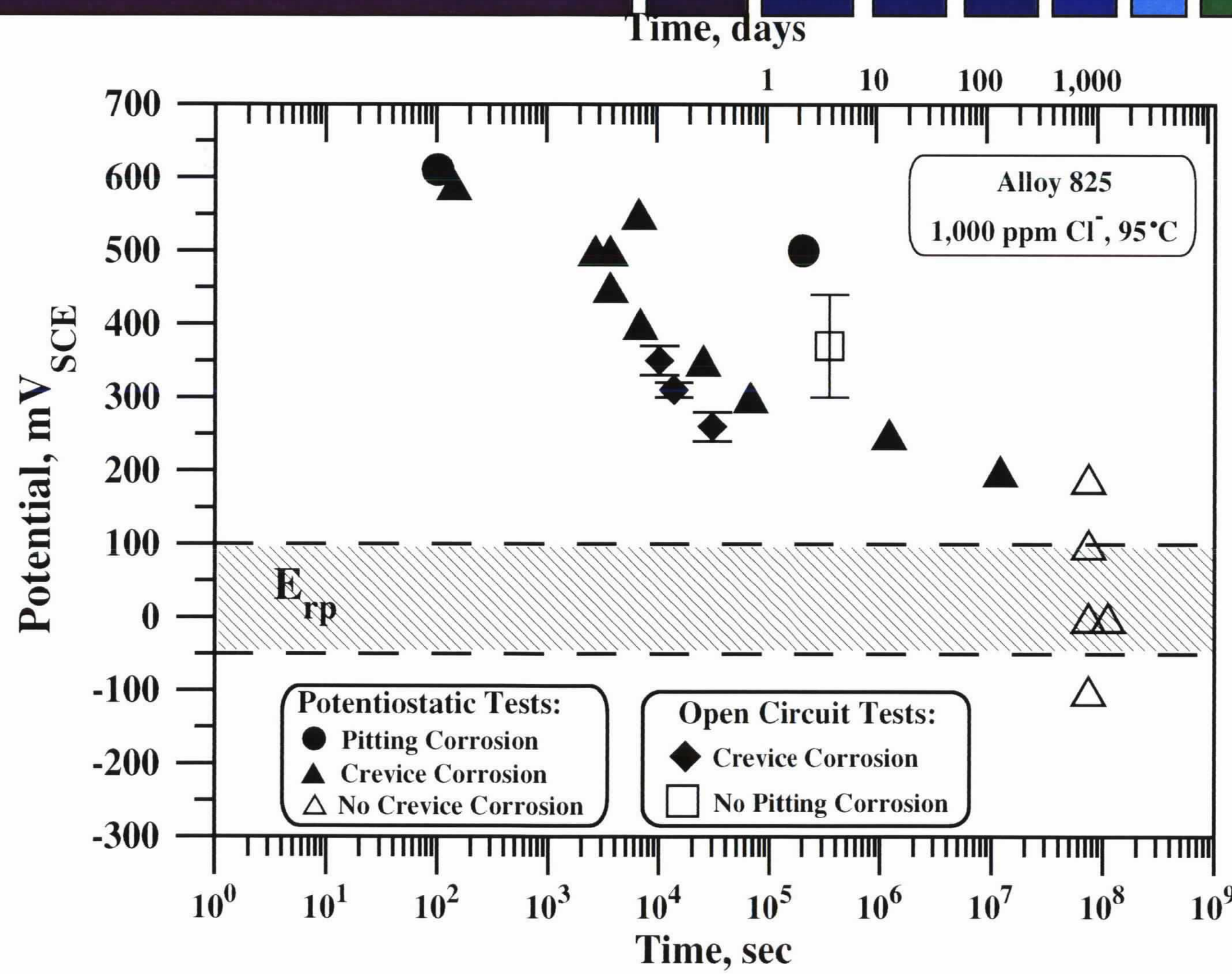


- Repassivation potential, E_{rp}, is affected mainly by anionic concentrations, temperature, and metallurgy
- Corrosion potential, E_{corr}, is affected mainly by redox kinetics, surface state, pH, temperature, and metallurgy
- Pit growth is affected mainly by transport processes within pits.

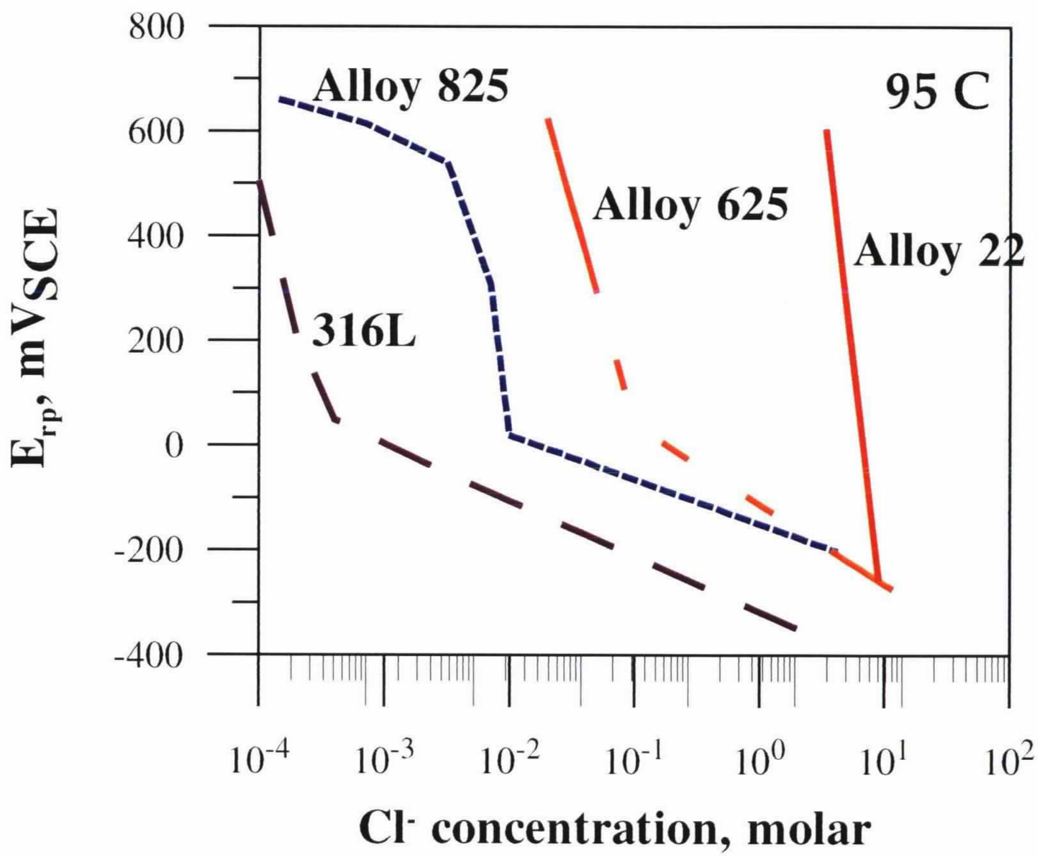
Issues Related to Container Corrosion

- Localized corrosion initiation and growth
  - Effect of near-field environment
  - Fabrication
  - Minor impurities in environment
- Passive, uniform dissolution
  - Measurement, modeling
- Stress corrosion cracking
  - Is there a critical potential?
  - Effect of cyclic loading
  - Minor impurities in environment

Validity Of Repassivation Potential

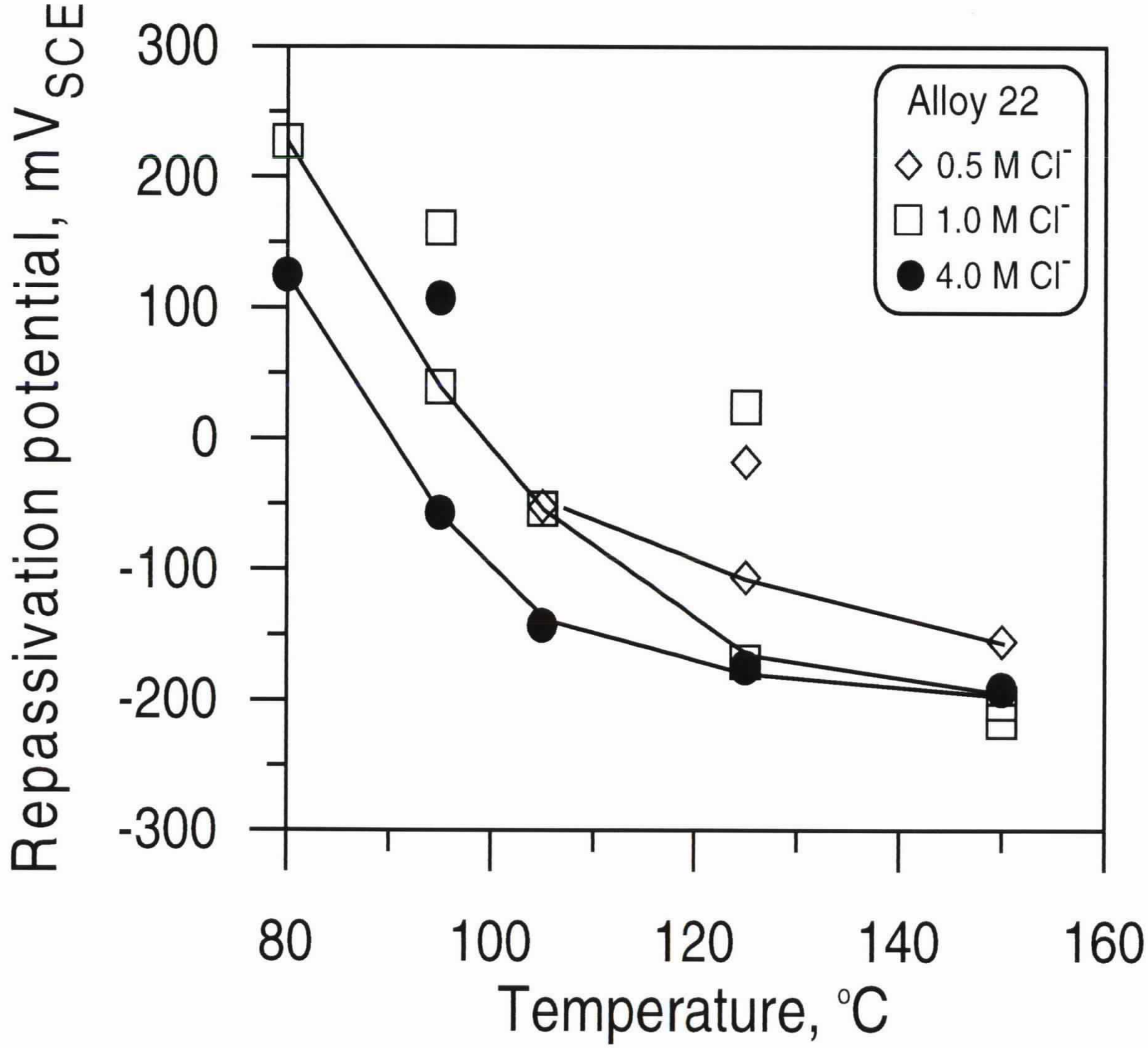


Conditions For Localized Corrosion Of Four Candidate Alloys

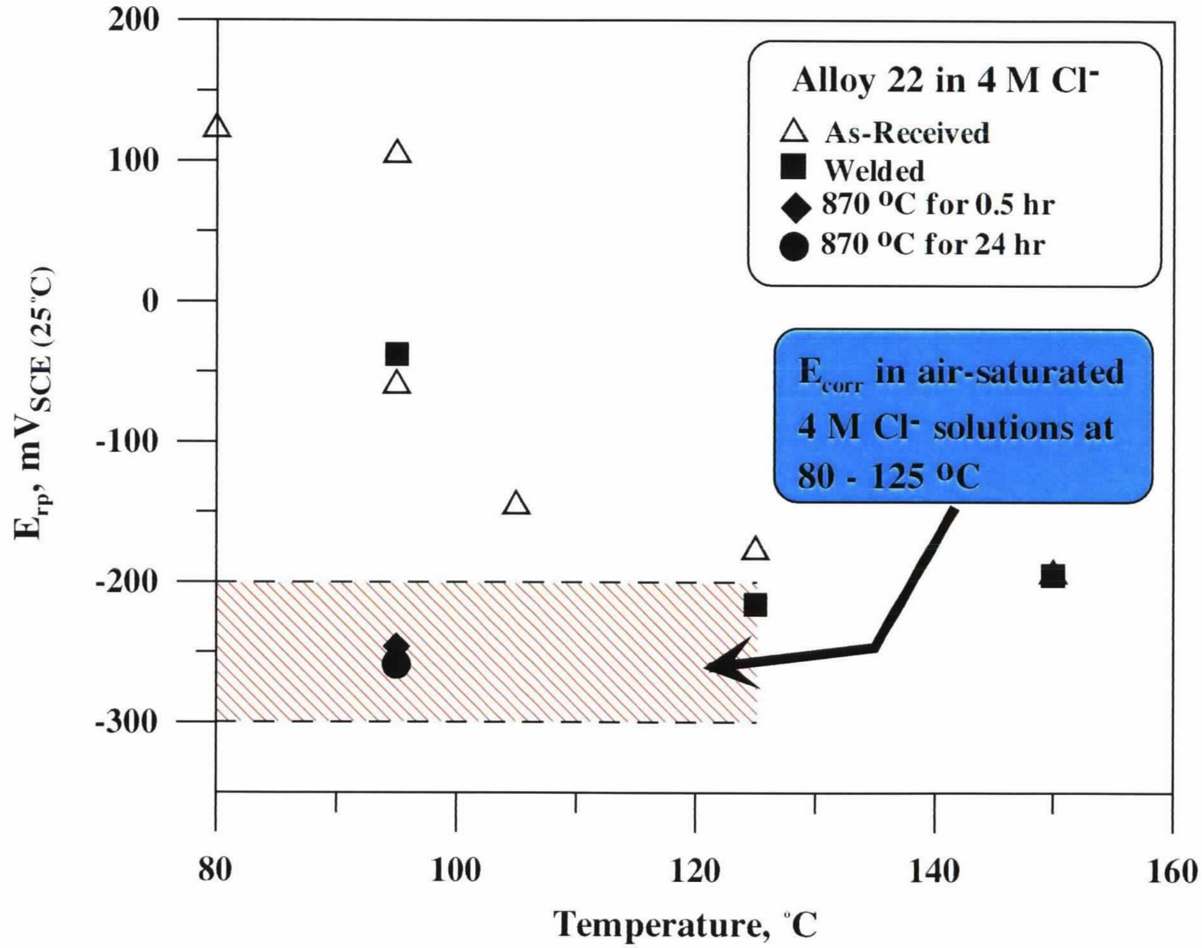


- Repassivation potential (E_{rcrev}) used as a critical potential for the initiation of localized (crevice) corrosion in NRC/CNWRA TPA code
- Improved corrosion resistance in the order 316L<825<625<C-22
- Critical chloride level for C-22 close to saturation of NaCl

Crevice Corrosion vs. Temperature



Effect Of Fabrication On Localized Corrosion

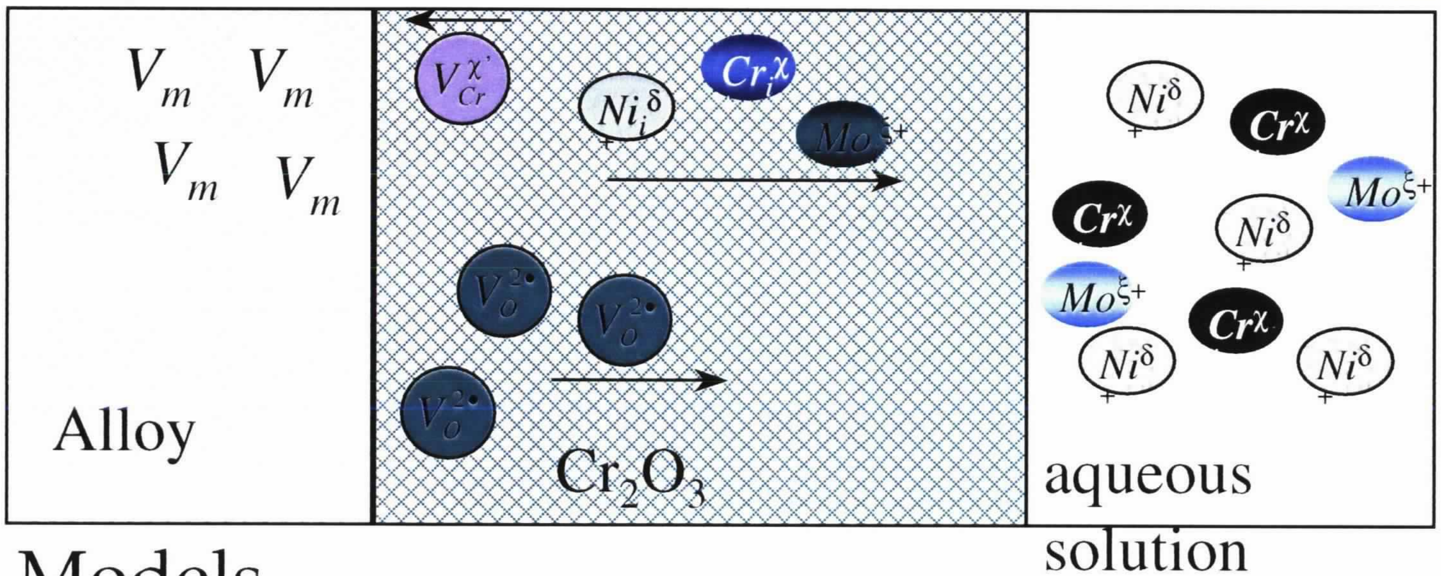


- Exposure to 870^0 C during thermal treatment may result in reduction of performance of alloy 22

Uniform Dissolution of Container

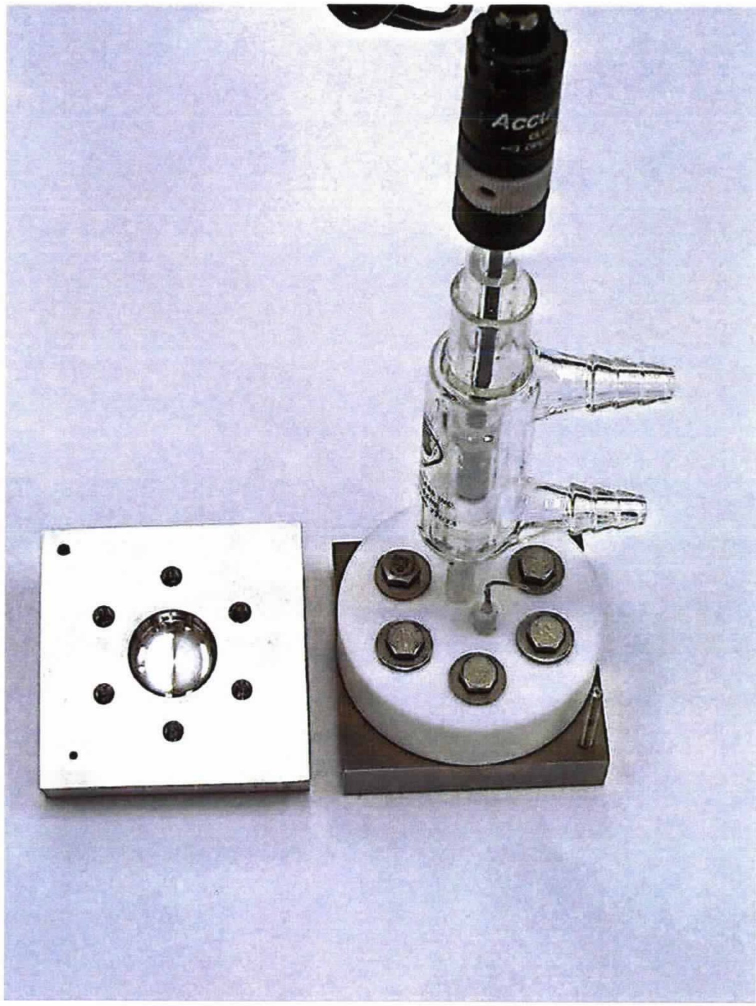
- The measured dissolution rates of alloy 22 range from $2x10^{-5}$ to $7x10^{-4}$ mm/y
- Assuming a constant dissolution rate, penetration of 20-mm wall would occur in 30,000 to 1 million years
- Short-term measurements do not consider defect generation or metastable events
- The effect of fabrication processes on dissolution rates are not considered

Long-term Prediction of Uniform Corrosion



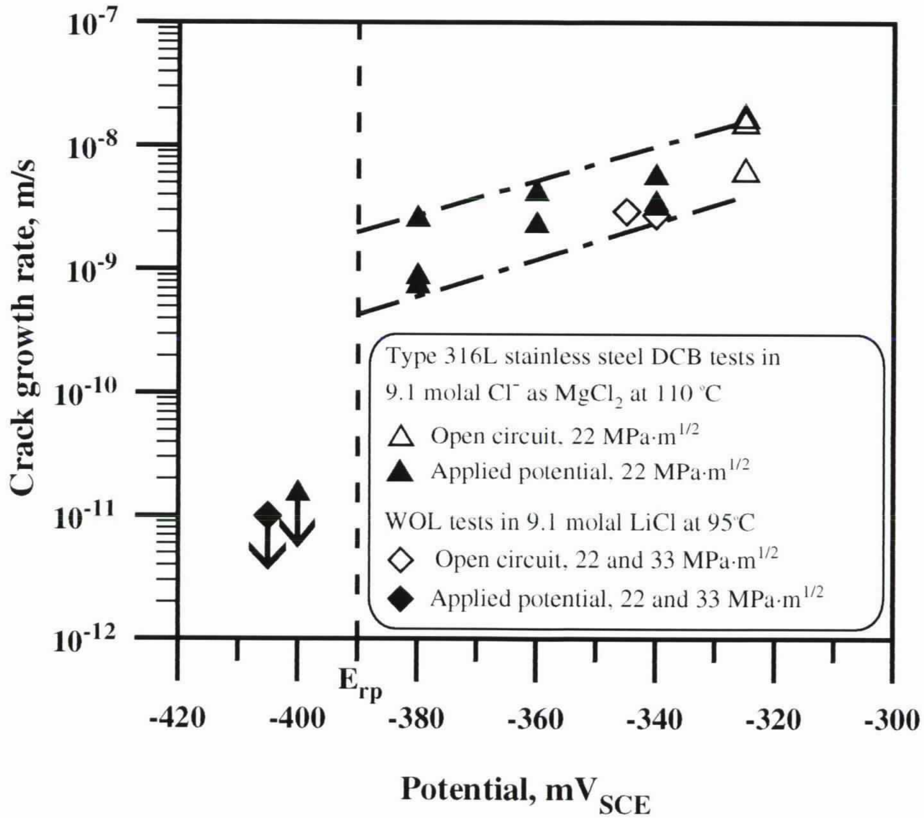
- ❖ Models
  - Point defect model
  - Semiconductive oxide model
- ❖ Experiments
  - Stoichiometry of dissolution
  - Dissolution rate

Uniform Dissolution Experiments



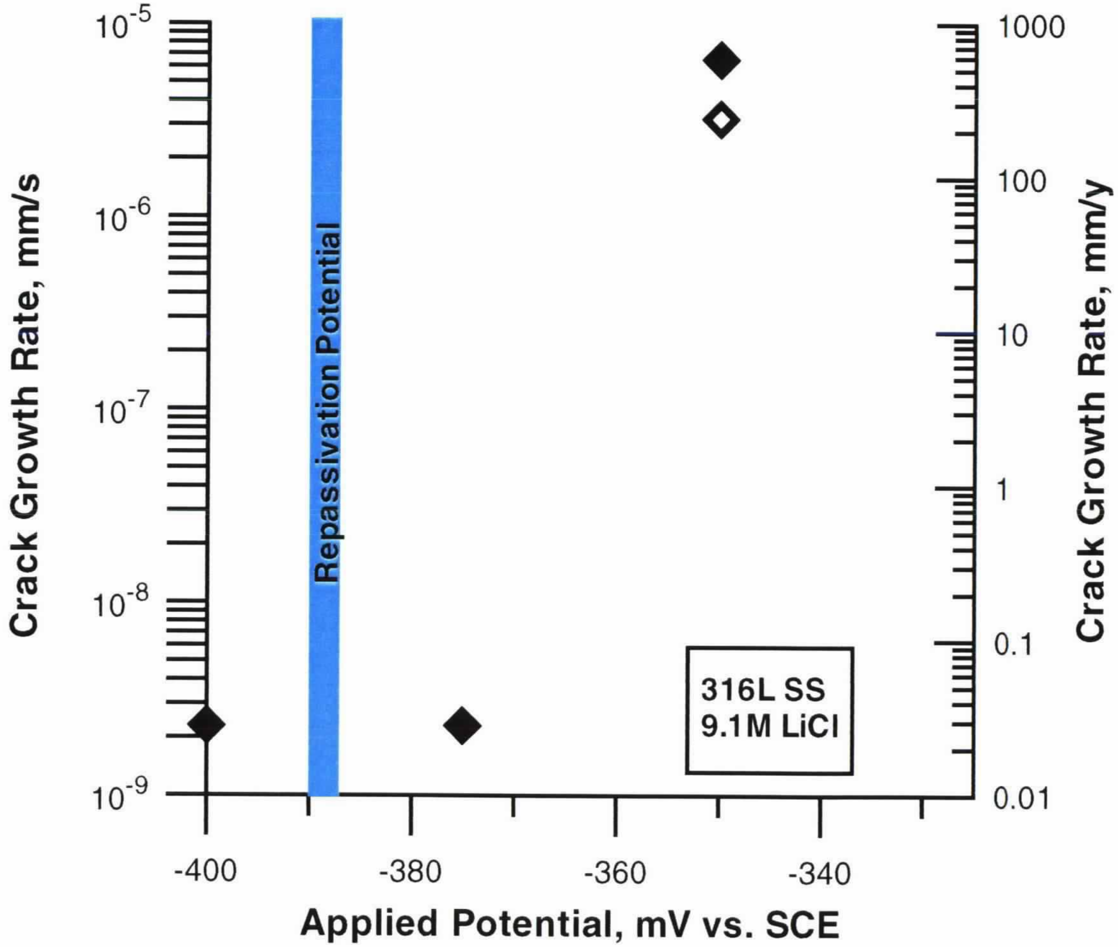
- Evaluate the stoichiometry of dissolution
- Sensitively measure rate of dissolution

Critical Potential for SCC



- Pre-cracked specimens
- Crack growth rate calculated by post-test SEM examination
- 1-month tests
- Some tests for 1 year

Critical Potential for SCC



- Compact tension specimens
- Static and cyclic loading (R=0.7)
- Test time: 1180 hour max
- No SCC in C-22 even with cyclic loading

Effect of Minor Environmental Species on SCC

- The effect of anticipated temperatures at the repository on corrosion and SCC
  - Test temperature used by the State much higher than expected for wet conditions
- The effect of anticipated pH of water contacting the containers
  - **cracking can be observed at low pH even without lead**
- The range of Pb, Hg, As concentrations needed to enhance SCC.
- The speciation of Pb in evaporated water
  - **Preliminary calculations using EQ3/6, to predict the effect of evaporation of J-13 water at 100°C**
  - **The pH is predicted to rise from ~8 to 10.5**
  - **The dominant dissolved species is $PbCO_3$(aq) at 1.2×10^{-3} molal**
- The range of potentials anticipated in the repository

Use of Analogues

- Archeological and natural analogues have been proposed and studied
  - Josephenite (Ni_3Fe type)
  - Iron
  - Bronze/copper
- Industrial experience with alloys similar to alloy 22 exist

Alloy 22 - Brief History

- Fourth generation in C-family of alloys
  - Haynes and others discovered Ni-Cr alloys ca. 1898
  - Alloy C developed by Union Carbide in 1930's
  - Alloy C-276 developed by BASF in early 1960's
  - Alloy C-4 developed in 1973
  - Alloy C-22 developed in 1981
  - Other equivalent alloys (59, 622, etc.) commercialized (ca. 1988)
- Major applications include flue gas scrubbers, chemical process fluids, down hole tubing, pulp and paper bleach systems
- Need to put these industrial experiences in a common framework - repassivation potential vs. corrosion potential

Considerations for Analogues

- Similarity in electrochemical response
  - Josephenite (Ni_3Fe,Co) vs. ferchromide ($Cr_3Fe_{0.4}$) vis a vis alloy 22
- Mechanistic information
  - localized corrosion of mineral analog
  - localized corrosion of meteorites/iron artifacts
- Improve confidence in conceptual model
  - Map performance in other industrial applications of a class of alloys

A Proposed Approach for Analog

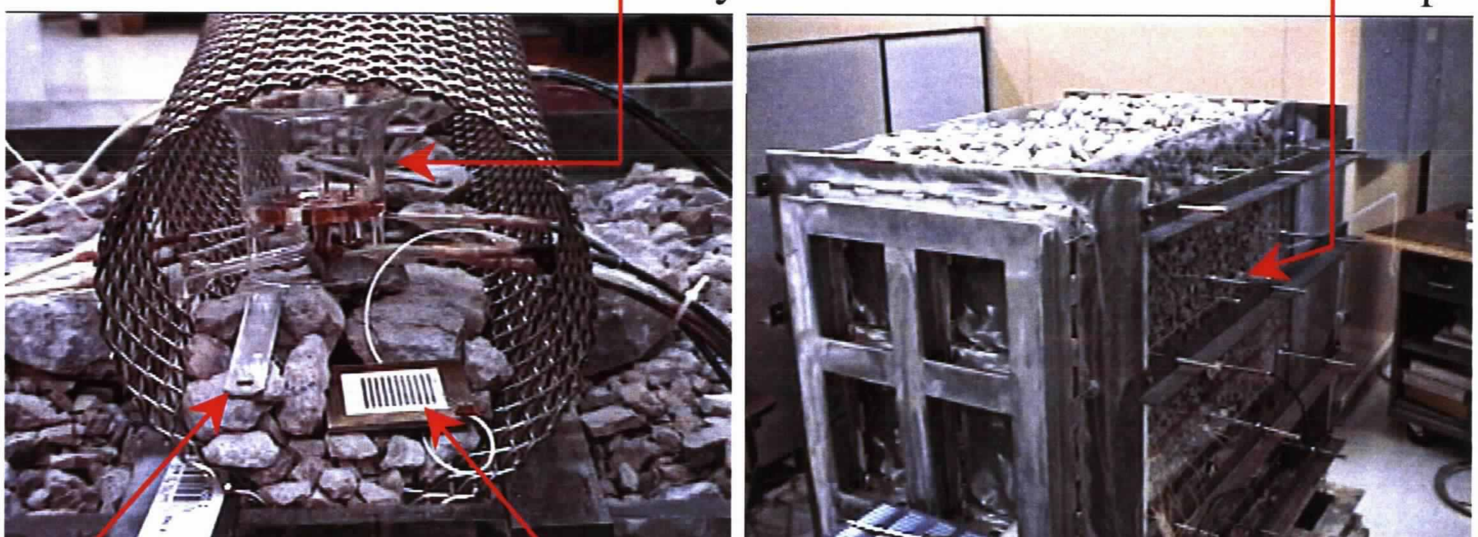
- Investigate mineral assemblage and morphology of ferchromide
- Identify whether any specific corrosion mode is present
- Assess the geochemical history associated with the mineral
- Compare to model prediction (e.g., repassivation vs. corrosion potential)

Performance Confirmation

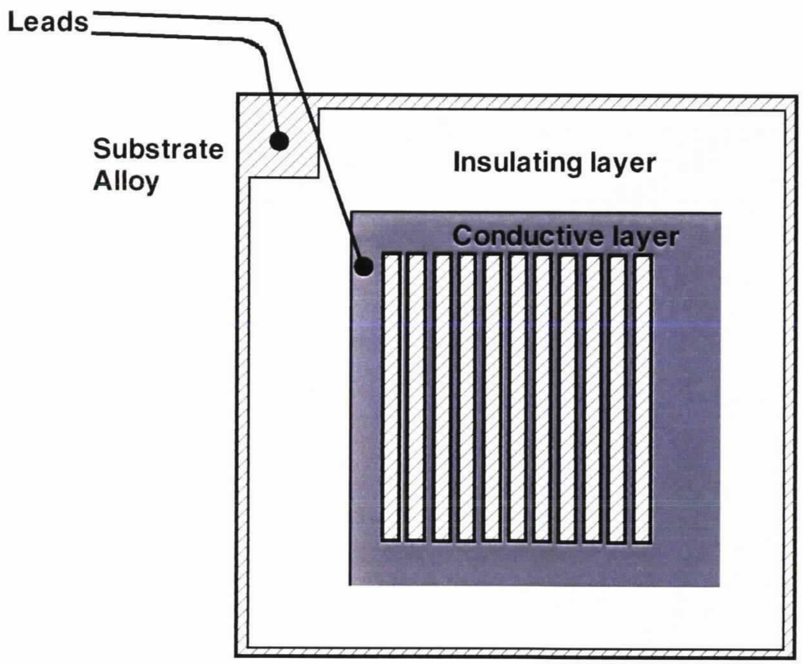
- PC improves confidence in models and laboratory tests
- PC can include many approaches, including laboratory and field tests and monitoring
- Sensor performance is an important consideration
- Different types of sensors can be evaluated in simulated heater tests in the lab

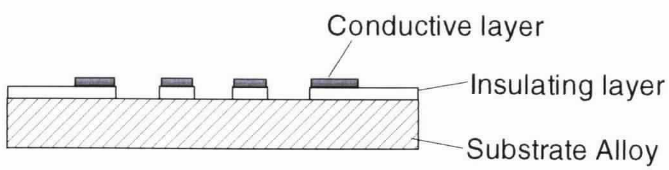
Simulated Drift

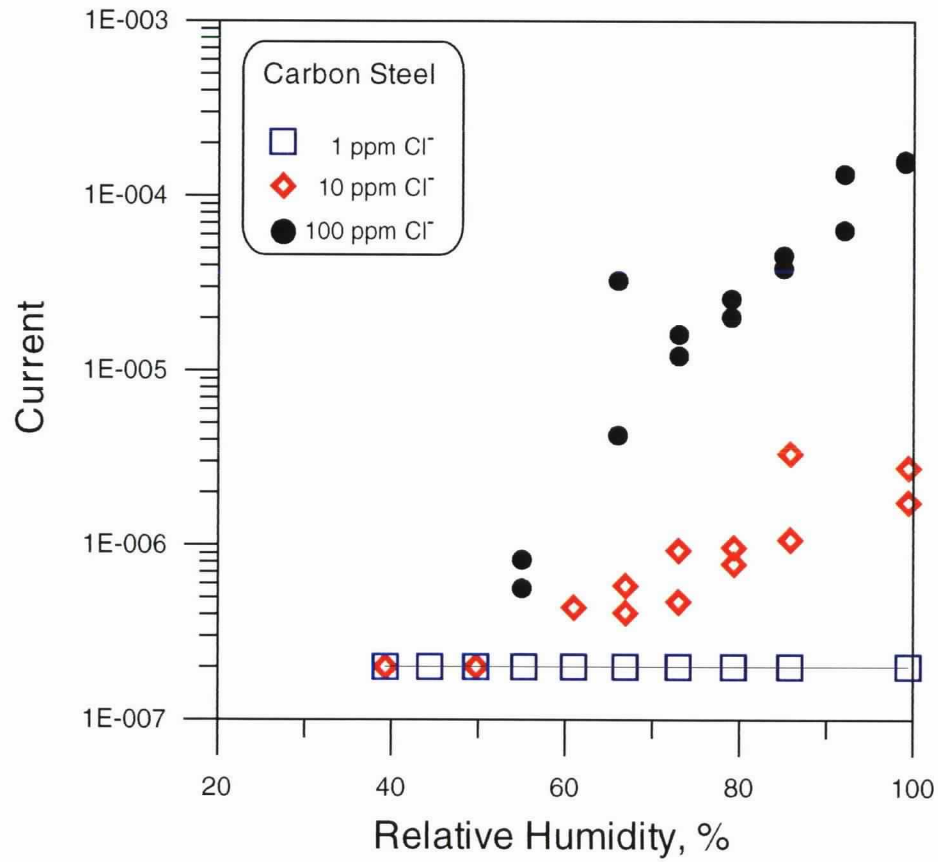
- Objective is to evaluate sensors, not hydrological models
- Crushed tuff from YM w/ 4" simulated drift space
- Tube heater to simulate heat from radioactive decay
- Water equilibrated w/ tuff to simulate ground water percolated in at 1-2 L/day



Galvanic Sensor



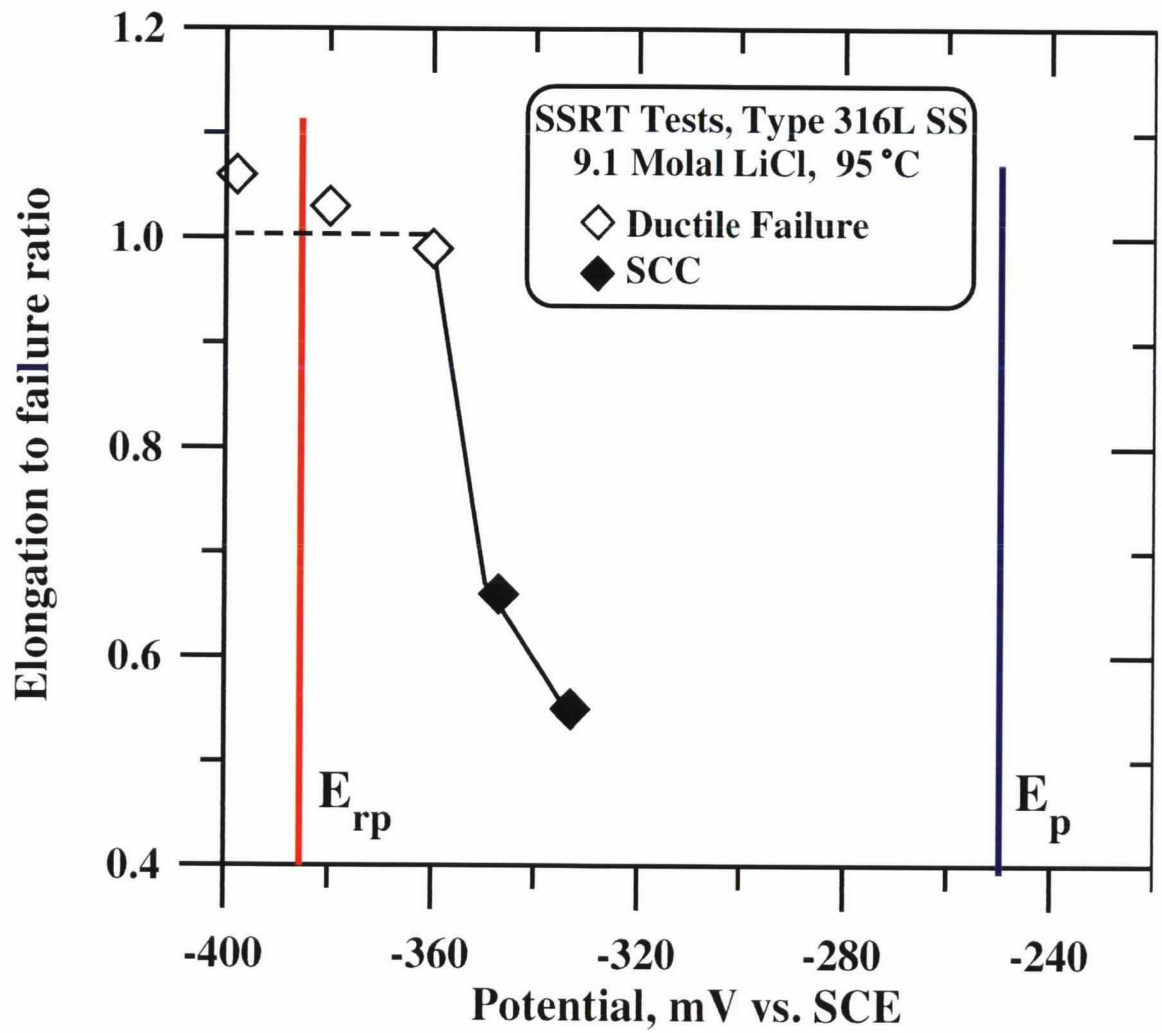




Summary

- Repassivation potential can be used to predict occurrence of localized corrosion and SCC
- Fabrication effects need to be studied
- Long-term passive dissolution needs to be better understood
- Sufficient thought should be given to the development and limitations of performance confirmation/monitoring tools

Critical Potential for SCC

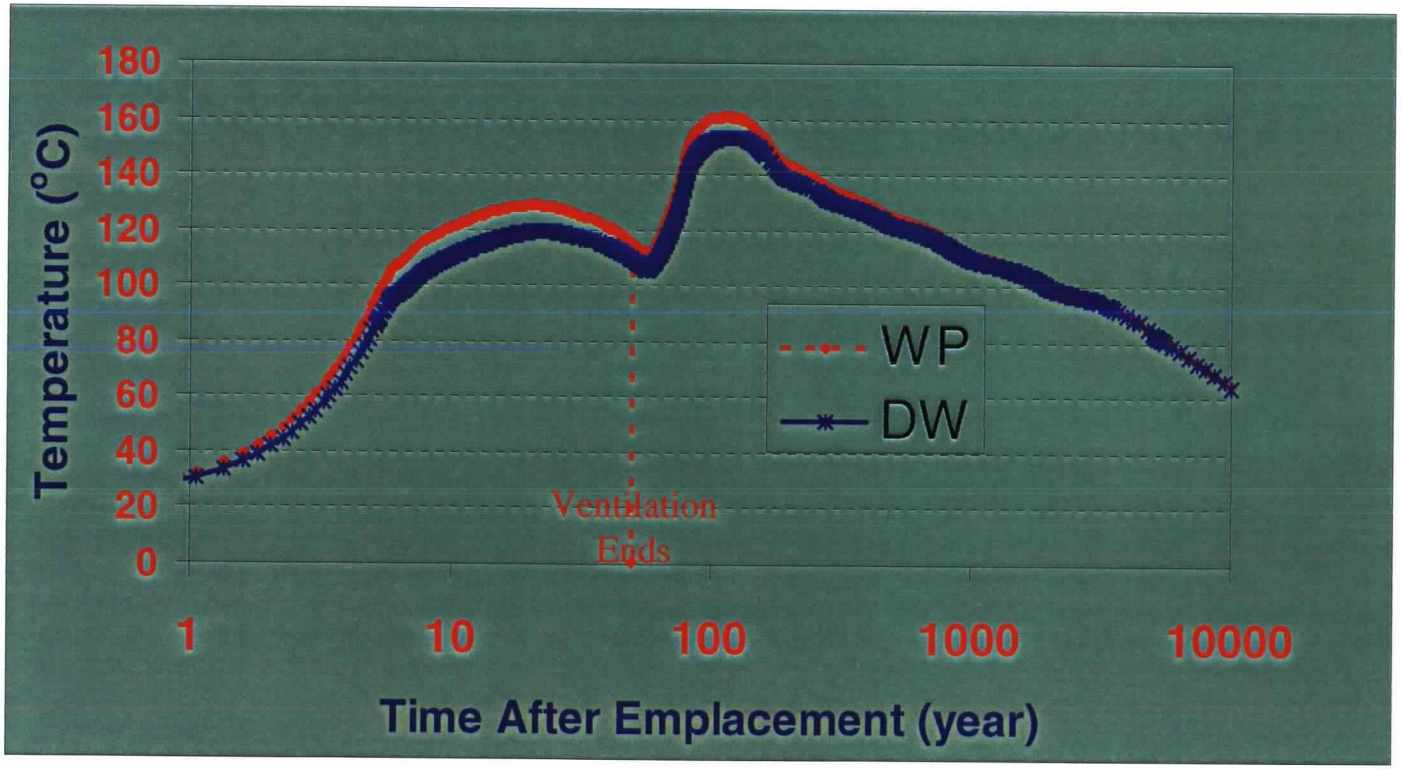


Backup Slides

Alloys

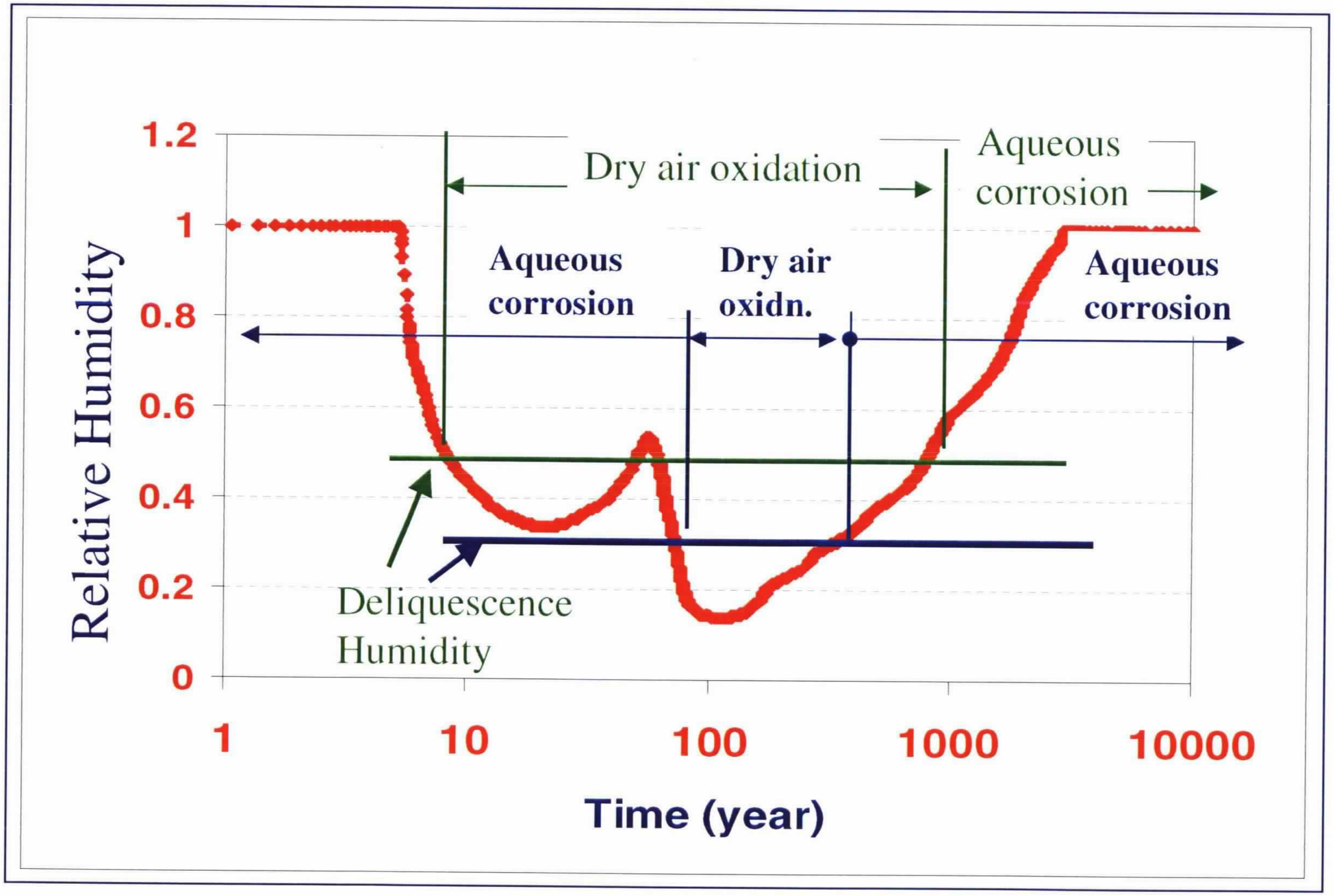
- Type 316L SS: Fe-17%Cr-10%Ni-2.5% Mo
- Alloy 825: Fe-42%Ni-21.5%Cr-2%Cu-3%Mo
- Alloy 625: Ni-21.5%Cr-9%Mo-3.7%Nb
- Alloy C-22:Ni-3%Fe-21.5%Cr-13.5%Mo-3%W

Background: Repository Temperature

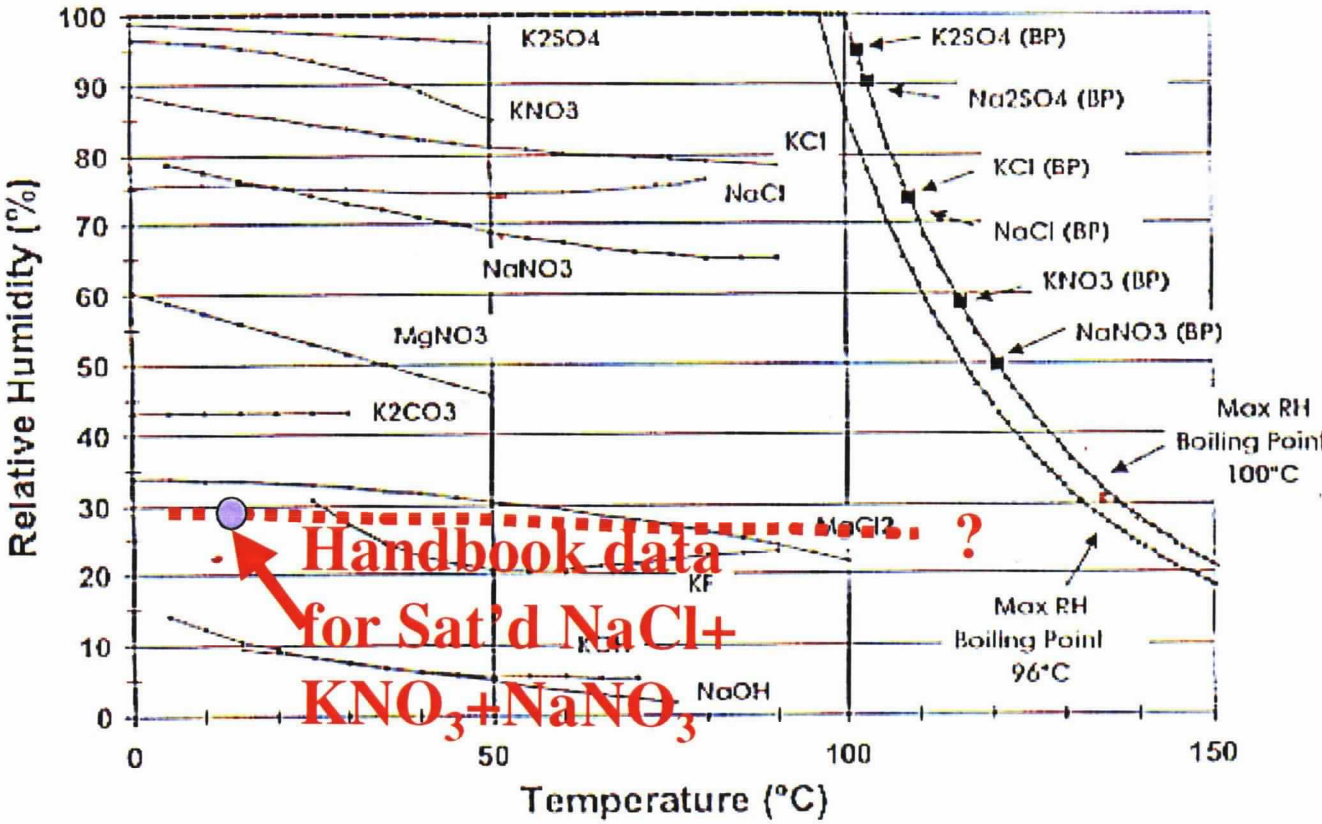


Preliminary MULTIFLO Result
provided by Debra Hughson, 02/20/01

Deliquescence Humidity and Aqueous or Dry Air Corrosion



Likely Deliquescence Humidity for Concentrated J13 Water



Uniform Corrosion Rates

Starting Condition of Alloy C-22	$[Cl^-]$, molar	pH	Temp, °C	Potential, mV_{SCE}	Anodic Current Density, A/cm^2	Corrosion Rate, mm/yr	Lifetime of 20 mm Thick WP Barrier, Years
As-received	0.028	8	20	200	2×10^{-9}	2×10^{-5}	1,007,455
As-received	0.028	8	95	200	3×10^{-8}	3×10^{-4}	67,163
As-received	0.028	0.7	95	200	7×10^{-8}	7×10^{-4}	28,784
As-received	4	8	95	200	3×10^{-8}	3×10^{-4}	67,163
As-received	4	8	95	400	4×10^{-8}	4×10^{-4}	50,372
TPA 3.2 Calculation Low Dissolution Rate					6×10^{-8}	7×10^{-4}	33,581
TPA 3.2 Calculation High Dissolution Rate					2×10^{-7}	2×10^{-3}	10,074

Uniform Corrosion