



U.S. Department of Energy  
Office of Civilian Radioactive Waste Management

# Evaluation of Corrosion Processes: Summary of Current Status and Approach for Extrapolation to Long Times

Presented to:  
**Nuclear Waste Technical Review Board**

Presented by:  
**Gerald Gordon**  
**Framatome Advanced Nuclear Power**  
**Bechtel SAIC Company, LLC**

**June 20-21, 2001**  
**Las Vegas, NV**

YUCCA  
MOUNTAIN  
PROJECT

# Outline

- **Corrosion Process Evaluation Status/Understanding**
  - Establishment of long-term corrosion rates
  - Characterization of passive film structure and growth kinetics
  - Potential passive film degradation mechanisms
  - Development of a mechanistic general corrosion model
  - Localized corrosion status
- **Conclusions**
- **Backups (including Path Forward to reduce uncertainty)**

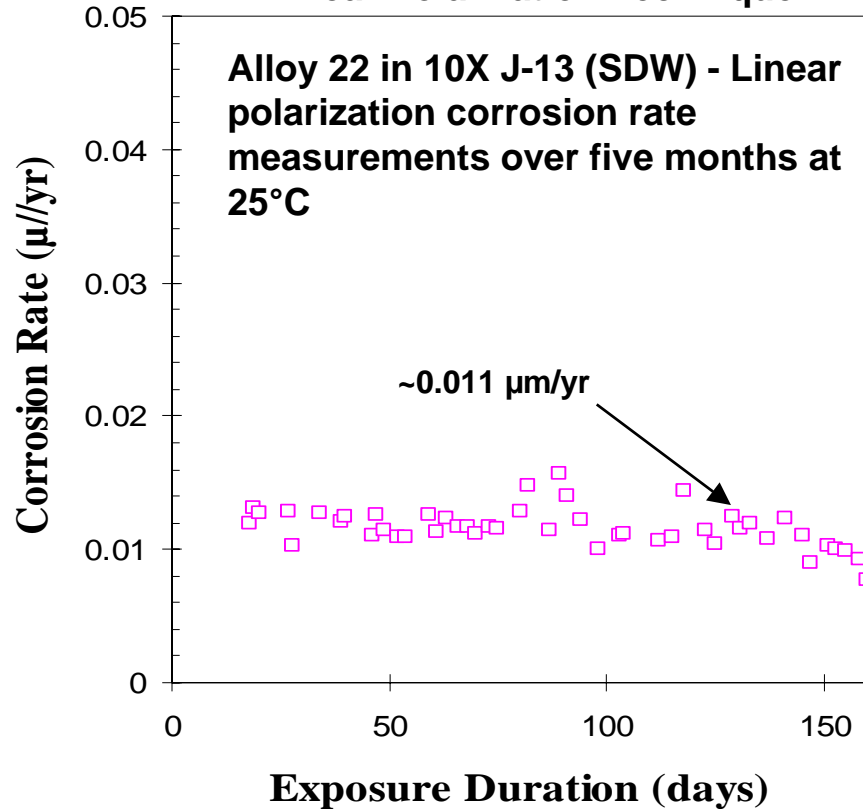
# Establishment of Long-Term Corrosion Rates

- **Long term corrosion test facility (LTCTF) weight loss and localized corrosion test results currently available for  $\leq 2.3$  years exposure times**
  - **Very low observed corrosion rates coupled with measurement uncertainties limits ability to discern small temperature and environmental effects on corrosion rates**
  - **Experimental and modeling program underway to corroborate LTCTF measured rates, to establish temperature and environmental dependencies and to provide mechanistic basis for extrapolation over very long times**

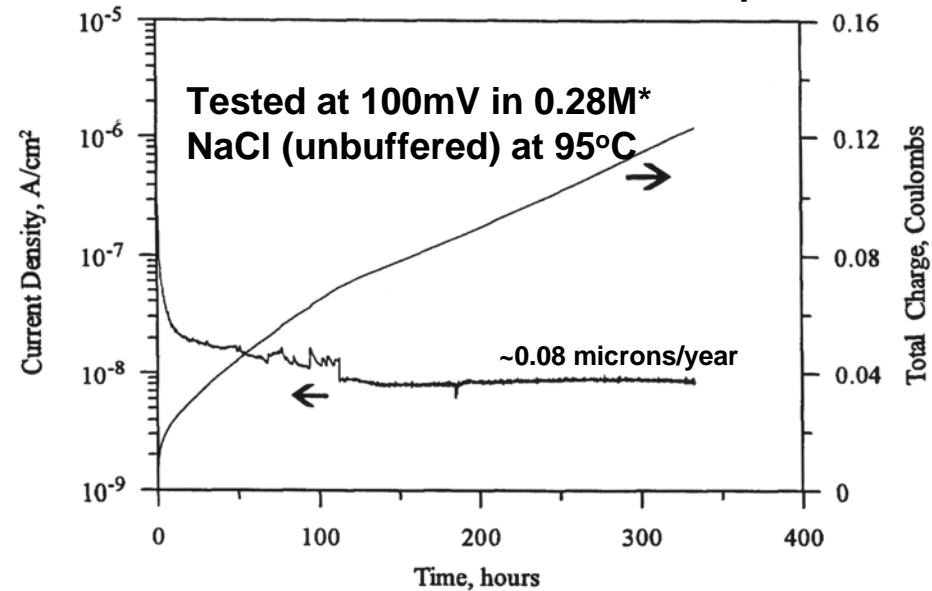
# **Electrochemical and Microscopic Corroboration of Long Term Corrosion Test Facility Results (Results from Project plus Literature)**

# Electrochemical Techniques for Confirmation of Corrosion Rate Measurement

## Linear Polarization Technique



## Potentiostatic Polarization Technique



(from Corrosion 2001, Paper 01125, Dunn, D.S. et al)

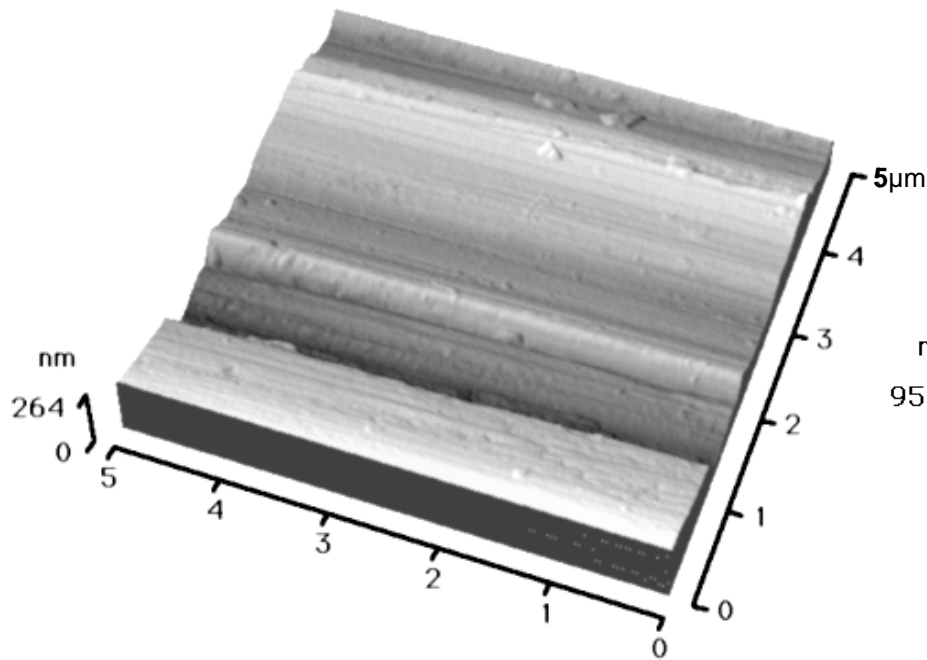
Test program underway to obtain high resolution corrosion rate measurements = f(time, environment, applied potential and metallurgical condition)

# Characterization of Alloy 22 Passive Film

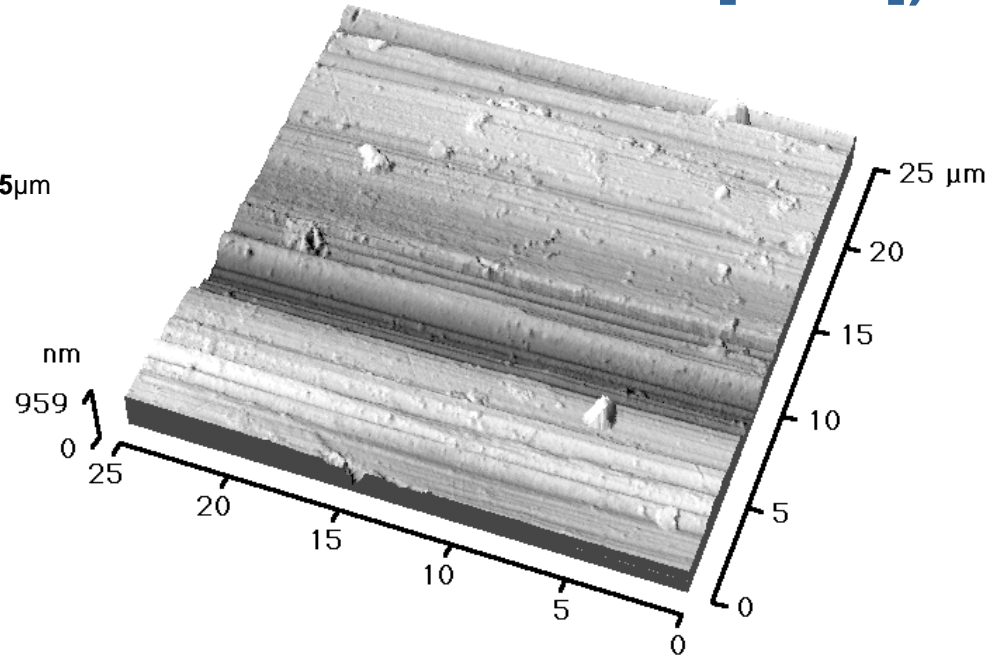
- **Ni-Cr-Mo alloy corrosion films in general consist of at least two layers**
  - A very thin (~10-100 angstroms), thermodynamically stable  $\text{Cr}_2\text{O}_3$  rich protective layer containing Mo, Ni and W (for Alloy 22)
  - A generally less protective precipitated oxide, hydroxide, or oxyhydroxide containing outer layer
- **Characterization of passive films on Alloy 22 has been conducted utilizing**
  - Atomic Force Microscopy (AFM) and Tunneling AFM
  - X-ray photoelectron spectroscopy (XPS)
  - Time-of-Flight Ion Mass Spectrometry (TOF SIMS)

# Atomic Force Microscopy of Alloy 22 Surface Exposed to Vapor Phase

(1 year at 90°C in simulated concentrated water [SCW])



Control Coupon DWA163 pb990607.020 AFM Image



SCW, 90°C, Vapor DWA117 pb990607.044 AFM Image

**Microscopic observations on specimen with minimal surface deposits show no evident roughening or fine scratch removal - consistent with one year descaled weight loss measurements (<60 nm equivalent metal loss)**

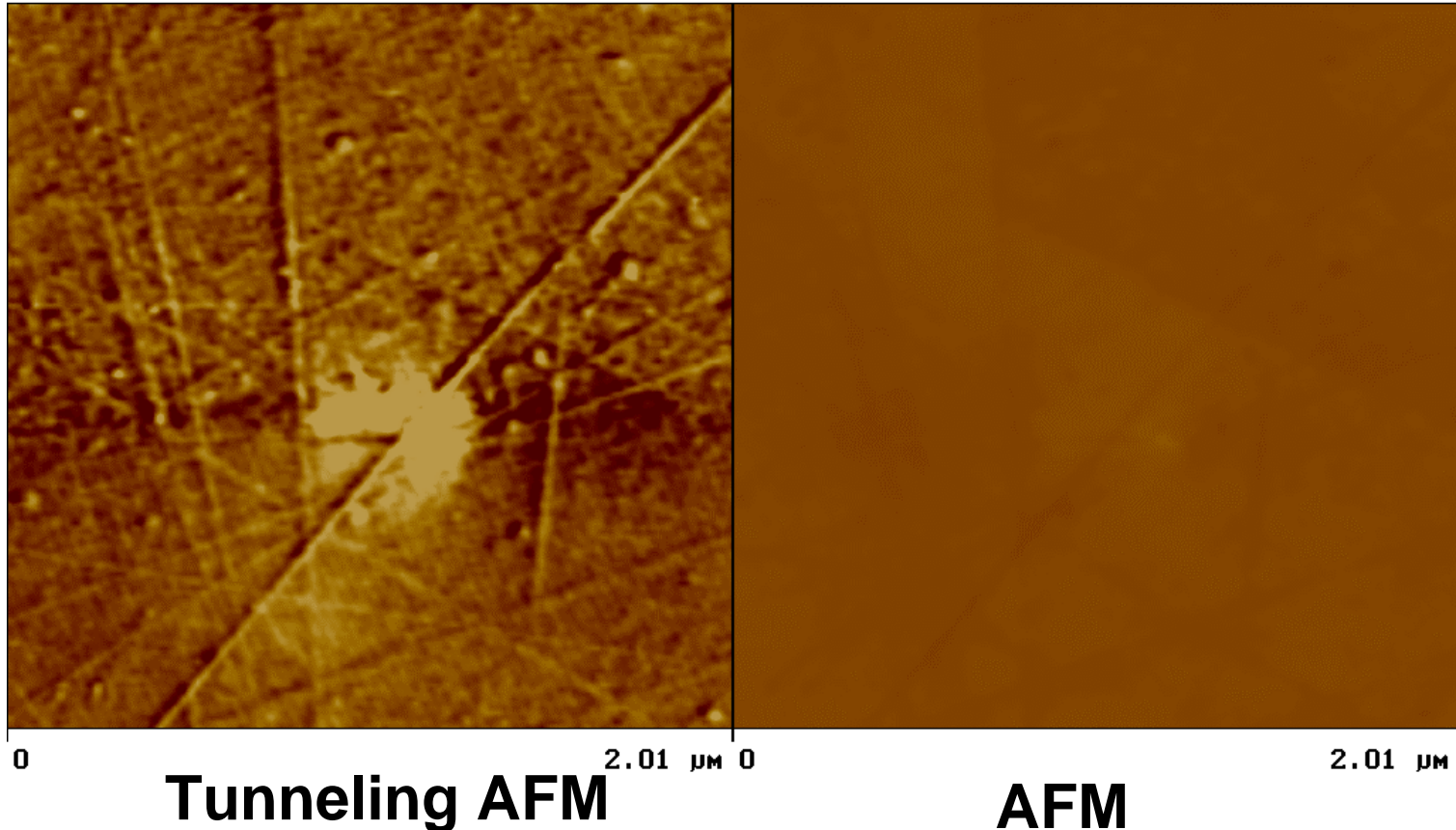
# Characterization of Film Growth Kinetics using Tunneling AFM

- Whereas conventional Atomic Force Microscopy (AFM) measures surface topography, Tunneling AFM (TUNA) measures a tunneling current through a surface dielectric (oxide)
- Tunneling AFM is very sensitive to changes in electrical properties of oxide and can detect small variations across a surface
  - Also used in semi-conductor industry
- The Tunneling AFM technique can also detect small changes in oxide thickness



# Surface Topography by Tunneling AFM and AFM

Alloy 22 surface after 45 days in air at 200°C



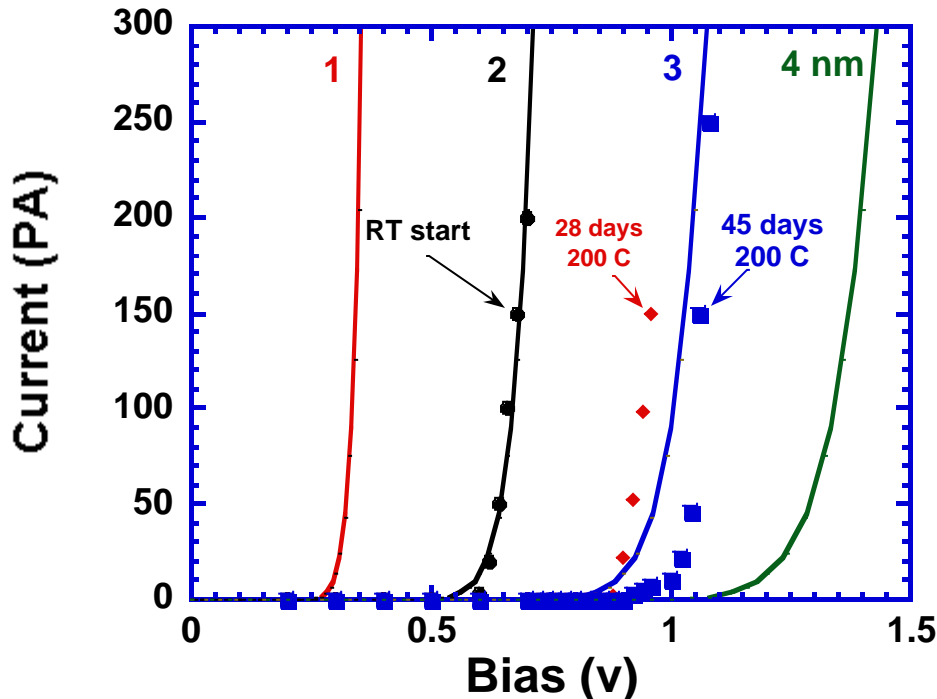
Tunneling AFM characterization of thin Alloy 22 surface oxide yields high resolution image compared to AFM

# Characterizing Film Thickness/Composition

1M NaCl, pH 1, 85°C

Time of Flight Secondary Ion Mass Spectrometry (TOF SIMS)

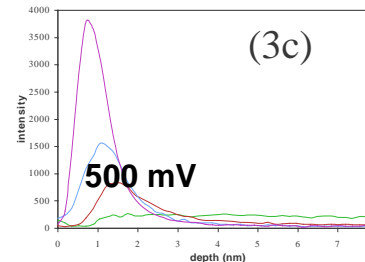
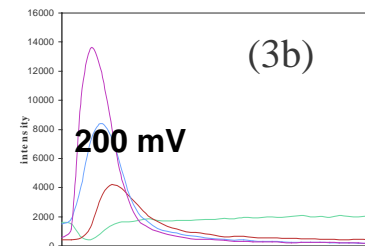
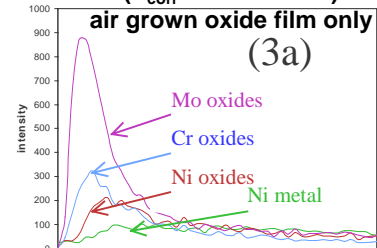
Tunneling AFM oxide thickness in 200°C air



- Oxide film growth after 45 days at 200 C in air estimated at 3.2 nm
- Little if any additional growth after 120 days
- Measurements in relevant aqueous environments planned for late FY01

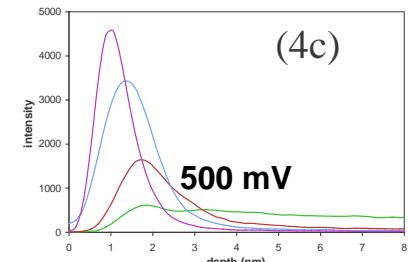
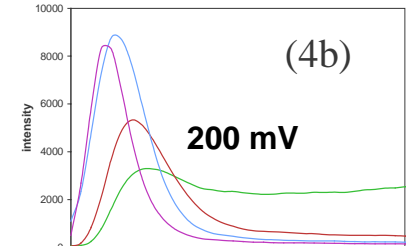
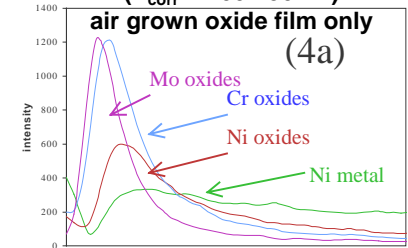
Alloy C-4

( $E_{corr} = 100-150mV$ )



Alloy C-22

( $E_{corr} = 100-150mV$ )



- ~3nm thick Alloy 22 surface oxide layer for both air-formed and aqueous films
- Cr/Mo coexist in outer surface of aqueous-formed passive films
- Only  $Cr^{3+}$  valence state present in oxide layer - Consistent with  $Cr_2O_3$  rich passive film expected from thermodynamic considerations

# Potential Passive Film Degradation Mechanisms

- **To decrease uncertainty, need to better understand fundamental mechanisms that, although unlikely for Alloy 22 in repository conditions, could degrade passive layer protectiveness over time, e.g.**
  - **Defect accumulation as layer sweeps through metal**
  - **Debris accumulation — long term corrosion product effects on layer**
  - **Quasi-transpassive dissolution — if corrosion potential increases over time, transpassive dissolution may occur aided by high Mo content**
  - **Coalescence of metastable pits**
  - **Diffusion induced grain boundary migration**
- **Test plans are being developed to address these and other identified potential film degradation mechanisms**

# Potential Passive Film Degradation Mechanisms

(Continued)

- **Project International Waste Package Performance Peer Review Panel has been convened and will address the appropriateness of these plans and current path forward efforts**
- **NWTRB Workshop on July 19-20 will also address this issue**

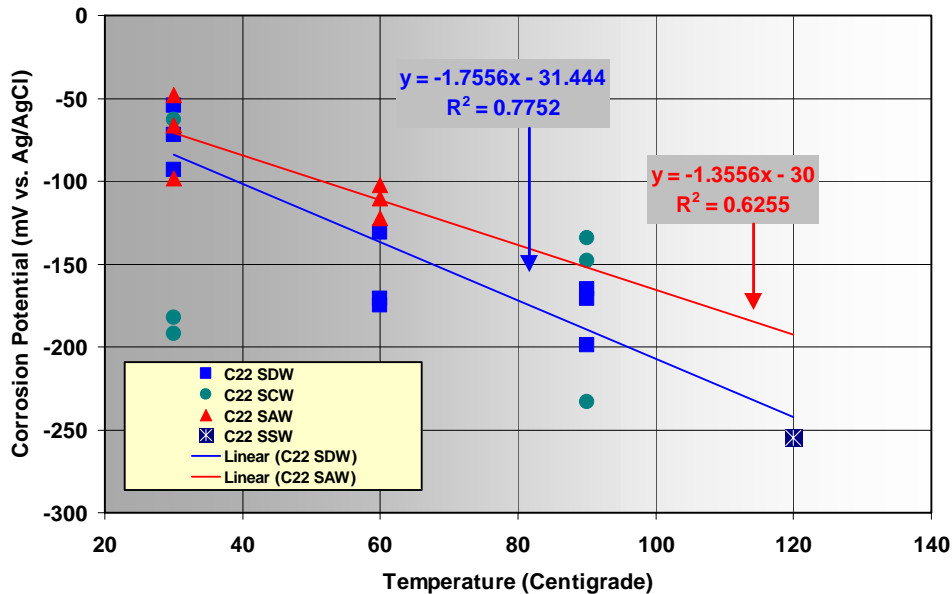
# Development of General Corrosion Model for Long Term Prediction of Corrosion Damage

- **Short term corrosion experience base (<100 years) makes effective extrapolation challenging**
- **Deterministic approach offers potential to reduce uncertainties associated with empirical extrapolation**
- **Current mechanistic models to describe passive film kinetic behavior include**
  - **Point defect model and mixed potential model**
  - **Semi-conductive oxide model**
- **Project currently developing a point defect based generalized corrosion model for predicting accumulated general corrosion damage**

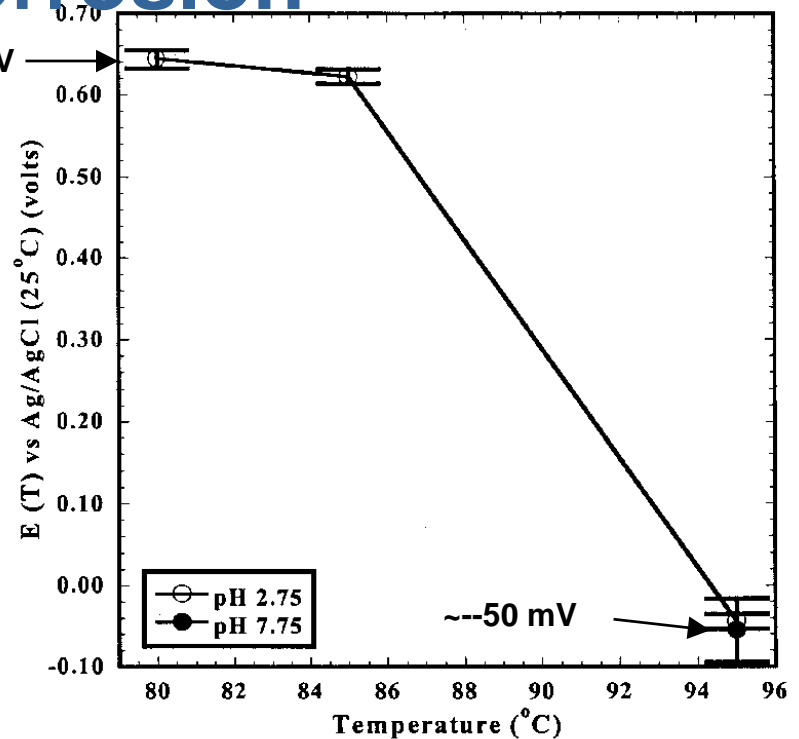
# Localized Corrosion Status

- **Localized corrosion not expected under range of potential repository relevant aqueous conditions [i.e. buffer ion(s) present at anion ratios of (Cl<sup>-</sup>/NO<sub>3</sub><sup>-</sup> + SO<sub>4</sub><sup>=</sup>) <2:1 and E<sub>corr</sub> <E<sub>crit</sub>.]**
  - Resistance confirmed by project and literature data
  - However, localized corrosion of Alloy 22 can occur under very oxidizing conditions in concentrated chloride solutions at high molar anion ratios (Cl<sup>-</sup>/NO<sub>3</sub><sup>-</sup> + SO<sub>4</sub><sup>=</sup>) >~10:1

# Temperature Dependency for Localized Corrosion



Corrosion potential vs temperature for range of relevant environments



Crevice repassivation potential\* vs temperature in more aggressive, partially buffered 4M LiCl ( $[Cl^-/NO_3^- + SO_4^{2-}] = 10:1$ ) (from Kehler et al., Corrosion 2001, Paper No. 01141)

Repassivation potential\* increases rapidly and  $E_{corr}$  more slowly as temperature drops leading to increased crevice corrosion margin at lower temperatures [\* minimum potential for localized corrosion]

# Comparison of Alloy 22 General and Localized Corrosion versus other Nickel-Base Alloys

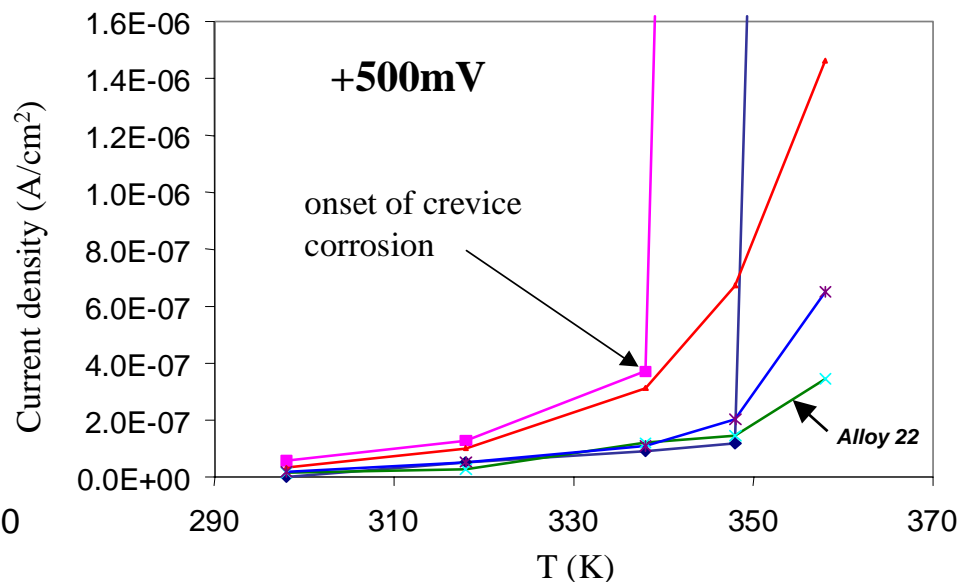
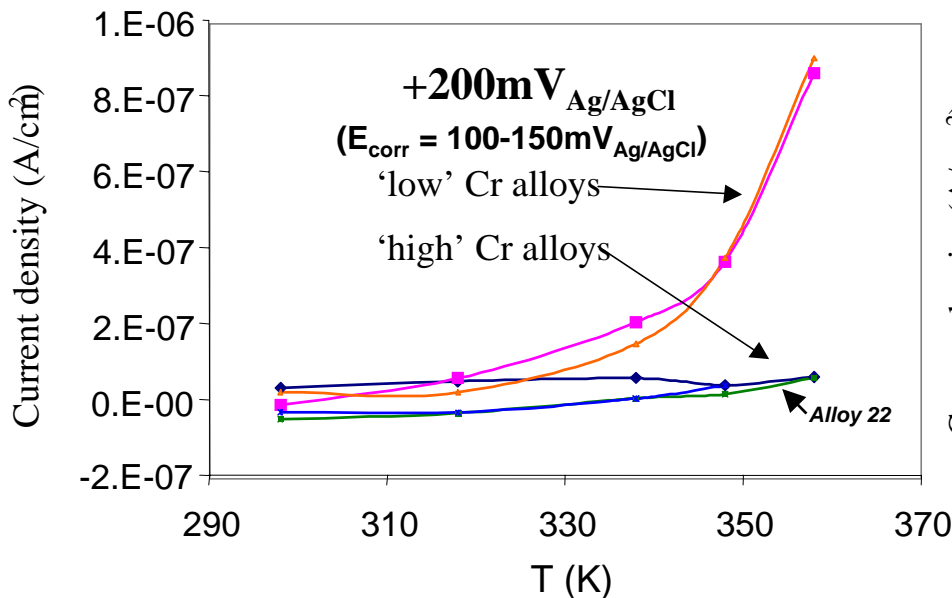
(Potentiostatic Polarization Rates in deaerated 1 M NaCl, pH 1)

(data from A.C. Lloyd, D.W. Shoesmith, et al, Stainless Steel World, 2001)

Component	C-4	C-276	C-22	C-2000	625
Cr	14-18	16.5-14.5	22	23	21
Ni	Bal	Bal	Bal	Bal	Bal
Mo	14-17	17-15	13	16	9
W	0	4.5-3	3	0	0
C	Max 0.01	Max 0.01	Max 0.01	Max 0.01	Max 0.1
Co	Max 20	Max 2.5	Max 2.5		Max 1.0
Fe	Max 3	7-4	3		Max 5.0
Si	Max 0.08	Max 0.08	Max 0.08	Max 0.08	Max 0.5
Mn	Max 1	Max 1	Max 0.5		Max 0.5
Ti	Max 0.7	0	0		Max 0.4
Cu				1.6	

**Calculated Alloy 22 activation energy at +350mV = 32 kJ/mole**

**Alloys tested include 625, C-4, C-276, C-2000 and Alloy 22**



**Alloy 22 one of most corrosion resistant nickel-base alloys**  
**No Alloy 22 crevice corrosion observed up to 500mV applied potential**



# Conclusions

- **Project and Literature results plus other multiple lines of evidence such as commercial analog performance support basis for extrapolation of corrosion rate over long times**
- **Resistance to localized corrosion high in expected range of repository relevant environments. Margin increases further with lower temperature**
- **Comprehensive experimental and passive film modeling programs defined and underway to decrease remaining uncertainties**
  - **Extensive confirmatory experimental results expected by October-December, 2001**

# Conclusions

- **The Waste Package Performance Peer Review Panel has been convened and will assess adequacy of current approaches and paths forward to resolve remaining uncertainties, particularly in the areas of**
  - **Extrapolation of corrosion data over long time periods**
  - **Long-term passive film stability**
  - **Confidence in long-term margin for localized corrosion threshold potentials**


# Backup



# Corrosion Resistant Ni-Cr-Mo Base Alloys

## Chemical Compositions (Weight %)

<u>Alloy</u>	<u>Nickel</u>	<u>Chromium</u>	<u>Molybdenum</u>	<u>Iron</u>	<u>Other (maximum values)</u>
59	59	23	16	1	0.4Al, .010C
C-2000	59	23	16	-	1.6 Cu, .015C
22	56	22	13	3	2.5Co, 3.5W, 0.35V, .015C
C-4	63	16	16	3	2.0 Co, 0.7Ti, .015C
C-276	59	15.5	16	5	2.5 Co, 4W, 0.35V, .02C
C	56	16.5	17	6	4.5W, 0.15C
625	60	22	9	5	4.0Nb, 0.4Ti, 0.4Al, .10C
825	40	22	3	32	2.2 Cu, 1.0Ti, 0.2Al, .05C


  
 Similar

### Ni-Cr Alloys without Mo

600	76	16	-	8
690	62	29	-	9

#### Legend:

Co - cobalt  
 W - tungsten  
 Ti - titanium  
 Nb - niobium  
 Al - aluminum  
 Cu - copper

# Plan to Verify Long-Term Corrosion Performance

## Technical Oversight and Direction DOE/BSC

Prof. L. Kaufman, MIT  
Prof. D. MacDonald  
Penn State Univ.

Prof. D. Shoesmith  
Univ. of Western Ontario  
Prof. J. Scully, U of VA

Dr. P. Andresen  
GE Corp. R&D

Prof. Denny Jones  
Univ. of Nevada -Reno

Drs. McCright Gdowski,  
Summers, Lawrence Livermore  
National Lab.

### Confirm Long-Term Passive Film Stability

- Demonstrate film is thermodynamically stable =  $f(\Delta x, \text{environment}, t, T, \text{ECP}, \text{etc.})$ 
  - Calculate Pourbaix diagram and compare to measured film compositions
- Compare passive films on Josephinite and commercial alloy analogs with Alloy 22
- **Utilize mechanistic model to extrapolate expected behavior over time**

### Characterize Corrosion Mechanism(s)

- Develop mechanistic model (e.g. Point Defect/Mixed Potential General Corrosion Model)
- Characterize film structure =  $f(\Delta x, t, T, \text{ECP}, \text{etc.})$ 
  - Evaluate film structure on specimens from LTCTF, CP, potentiostatic exposures, higher temp. autoclave exposures, Josephinite, etc.
    - AFM, TEM, AES, XPS, SIMS, etc.
- Evaluate film defect structure, diffusing species and diffusivities
  - CP, CER, EIS, TEM, etc.
- Characterize solution interface reactions

### Confirm Expected Corrosion Rates

- Characterize LTCTF weight loss specimens
  - Evaluate  $E_{\text{corr}}$  of 2-4 year specimens in each environment and compare to  $E_{\text{corr}}$  during initial exposures
- Add new LTCTF tanks with BSW @ 110°C and SSW @ 120°C
- Add high sensitivity weight loss and on-line monitoring of specimens in LTCTF
- Measure rates in situ in AFM =  $f(\Delta x, t, T, \text{ECP}, \text{etc.})$  using photolithographic height grid
- Run long-term potentiostatic tests =  $f(\text{ECP}, t, \text{environ.}, T, \text{welded}, \text{aged}, \text{etc.})$  to measure corr rate &  $E_{\text{rp}} = f(\text{time})$
- Confirm that environments evaluated to date represent bounding environments including trace elements

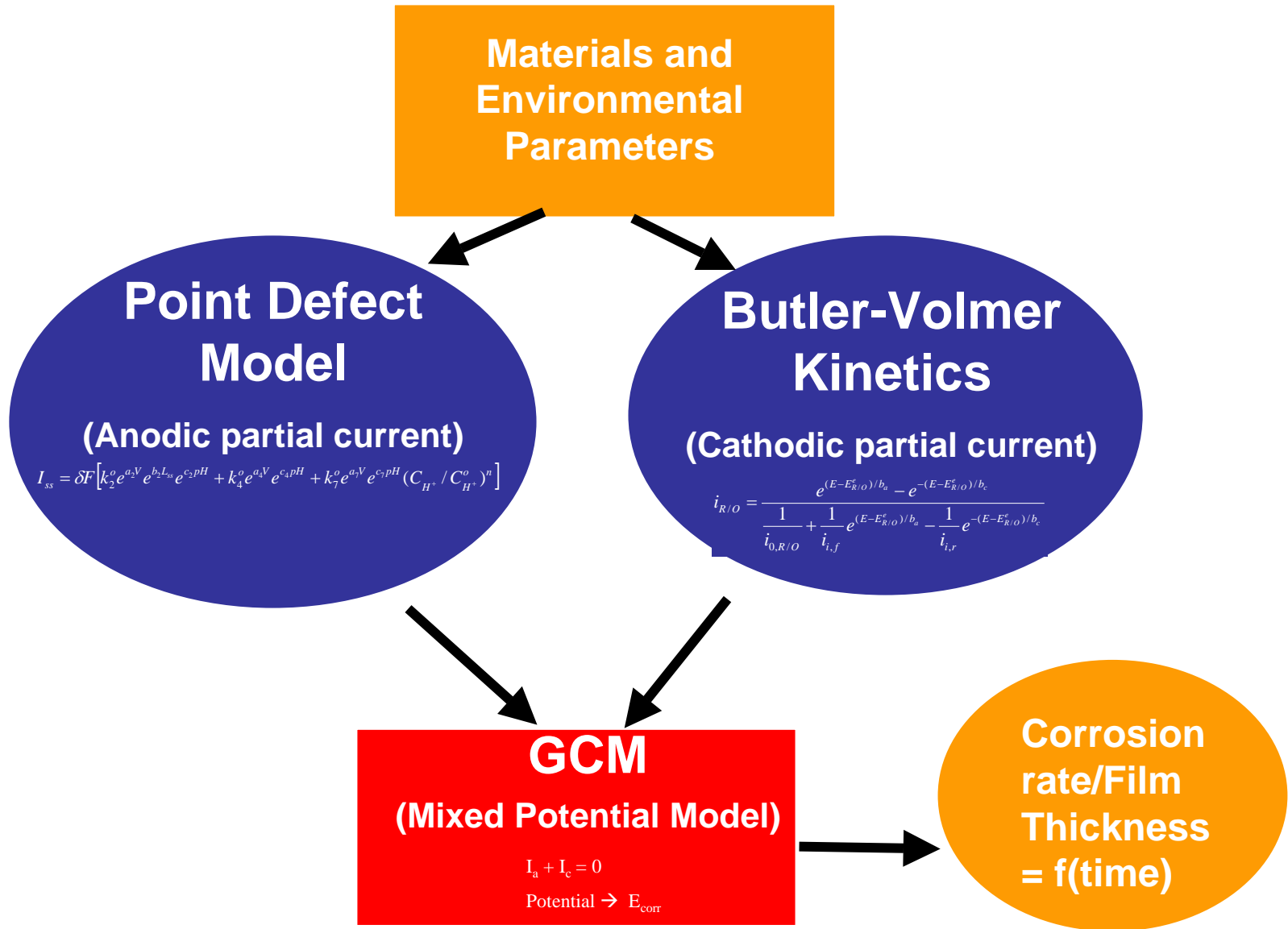
# Key Path Forward Elements

- **Path Forward to reduce remaining uncertainties**  
[Path forward agreement reviewed with Nuclear Regulatory Commission (NRC)]
  - **Benchmark mechanistic general corrosion model**
  - **High sensitivity corrosion rate measurements to establish passive film growth rate and metal loss rate**
  - **Characterize passive film structure, stability and potential degradation mechanisms over range of electrochemical potentials**

# Features of Current General Corrosion Model

- **Assumes thin electrolyte film (HCl/NaCl) on metal surface in equilibrium with oxygen in ambient air**
- **Corrects oxygen solubility for salting in / salting out effects**
- **Currently assumes transmission of cation interstitials in barrier layer is rate controlling for the partial anodic current**
- **Yields corrosion potential and corrosion current density corrected for temperature**
- **Not yet optimized because of lack of measured values for some parameters and because principal defect in Alloy 22 barrier layer not firmly established**
- **Yields realistic results for stainless steels**

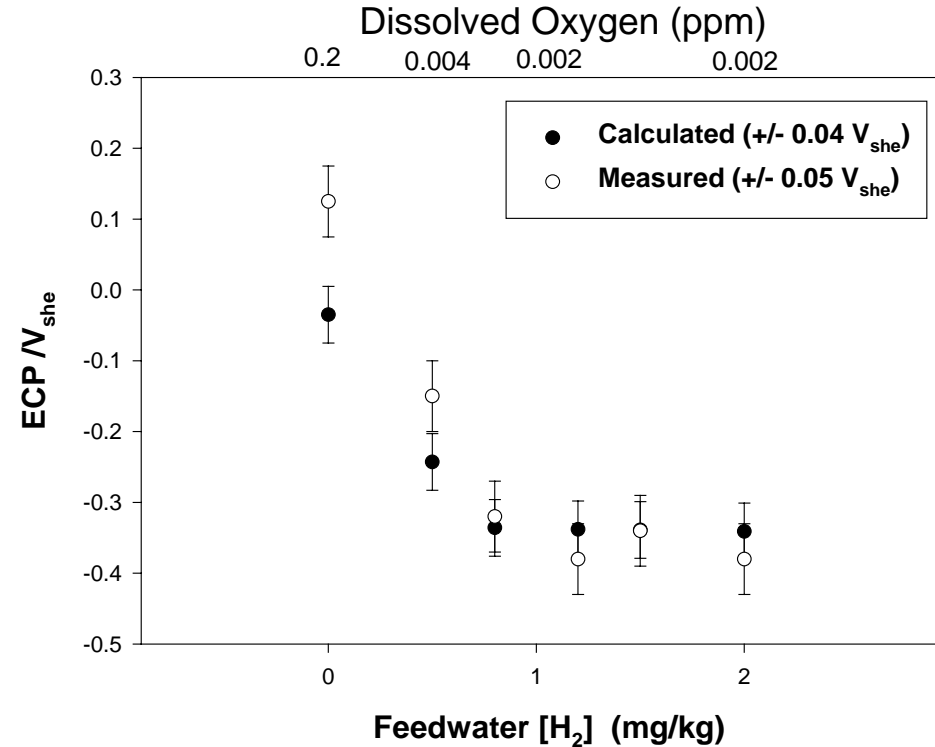
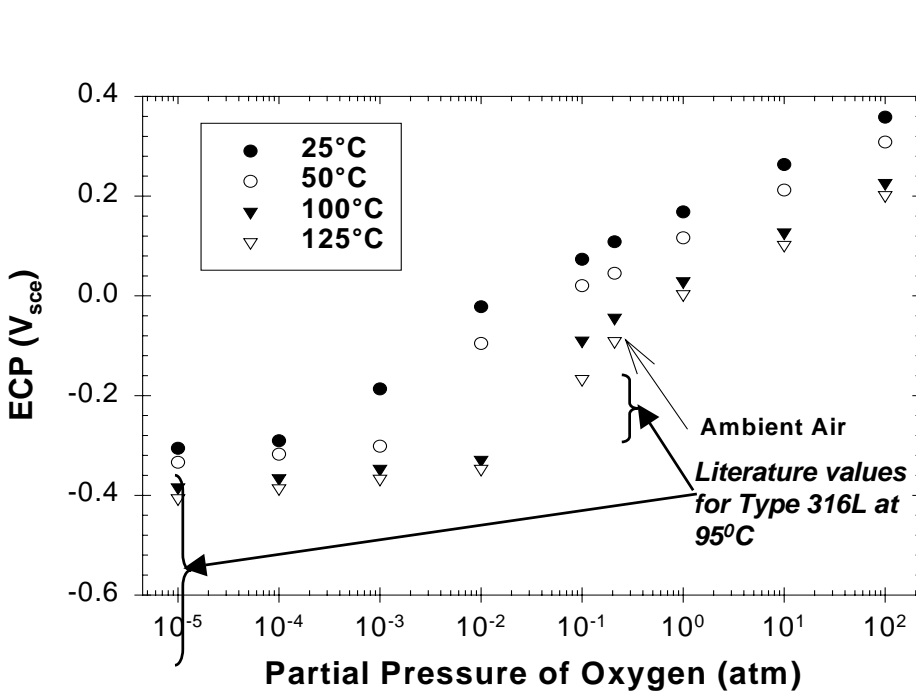
# Structure of the GCM\*





# Calculated Corrosion Potential vs. Dissolved Oxygen

## (Comparison of calculated versus measured values)



**NOTE:** The following parameter values were assumed: Stainless Steel, pH= 3, saturated NaCl solution, electrolyte film thickness = 0.01 cm.

**Comparison of calculated and measured ECP for Leibstadt BWR.**

# Details of General Corrosion Model (GCM)

## Butler-Volmer Kinetics of the Cathodic Processes

- **Two cathodic processes assumed –  $\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2$  (HER) and  $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$  (OER)**
- **Kinetics described by a generalized Butler-Volmer equation**
- **Kinetic parameters yet to be determined**
- **Used extensively in modeling corrosion processes in the heat transport circuits of water cooled nuclear reactors**

# Benchmark GCM - Path Forward

- Measure kinetic parameters for cathodic reactions (oxygen reduction and hydrogen evolution) and metal dissolution in passive state to obtain exchange current densities over a range of temperatures
- Obtain electrochemical impedance data (at frequencies from 10 kHz down to ~0.1 mHz) to quantify parameters in point defect model
- Measure kinetics of passive film growth under potentiostatic polarization and determine film thicknesses using ellipsometry or capacitance measurements
- Measure the (indirect) quantum tunneling constants using a fast redox couple, such as  $\text{Fe}(\text{CN})_6^{3-/4-}$ , by determining charge transfer rate across passive interface
  - Constants will be used to correct  $i_0$  values for redox reactions as  $f(\text{film thickness over time})$

# GCM Path Forward

(Continued)

- **Experimentally measured Alloy 22 values for various model parameters will be incorporated**
- **A localized corrosion damage algorithm being developed by Dr. Macdonald for predicting pitting damage function will be incorporated in future work**
- **Complete benchmarking of mechanistic model and compare predictions with relevant kinetic data**

# High Sensitivity Corrosion Rate Measurements

## Path Forward

- **Adding new ‘bounding’ test environments (Basic Saturated Water [BSW] at 110°C and Simulated Saturated Water [SSW] at 120°C) to long term corrosion tests**
  - Testing in all environments continues (5 and 10 years)
- **Since very low measured two year corrosion rate values approximate measurement uncertainty range**
  - Installing thinner, larger surface area coupons and high sensitivity corrosion probes in LTCTF
  - Continuing Atomic Force Microscope (AFM) studies on polished specimens with inert masked areas (markers)
    - ◆ Quantifies rates and reveals how ‘uniform’ attack is (nanometer scale)

# High Sensitivity Corrosion Rate Measurements

## Path Forward

(Continued)

- **Using electrochemical impedance spectroscopy and linear polarization (LP) as other test methods to corroborate very small corrosion rates**
  - ◆ **Corroborate weight loss data from long term tests**
  - ◆ **Evaluate effects of films formed during container fabrication and welding and from long term thermal exposure in repository**
- **Running long term potentiostatic tests over range of passive potentials, environments, temperatures, metallurgical conditions, etc. to establish corrosion rates and to compare to weight loss measured rates**

# Characterize Passive Film Structure, Stability and Potential Degradation Mechanisms - Path Forward

- **Calculating Pourbaix diagram to establish expected thermodynamically stable phases in surface film**
- **Growing thicker oxide films at higher temperatures (90°-175°C) using autoclaves, humid air and/or electrochemical techniques (anoxic polarization) to accelerate growth for compositional/structural studies**
- **Determining chemical, structural, and mechanical properties of films, including thickened films using ‘battery’ of surface analytical techniques**
  - **Need multiple techniques to resolve ambiguities where spectral lines coincide or when different morphological forms of the oxide film exist**

# Path Forward: Pourbaix Analysis of Passive Film Stability of Alloy 22

## Objective:

Pourbaix diagrams for Alloy 22 under various repository environments to determine: (1) the regions of thermodynamic stability of the metals, their oxides, and soluble ions, and (2) the environmental conditions under which Alloy 22 passivates.

Activity of each metal in Alloy 22 will determine the phase stability regions in the Pourbaix diagrams.

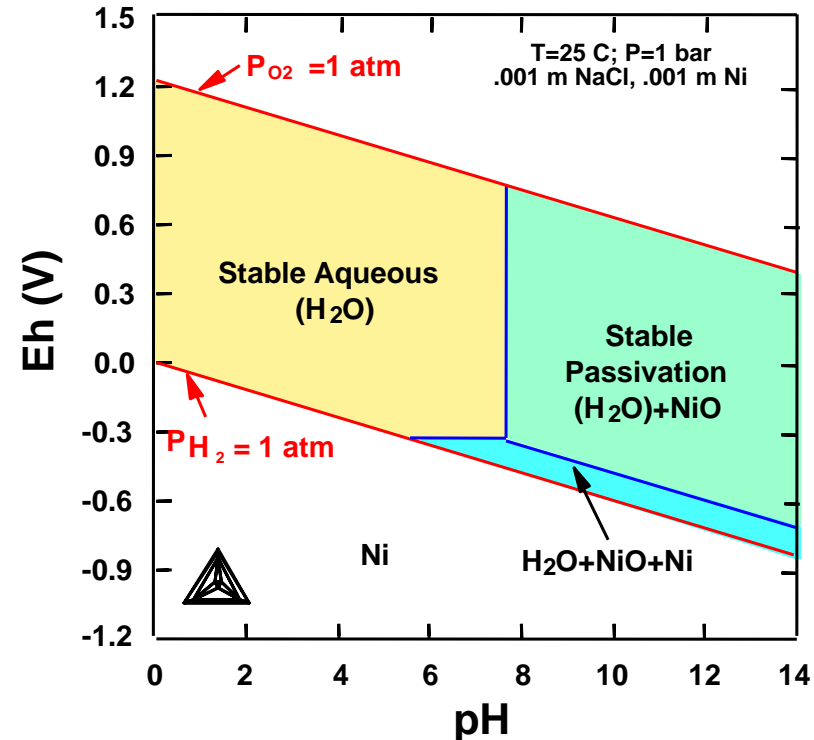
## Projected Schedule of Activities:

Step 1: Pure metals (code validation)-- example shown for Ni

Step 2: Binary alloy, Ni-Cr, in a simple moderately concentrated environment

Step 3: Ternary alloy Ni-Cr-Mo, and role of additions such as W and Fe, in the same environment

Step 4: Repeat steps 1-3 by considering as variables: Temperature, and solution composition (e.g., chloride ion at high concentration, sulfur containing species, and other species)



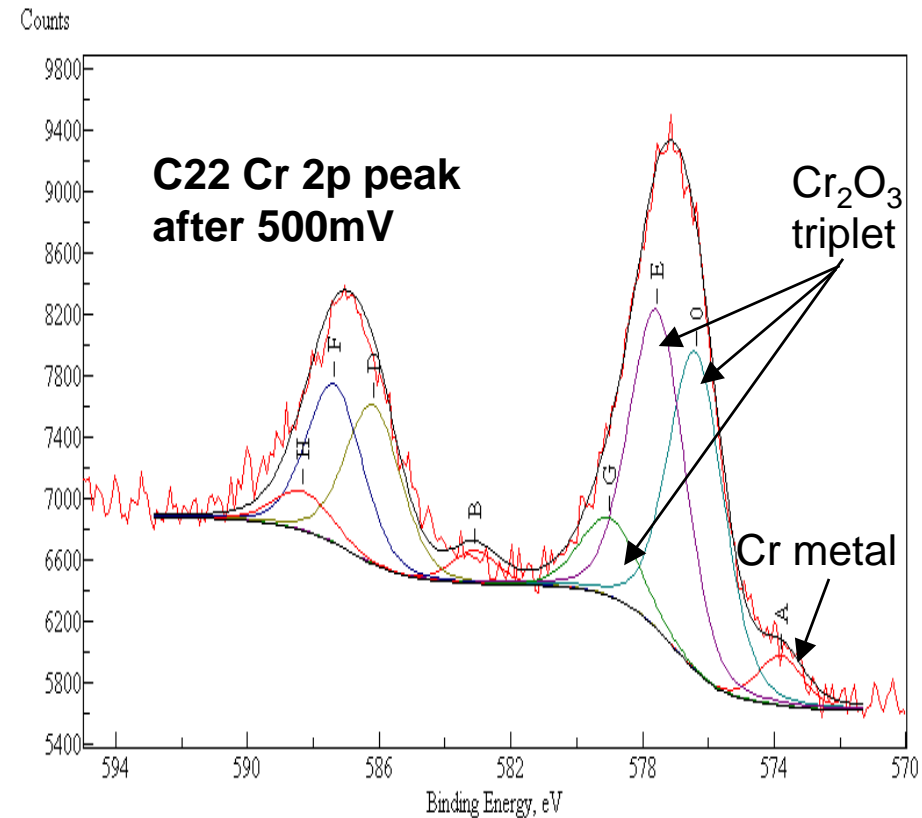
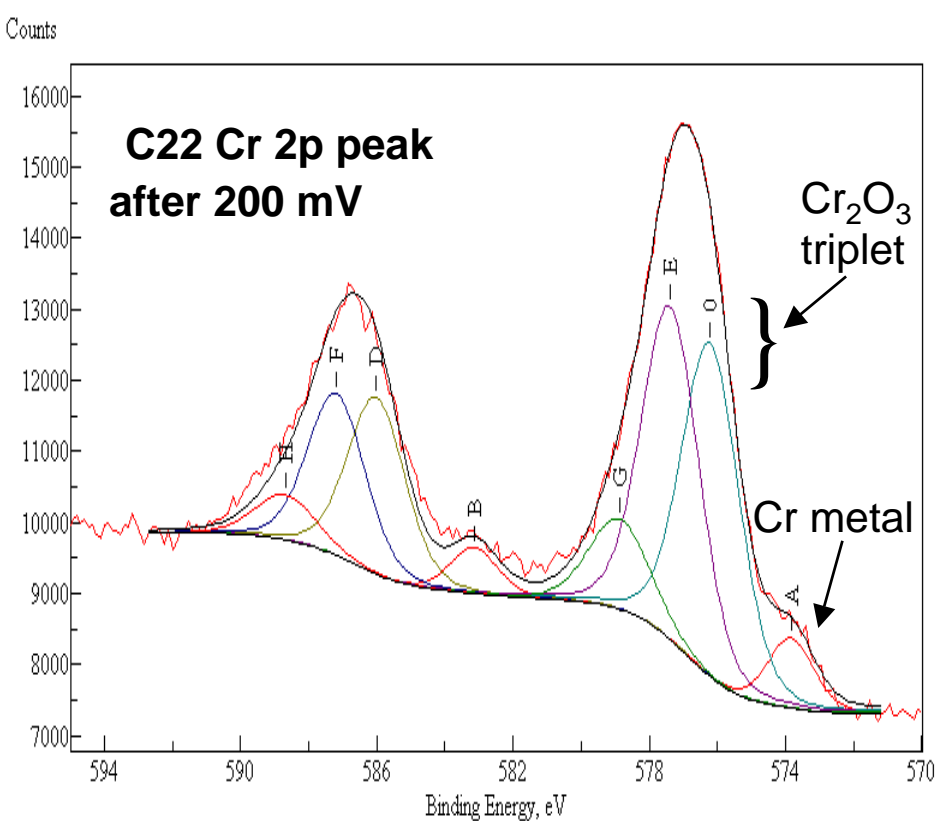


# Literature Characterization of Alloy 22 Films

## X-Ray Photoelectron Spectroscopy (XPS)

(1M NaCl, pH 1, 85°C)

( A.C. Lloyd, D.W. Shoemith, Corrosion 2001 Poster Session)



- Only Cr<sup>3+</sup> present in oxide at both potentials
- Based on Cr<sub>oxide</sub>/Cr<sub>metal</sub> signal ratio, oxide significantly thicker at 500mV

# Characterize Passive Film Structure, Stability and Potential Degradation Mechanisms - Path Forward

(Continued)

- **Correlating changes in  $E_{\text{corr}}$  measured in LTCTF with compositional changes in passive film over time**
- **Determining changes in film structure/ properties on high defect concentration cold-worked materials**
- **Comparing films formed on Alloy 22 with other similar passive film alloys with longer industrial experience such as Alloys C, C-4, C-276 and 625**

# Characterize Passive Film Structure, Stability and Potential Degradation Mechanisms - Path Forward

(Continued)

- **Resolving kinetics of film growth and metal loss:**
  - Logarithmic, parabolic or higher order?
  - Does film growth become linear as it thickens?
  - Does film become brittle and spall off?
  - What are film dissolution kinetics?
- **Assessing film defect structures, diffusing species and film/solution interface reactions**
  - AC impedance
  - Cyclic polarization
  - Contact electrical resistance
- **Utilizing focused tests to resolve relevance of potential film degradation mechanisms**

# Thermodynamic Considerations

- **Surface analyses indicate rate controlling Alloy 22 corrosion film is likely a Mo, Ni and W containing  $\text{Cr}_2\text{O}_3$**
- **These observations are consistent with Pourbaix diagram predictions, i.e.  $\text{Cr}_2\text{O}_3$  is one of the thermodynamically predicted oxide phases over a range of pH and corrosion potential and thus is likely to persist over time**
  - **Estimated potential-pH range for waste package relevant environments mostly overlays  $\text{Cr}_2\text{O}_3$  stability range**
  - **Detailed calculation of Alloy 22 specific Pourbaix diagrams over range of relevant environments and temperatures in Path Forward effort**

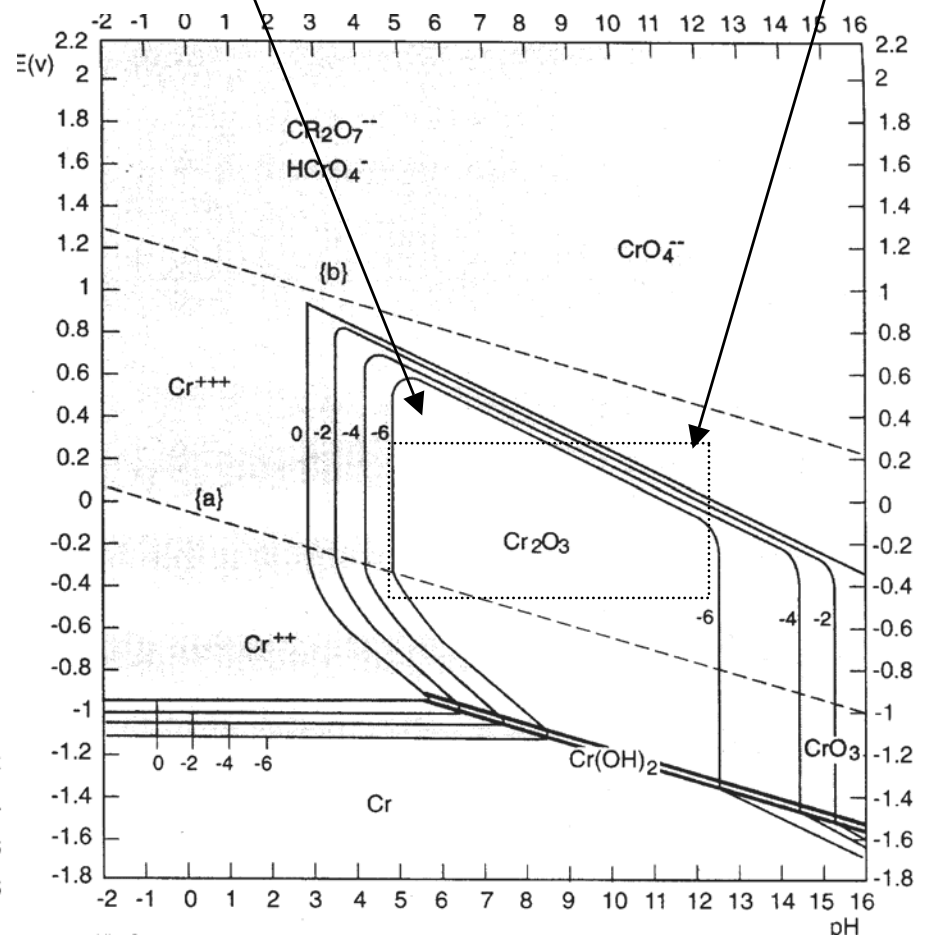
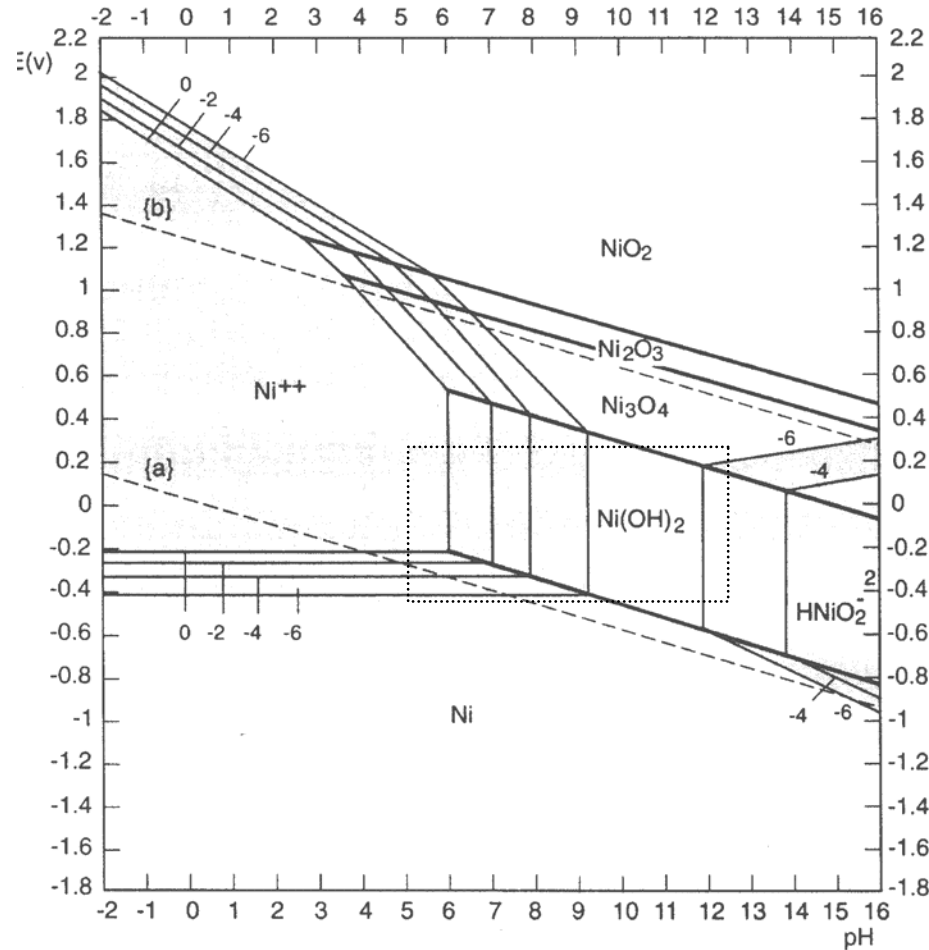
# Thermodynamic stability domain of $\text{Cr}_2\text{O}_3$ corrosion film on Alloy 22 (Ni-22 Cr-13 Mo-3.5 W) indicated qualitatively by 25°C Pourbaix Diagrams

Ni

$\text{Cr}_2\text{O}_3$  stability domain

Cr

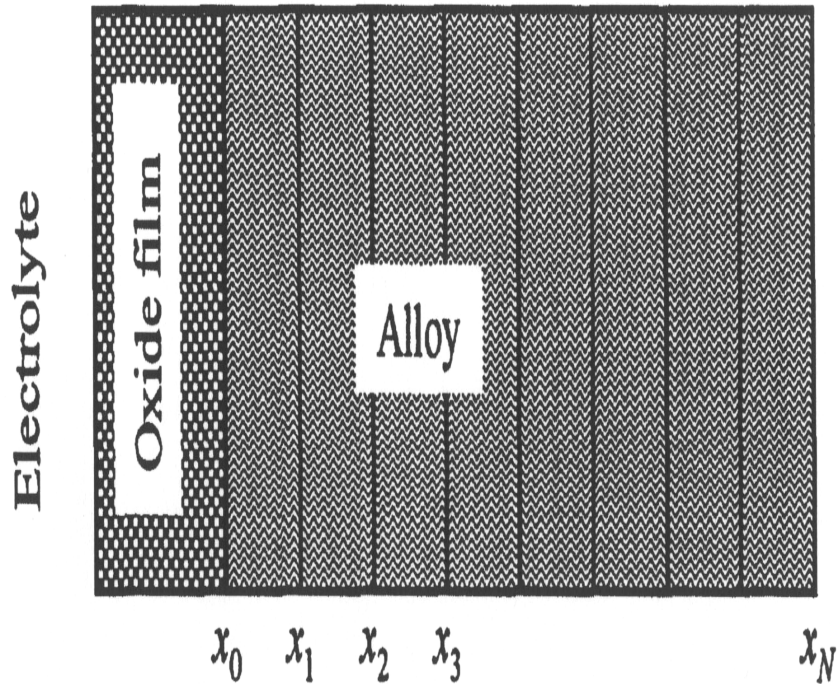
Estimated potential-pH range for relevant environments



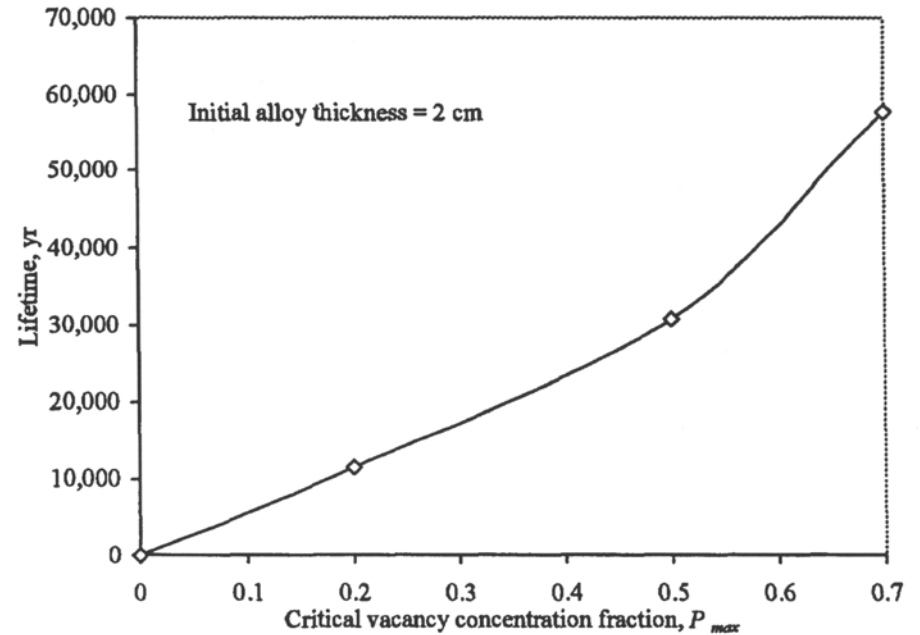
# Potential Passive Film Degradation Mechanisms

- **To decrease uncertainty, need to better understand fundamental mechanisms that, although unlikely for Alloy 22 in repository conditions, could degrade passive layer protectiveness over time, e.g.**
  - **Defect accumulation as layer sweeps through metal**
    - ◆ **NRC is modeling effect of vacancy accumulation at metal interface - depending on film “spalling” threshold, vacancy concentration could accelerate effective corrosion rate if applicable (see next chart)**
  - **Debris accumulation — long term corrosion product effects on layer**
    - ◆ **In LTCTF, silica deposition appears protective. Other “buffer” ions may also form beneficial surface deposits (e.g.  $\text{SO}_4=$ ,  $\text{CO}_3=$ )**
    - ◆ **However, it is possible that deposits could lead to selective removal of protective ions reaching passive film**

# Vacancy Defect Accumulation Degradation Model (D.S. Dunn et al, Paper 01125, Corrosion 2001)



Once vacancy fraction between  $x_0$  and  $x_1$  exceeds threshold,  $P_{max}$ , new metal/film interface defined as  $x_1$ . Process repeats until corrosion front penetrates alloy thickness



Calculated lifetime of Alloy 22 plate versus critical vacancy concentration,  $P_{max}$

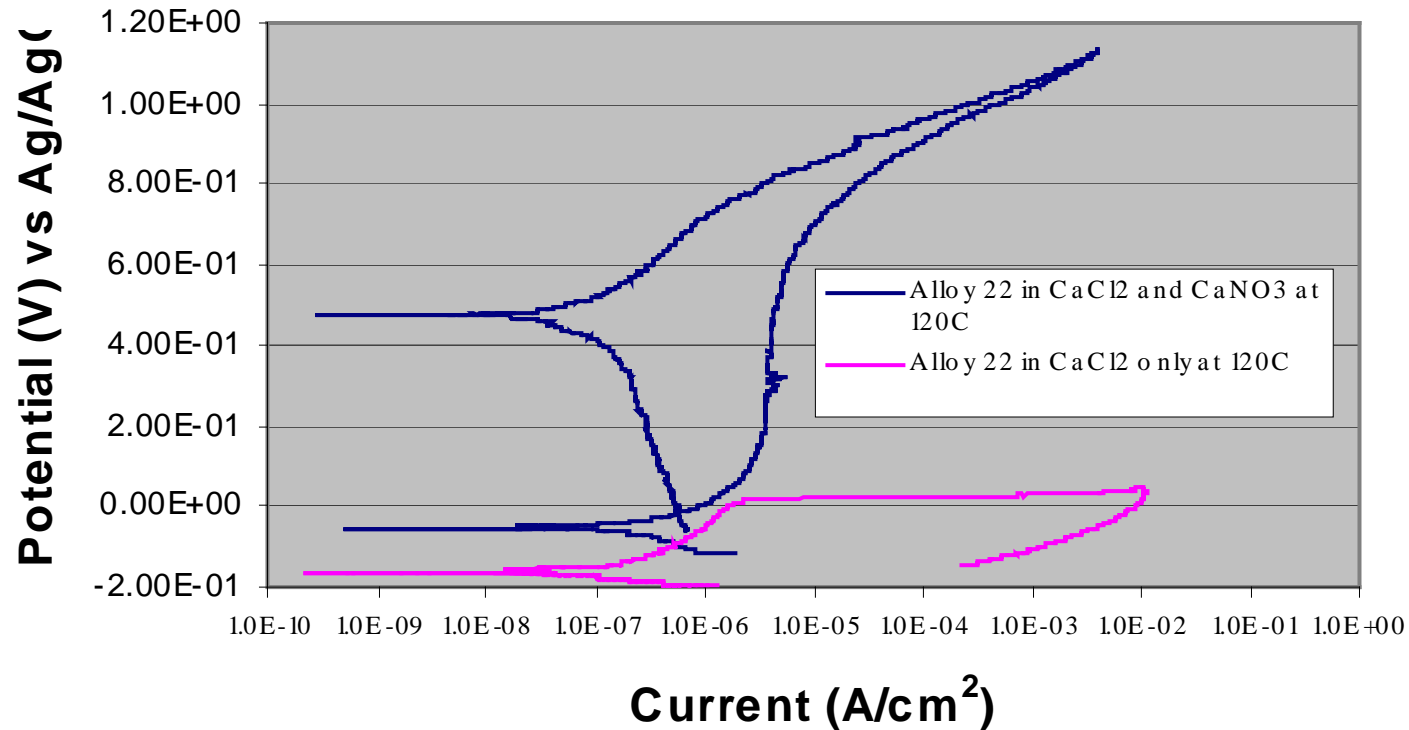
# Potential Passive Film Degradation Mechanisms

(Continued)

- **Quasi-transpassive dissolution — if corrosion potential increases over time, transpassive dissolution may occur aided by high Mo content**
  - ◆ LLNL running long-term potentiostatic tests as  $f(\text{applied potential})$  to establish passive/transpassive transition potential
  - ◆ Corrosion potential measurements as  $f(\text{time})$  up to four years exposure in range of relevant environments, temperatures underway
- **Coalescence of metastable pits**
  - ◆ Could occur due to vacancy agglomeration or impurity precipitates in structure - long term potentiostatic tests will help resolve issue
- **Diffusion induced grain boundary migration**
  - ◆ Unlikely at waste package surface temperatures
- **Changes in film amorphous or crystalline structure or composition (metastable phases)**
  - ◆ Film structure will be characterized analytically and thermodynamically to confirm long term stability



# Effect of Near Saturation Chloride and Nitrate Variants on Transpassive Potentials of Alloy 22 at 120°C using Cyclic Polarization Technique



**Nitrate addition appears to mitigate against any possible localized corrosion effects**