Sandia National Laboratories
yucca mountain project
OCRWM Lead Laboratory for Repository Systems

SAND2008-0259C

Corrosion Testing to Support Performance Predictions for the Yucca Mountain Nuclear Waste Repository

Tampa, Florida

January 31, 2008

Doug Wall
Manager, YMP Corrosion Science Department
Yucca Mountain Project

Not LSN Relevant

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,
for the United States Department of Energy's National Nuclear Security Administration
under contract DE-AC04-94AL85000.

Sandia National Laboratories

Acknowledgements

- Kevin Mon - *Areva Np*
- Gopal De - *Apogen*
- Bryan Bullard - *Areva Np*
- David Enos - *Sandia National Laboratories*
- Charles Bryan - *Sandia National Laboratories*
- Russ Jarek - *Sandia National Laboratories*
- Peter Swift - *Sandia National Laboratories*

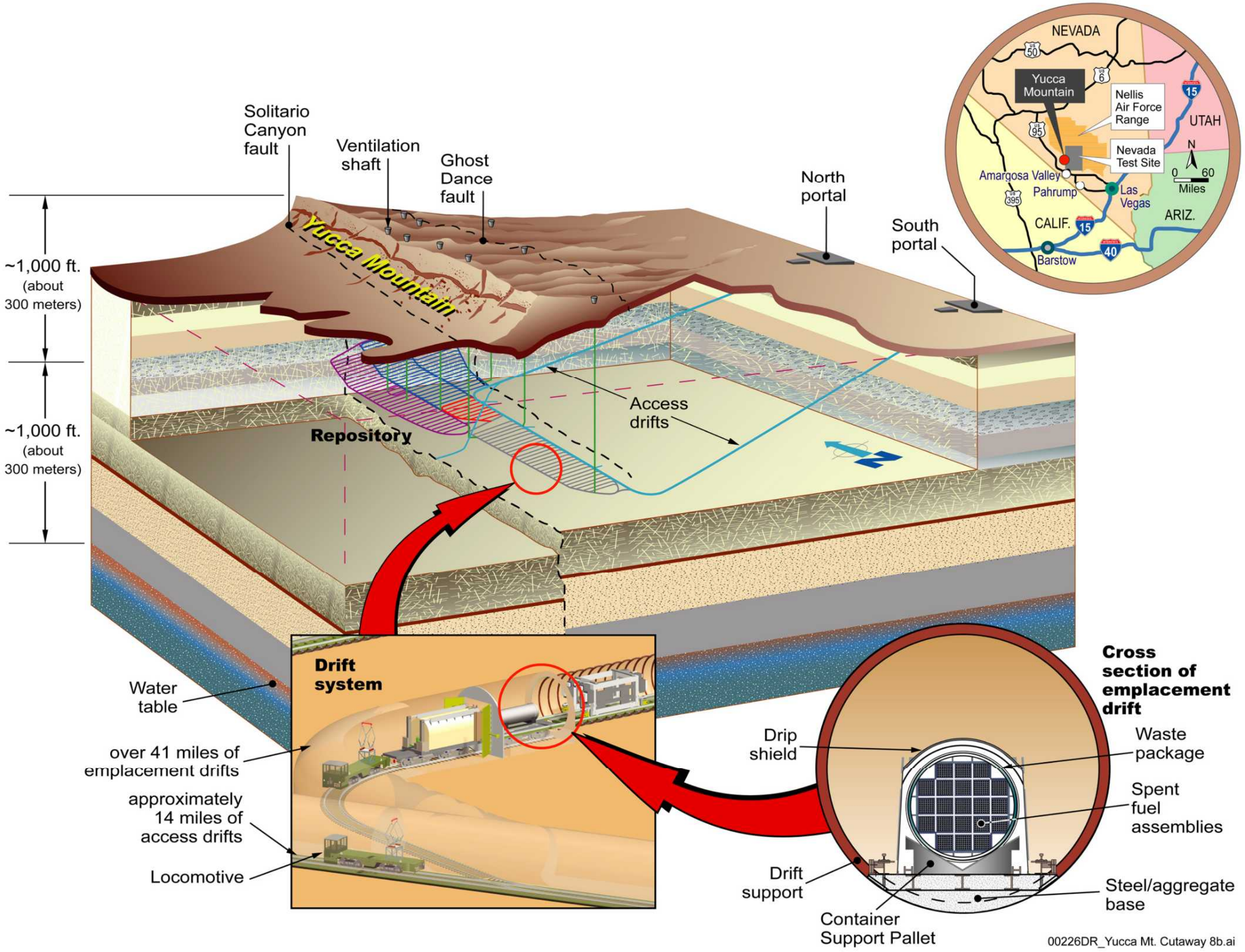
Motivation

- The Yucca Mountain Program (YMP) studies corrosion behavior of barrier materials in order to understand how corrosion-based failure modes could contribute to radionuclide release to the environment.
- A key goal of corrosion modeling is to not underestimate the frequency, rate or accumulated damage from corrosion processes.

Outline of Presentation

- Introduction to the YMP barrier system
- Total system performance assessment (TSPA)
- Role of the engineered barrier
- Corrosion processes considered for TSPA implementation
- Materials and environments
- General corrosion of Alloy 22 under seepage conditions
- Localized corrosion of Alloy 22 under seepage conditions
- Localized corrosion of Alloy 22 under deliquescence conditions

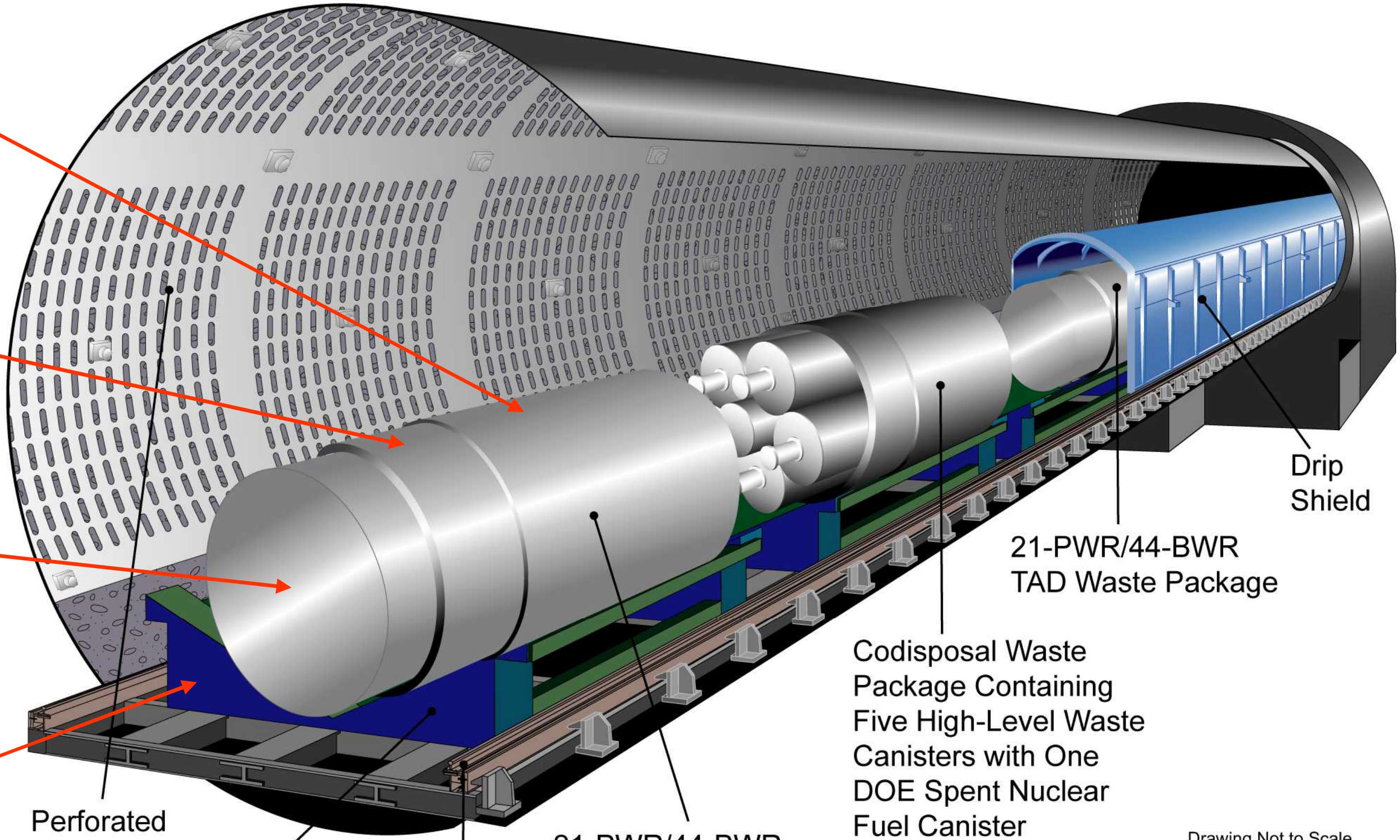
The Proposed Yucca Mountain HLNW Repository Relies on Natural and Engineered Barrier Systems to Meet Dose Regulations



Total System Performance Assessment – Key Attributes

- Estimates groundwater concentrations at the accessible environment
- Estimates dose to the reasonably maximally exposed individual who:
  - Lives in the accessible environment above the point of highest concentration in the contaminated plume
  - Has diet and lifestyle of today's inhabitants of Amargosa Valley
  - Drinks 2 liters of contaminated groundwater per day with concentrations based on annual water use of 3000 acre-feet
  - Is an adult
- Includes the effect of parameter and model uncertainty (Monte-Carlo-based analysis)
- Systematically addresses the questions in the 'risk-triplet'
  - What can happen?
  - How likely is it to happen?
  - What are the consequences if it does happen?

The Primary Purpose of the Engineered Barrier is to Reduce the Rate of Seepage Water Contacting the Inner Vessel



Drawing Not to Scale
00663DC_101a.ai

Corrosion Processes Considered for TSPA Implementation

- Error in waste emplacement
- *General corrosion of the waste package*
- *General corrosion of the drip shields*
- *SCC of waste packages*
- SCC of drip shields
- *Localized corrosion (LC) of waste packages*
- LC of drip shields
- Hydride cracking of waste packages
- Hydride cracking of drip shields
- *Microbiologically Influenced Corrosion (MIC) of the waste packages*
- MIC of drip shields
- Internal corrosion of waste packages prior to breach
- Mechanical impact on waste package
- Mechanical impact on drip shields
- *Early failure of waste packages*
- Early failure of drip shields
- Copper corrosion in EBS
- LC on the waste package outer barrier (WPOB) due to dust deliquescence
- *Physical form of waste package and drip shield*
- Oxygen embrittlement of the drip shields
- Mechanical effects at EBS component interfaces
- Rockfall
- Creep of metallic materials in the waste package
- Creep of metallic materials in the drip shield
- Volume increase of corrosion products impacts waste package
- Electrochemical effects in EBS
- Thermal sensitization of waste packages
- Thermal sensitization of drip shields
- Thermal expansion/Stress of in-drift EBS components
- Gas generation (H_2) from waste package corrosion
- Radiolysis
- Radiation damage in EBS

Differentiation of General and Localized Corrosion

- General Corrosion
  - The rate of material loss at every location is, on average, the same: results in uniform thinning rate for a structure
  - Is a direct function of the environment
  - Rate is affected by coupling to dissimilar metals
  - Typically of concern for corrosion allowance metals (e.g., carbon steel)
- Localized Corrosion
  - Non-uniform attack of a metal
  - The rate of attack at a small site (e.g., microns to millimeters) can be orders of magnitude greater than the general corrosion rate
  - A local environment develops that is more concentrated and more aggressive than the surrounding environment
  - Initiation is promoted by geometric constraints that result in diffusion barriers and cause concentration gradients to develop
  - Typically of concern for passive metals (e.g., nickel, titanium, stainless steels, aluminum, etc.)

Materials Receiving Credit for Barrier Function

- Drip Shield
  - Grade 7 Titanium plates
  - Grade 29 Titanium supports
  - Grade 7 / Grade 28 / Grade 29 welds

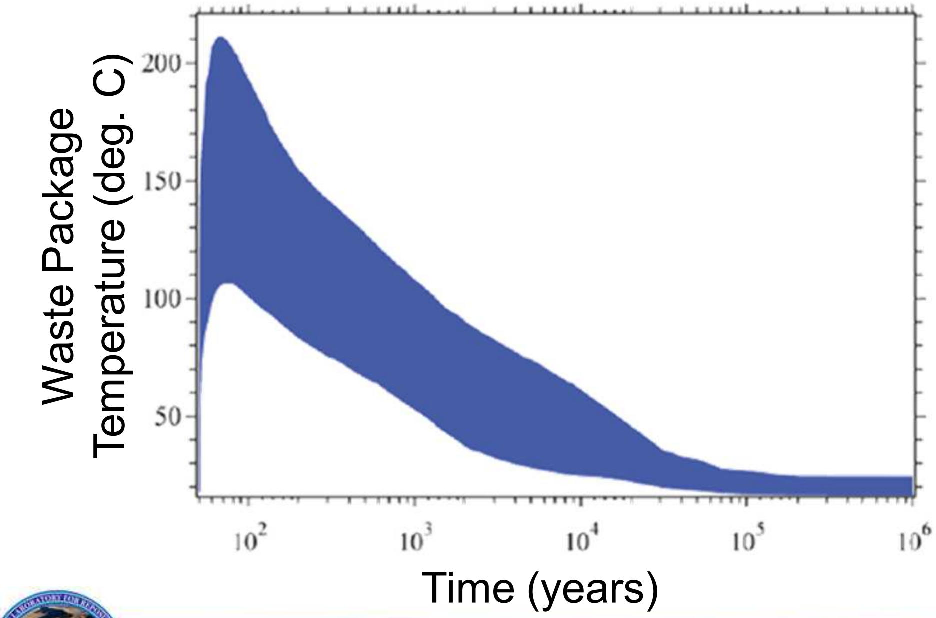
	Al	Pd	Ru	Ti	V
Grade 7	-	0.12-0.25	-	Bal.	-
Grade 28	2.5-3.5	-	0.08-0.14	Bal.	2-3
Grade 29	5.5-6.5	-	0.08-0.14	Bal.	3.5-4.5

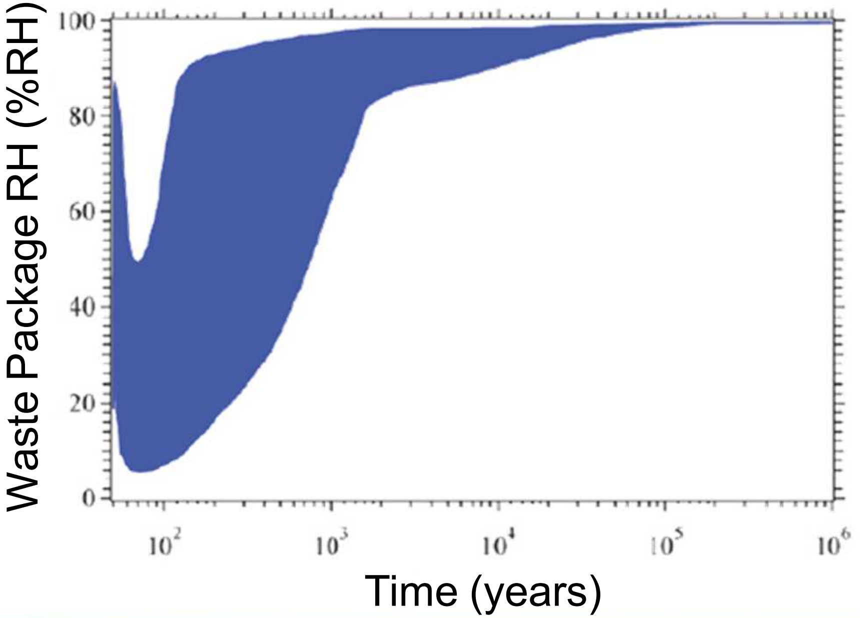
- Waste Package
  - Annealed Alloy 22
  - Annealed Alloy 22 welds (longitudinal weld)
  - Stress relieved Alloy 22 welds (circumferential closure weld)

Alloy 22 Composition (N06022)							
Co	Cr	Fe	Mn	Mo	Ni	V	W
2.5 max	20-22.5	2.0-6.0	0.5 max	12.5-14.5	Bal.	0.35 max	2.5-3.5

Environments that may potentially contact the barrier materials

- Seepage environments
  - Electrolyte chemistry defined by ambient water composition
  - Unlimited contaminant supply
  - Electrolyte may be continuous
- Deliquescent environments
  - Electrolyte chemistry defined by salt-bearing dusts deposited during repository ventilation
  - Limited contaminants
  - Electrolyte bound in the dust layer as droplets



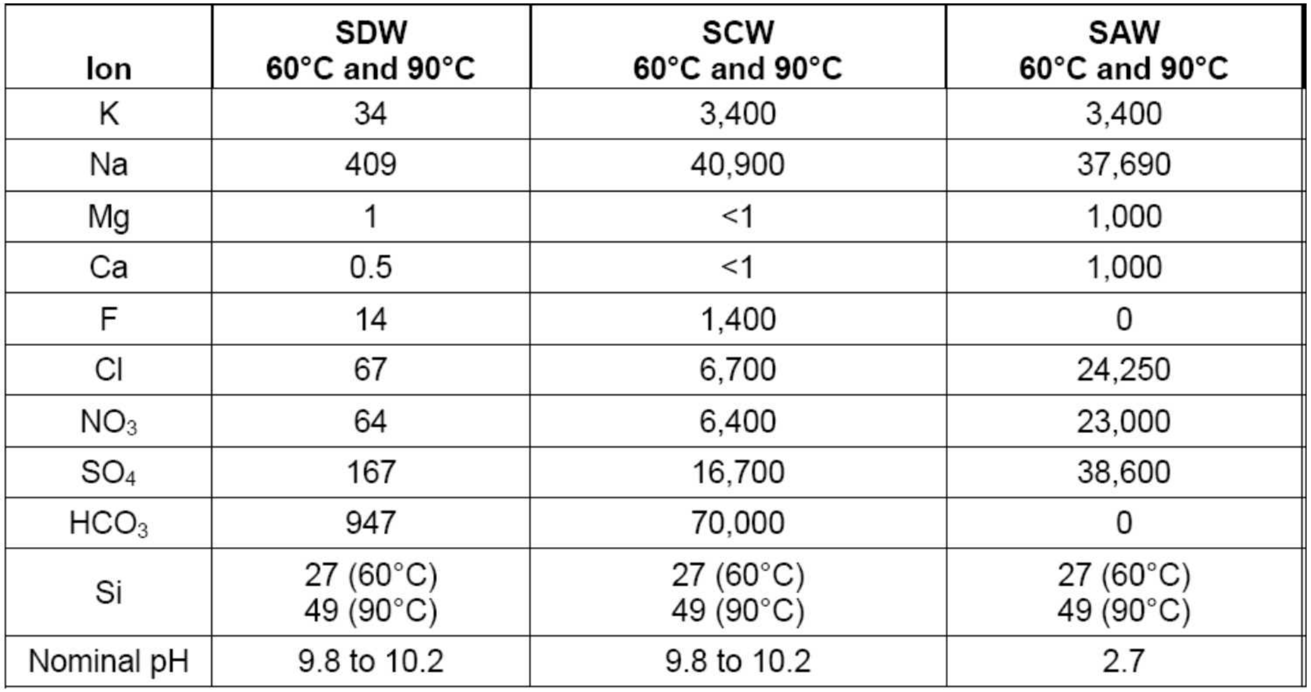


General Corrosion of Alloy 22 Under Seepage Conditions

- TSPA implementation
  - General corrosion process operates continuously following repository closure
  - No upper temperature threshold
  - Microbially influenced corrosion represented as a multiplication factor
  - Rate is dependent on
    - temperature
  - Rate is independent of
    - chemical environment
    - welding and thermal aging
    - time
- Experimental program
  - Weight change measurements following long-term exposures
    - Temperature dependence
    - Environmental independence
    - Variability in corrosion rate from sample-to-sample
    - Welding and thermal aging independence
  - Linear polarization testing following short-term equilibration
    - Temperature dependence
    - Welding and thermal aging independence

Long-Term Exposure Testing Conditions

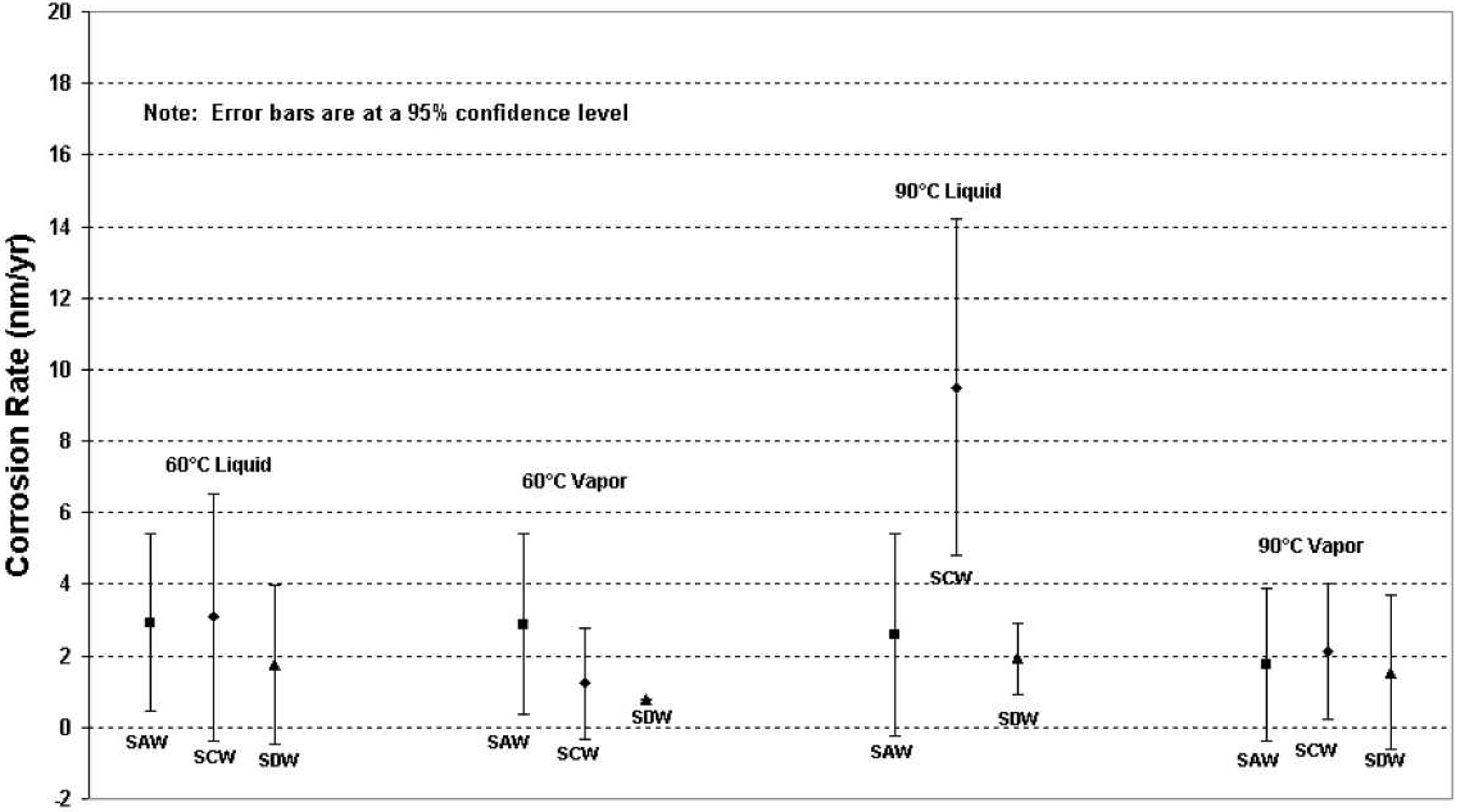
- Electrolytes: Simulated dilute water (SDW), Simulated acidified water (SAW) and Simulated concentrated water (SCW)
- Temperatures: 60ºC and 90ºC
- Specimen configurations: welded and non-welded, creviced and non-creviced
- Specimen locations: inundated, atmospheric and waterline



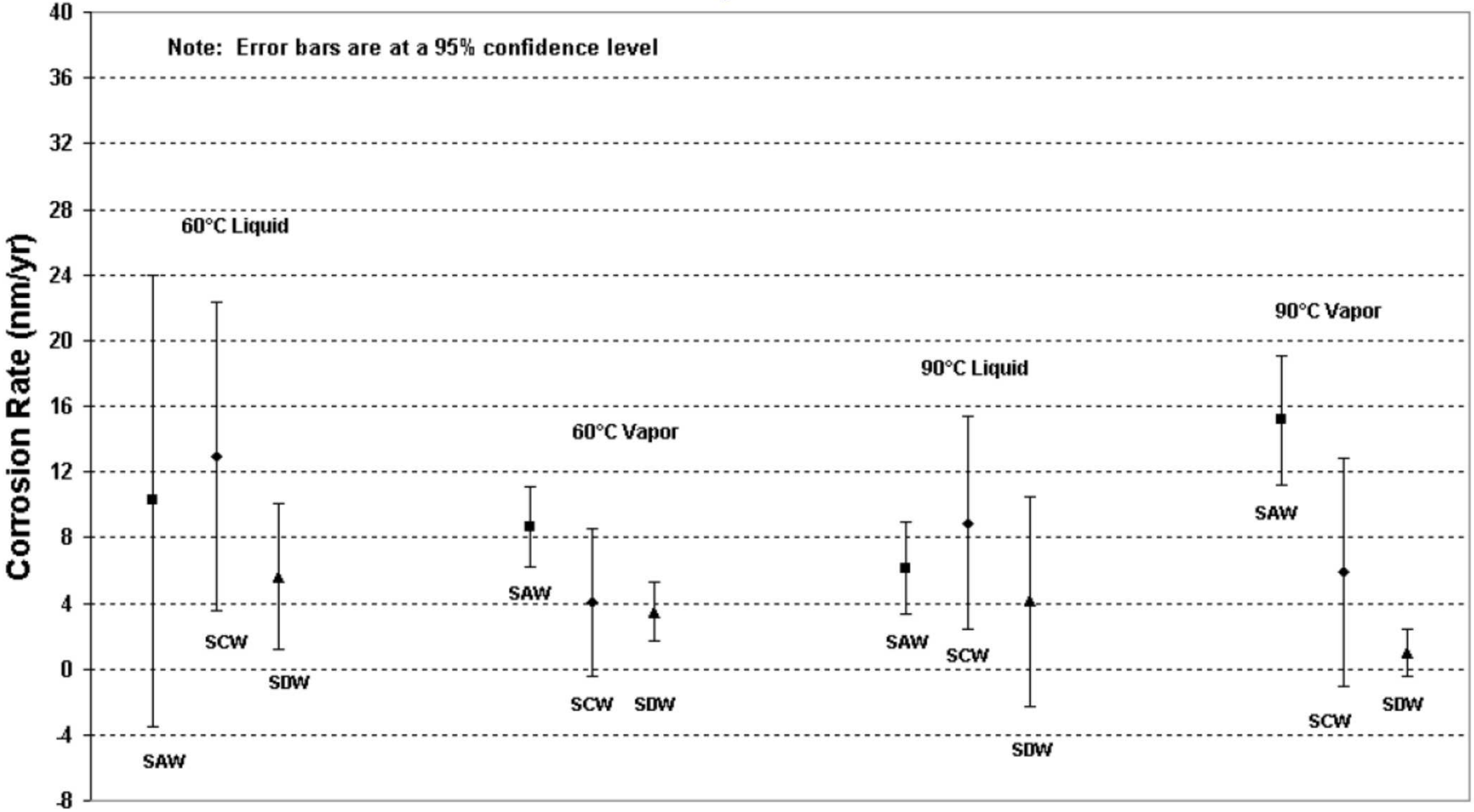
Ion	SDW 60°C and 90°C	SCW 60°C and 90°C	SAW 60°C and 90°C
K	34	3,400	3,400
Na	409	40,900	37,690
Mg	1	<1	1,000
Ca	0.5	<1	1,000
F	14	1,400	0
Cl	67	6,700	24,250
NO_3	64	6,400	23,000
SO_4	167	16,700	38,600
HCO_3	947	70,000	0
Si	27 (60°C) 49 (90°C)	27 (60°C) 49 (90°C)	27 (60°C) 49 (90°C)
Nominal pH	9.8 to 10.2	9.8 to 10.2	2.7

(concentrations are in parts per million)

Corrosion Rates for Non-Creviced Specimens After Five Years of Exposure

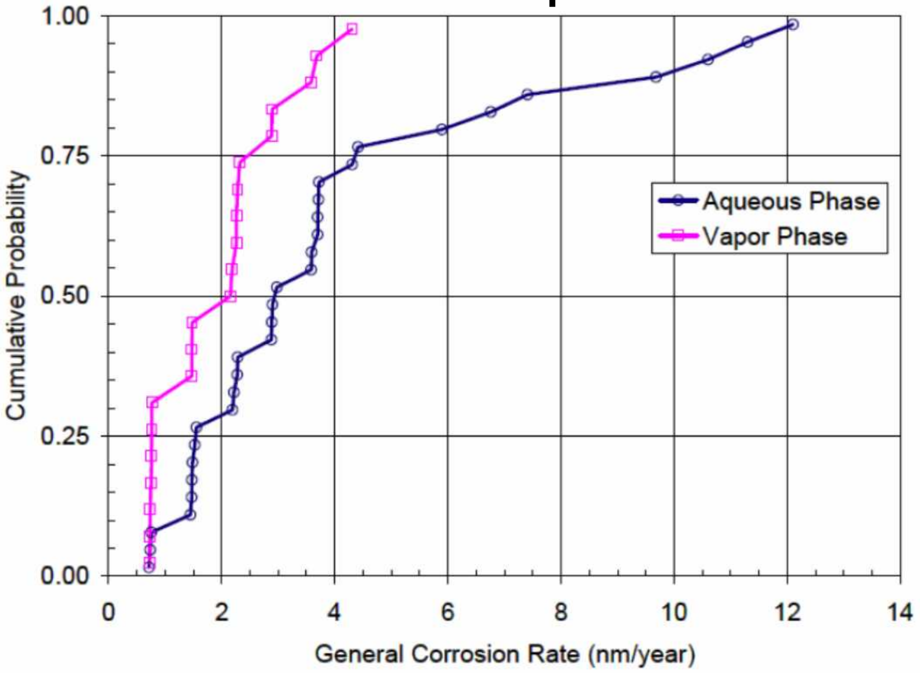


Corrosion Rates for Creviced Specimens After Five Years of Exposure

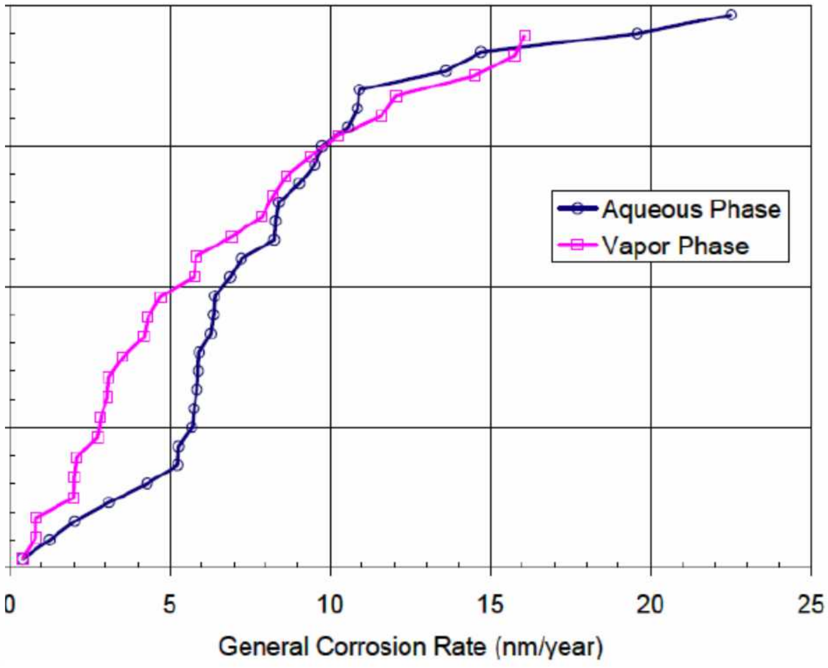


The Measured Corrosion Rates for Alloy 22 are Similar in the Aqueous and Vapor Phases

5-year, Alloy 22
non-creviced specimens

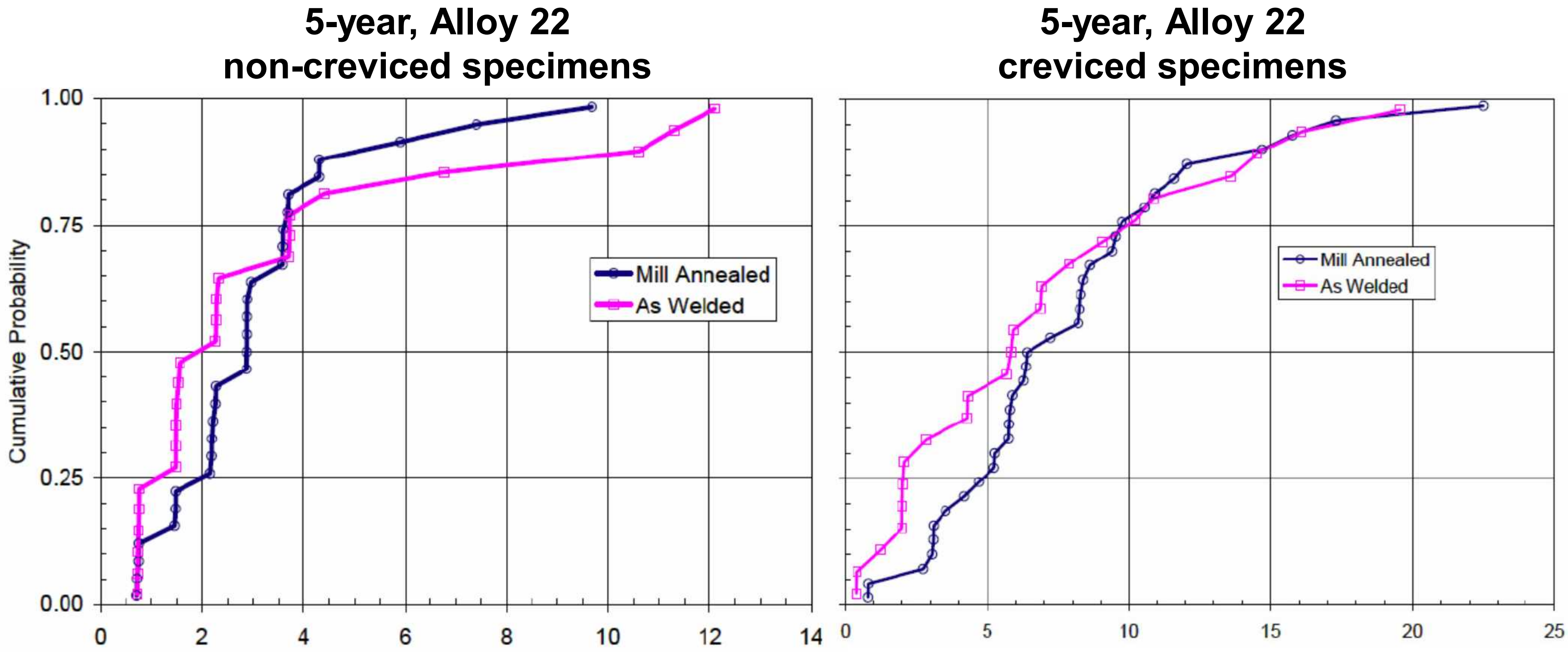


5-year, Alloy 22
creviced specimens



Data from the aqueous and vapor phases are combined in the model for general corrosion rate.

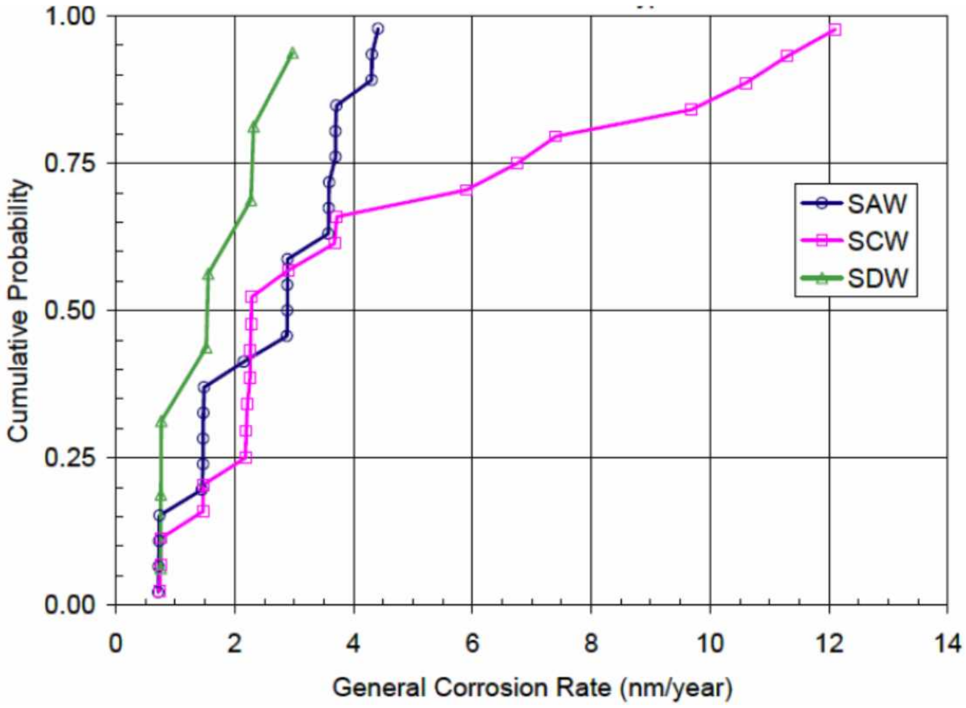
The Measured Corrosion Rates for Alloy 22 are Similar for Mill Annealed and As-Welded Specimens



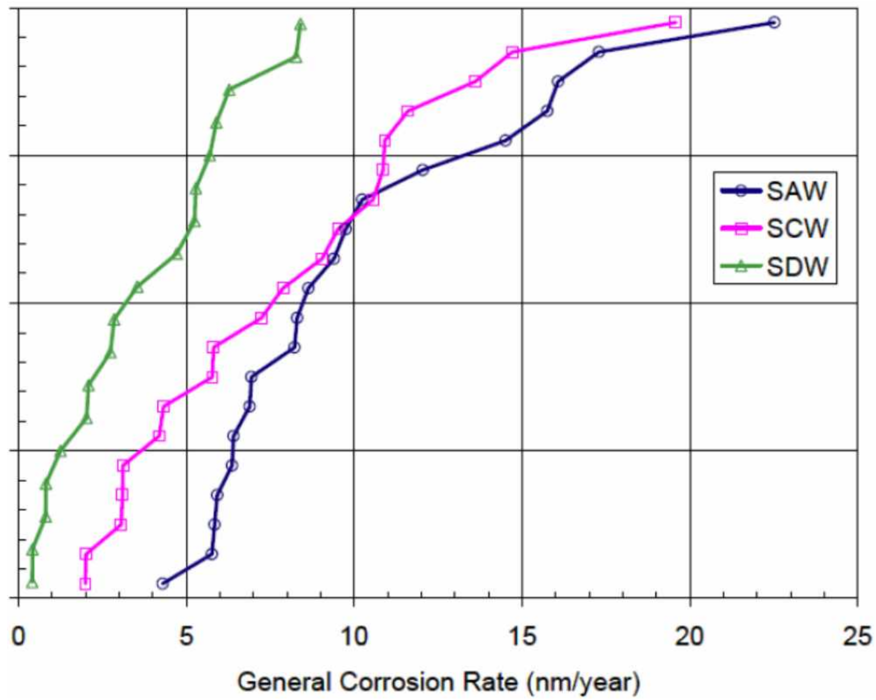
General corrosion rate is modeled as being independent of metallurgical condition.

The Measured Corrosion Rates for Alloy 22 are Similar for SAW, SDW and SCW Electrolytes

5-year, Alloy 22
non-creviced specimens

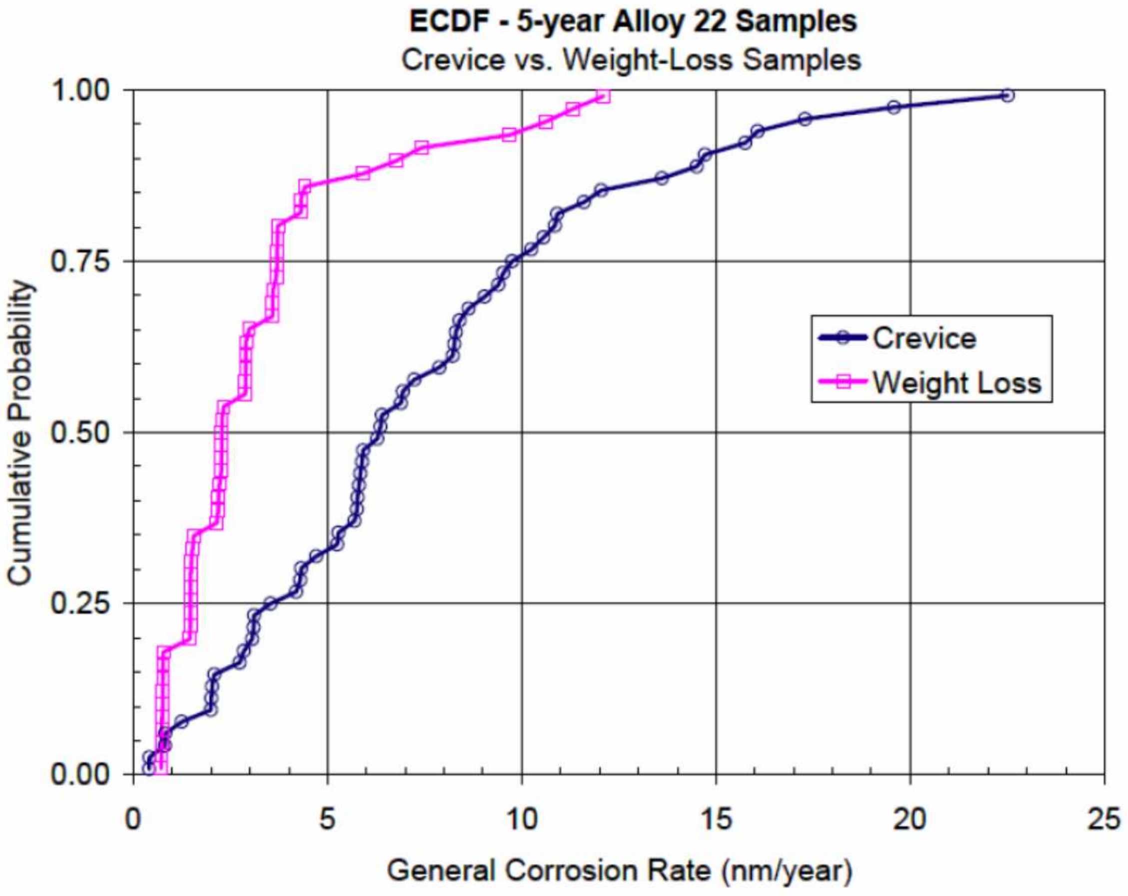


5-year, Alloy 22
creviced specimens



General corrosion rate is modeled as being independent of electrolyte composition.

The Measured Corrosion Rates for Creviced Alloy 22 Specimens are Higher than for Non-Creviced Alloy 22 Specimens



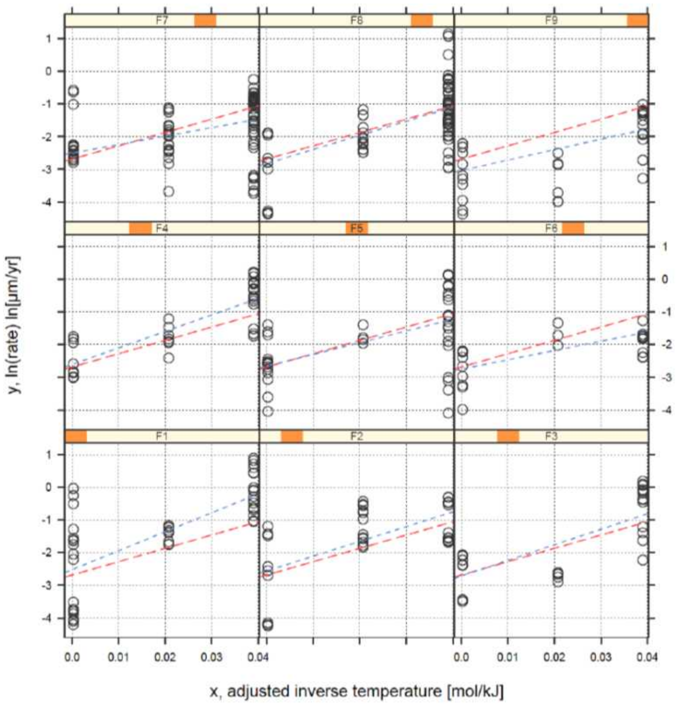
The ECDF for the creviced specimens is used as the general corrosion rate of Alloy 22 such that the rate is <u>not underestimated</u>.

Linear Polarization Test Conditions

- Specimen configuration: creviced
- Temperatures: 60ºC, 80ºC and 100ºC
- Electrolytes: multi-ionic salt solutions
- Test sequence
  - Sample polished to 600 grit
  - Immersed in electrolyte for 24 hours
  - Potential scanned from -20 to +20 mV vs. open circuit potential at 0.167 mV/s
- Data analysis
  - Fit data to Butler-Volmer equation to determine the corrosion current density
  - Convert corrosion current density to corrosion rate
  - Fit corrosion rate vs. T data to determine apparent activation energy

Example of a specimen configuration used for electrochemical testing. Other configurations were also used.

Linear Polarization Testing Yields an Environment-Independent Apparent Activation Energy of 40.78±11.75 kJ/mol



$$y = \ln(R_T) = \beta_0 + \beta_1 x$$

$$x = \left[\frac{1}{R \cdot T_0} - \frac{1}{R \cdot T}\right]$$

$$\beta_0 = \ln(R_o), \quad \beta_1 = E_a$$

Solutions used to determine temperature dependence

Solution	Solution Description	Activation Energy kJ/mol
F1	1 m NaCl + 0.05 m KNO_3	58.06
F2	1 m NaCl + 0.15 m KNO_3	45.22
F3	1 m NaCl + 0.5 m KNO_3	47.58
F4	3.5 m NaCl + 0.175 m KNO_3	50.63
F5	3.5 m NaCl + 0.525 m KNO_3	35.86
F6	3.5 m NaCl + 1.75 m KNO_3	28.46
F7	6 m NaCl + 0.3 m KNO_3	26.00
F8	6 m NaCl + 0.9 m KNO_3	43.24
F9	6 m NaCl + 3 m KNO_3	31.96

Output DTN: MO0612WPOUTERB.000, file: *Output_dataF-fit.txt*.

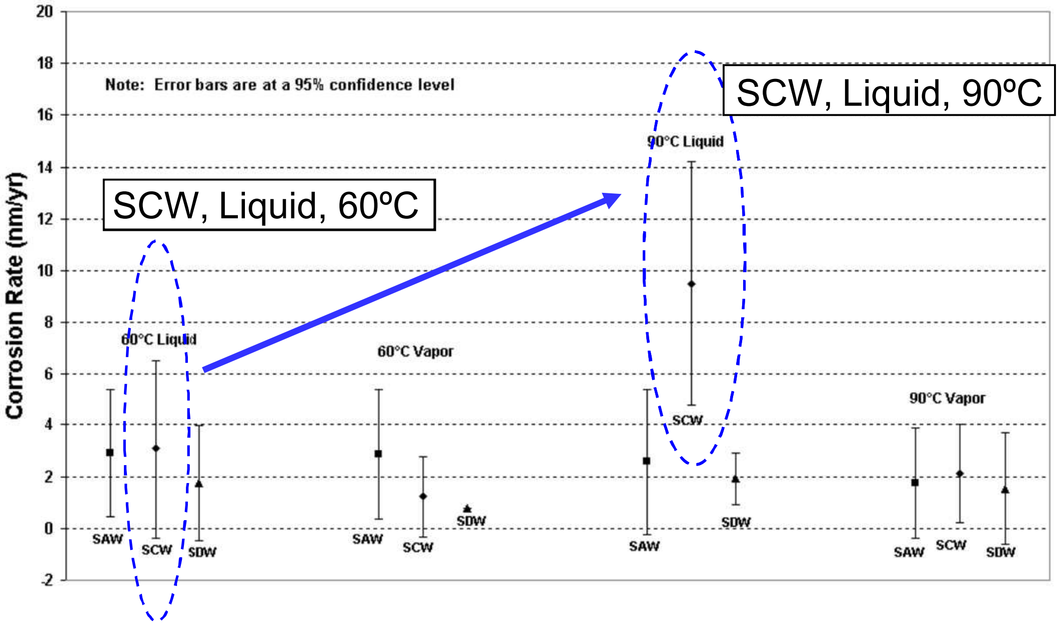
Solutions not used to determine temperature dependence

Solution Description	Temperature Range °C	Activation Energy kJ/mol
4 *M* NaCl	45 to 105	7.69
4 *M* NaCl + 0.04 *M* Na_2SO_4	45 to 105	51.03
4 *M* NaCl + 0.4 *M* Na_2SO_4	45 to 105	45.84
12 m $CaCl_2$ + 6 m $Ca(NO_3)_2$	100 to 150	35.61
5 *M* $CaCl_2$	30 to 120	28.07
5 *M* $CaCl_2$ + 0.5 *M* $Ca(NO_3)_2$	60 to 120	−15.13

N: MO0612WPOUTERB.000, file: *Output_data2-fit.txt*.

Long Term Data Establish the Range of Apparent Activation Energy

Non-creviced specimens exposed to SCW liquid phase comprised the only data set with a discernable temperature dependence.



SCW, Liquid, 60ºC

SCW, Liquid, 90ºC

100,000 bootstrap analyses were performed on these data sets to estimate apparent activation energy:

Mean = 40.51 kJ/mol

Min = 5.67 kJ/mol

Max = 64.94 kJ/mol

To include the observed long-term temperature dependence, the short term data are truncated at -3 and +2 standard deviations:

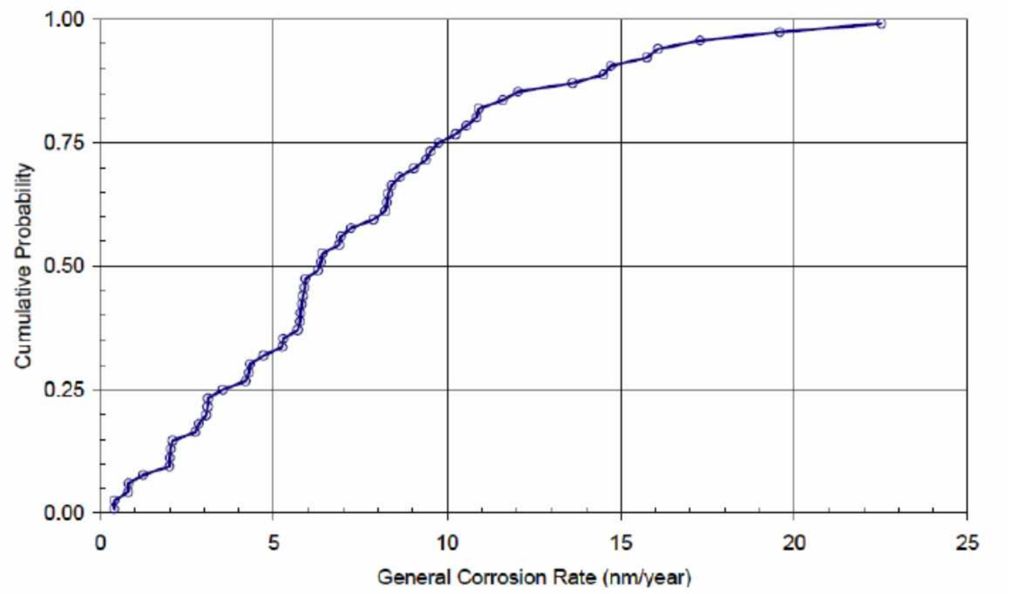
Mean = 40.78 kJ/mol

-3 stdev = 5.54 kJ/mol

+2 stdev = 64.28 kJ/mol

Summary of Alloy 22 General Corrosion Model Under Seepage Conditions

$$\ln(R_T) = \ln(R_0) + E_a\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

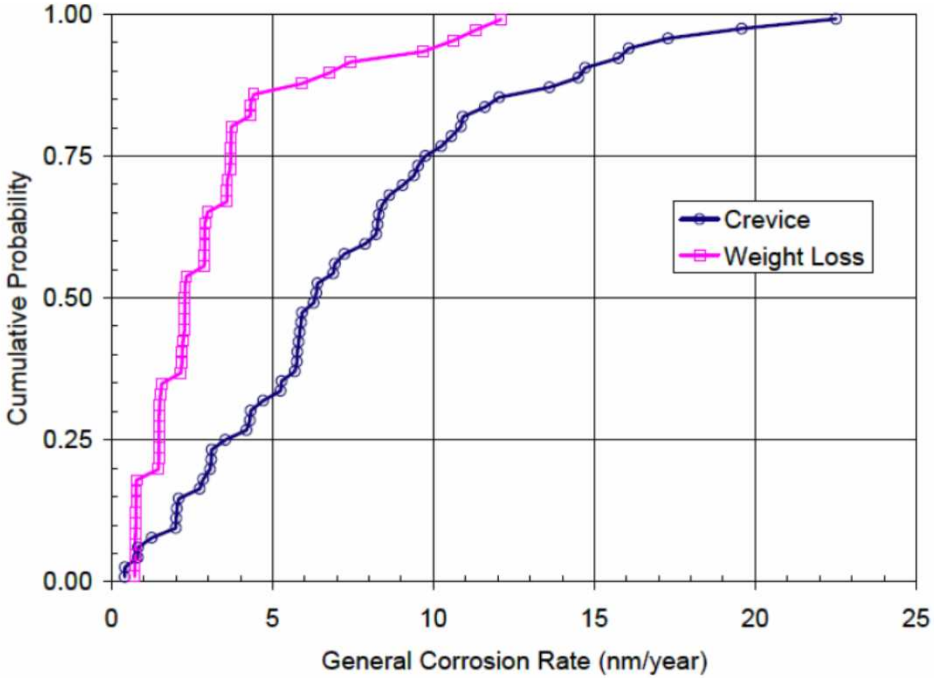


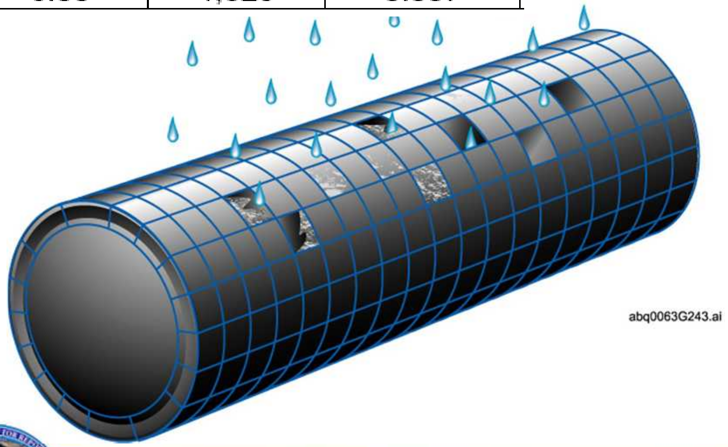
ECDF of crevice sample data used for R_0 at T_0 = 60°C

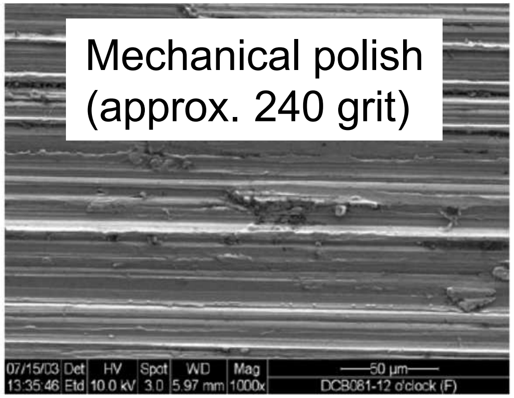
Mean	= 40.78 kJ/mol
-3 stdev	= 5.54 kJ/mol
+2 stdev	= 64.28 kJ/mol

The Corrosion Model is Expected to Overestimate General Corrosion of the Alloy 22 Waste Package

Exposure Time		Mean Rate
(years)	(days)	(µm/yr)
0.0027	1	0.460
0.0027	1	1.250
0.019	7	0.100
0.154	56	0.182
0.50	183	0.076
1.00	365	0.025
2.00	730	0.014
5.00	1,825	0.007




abq0063G243.ai


Mechanical polish (approx. 240 grit)

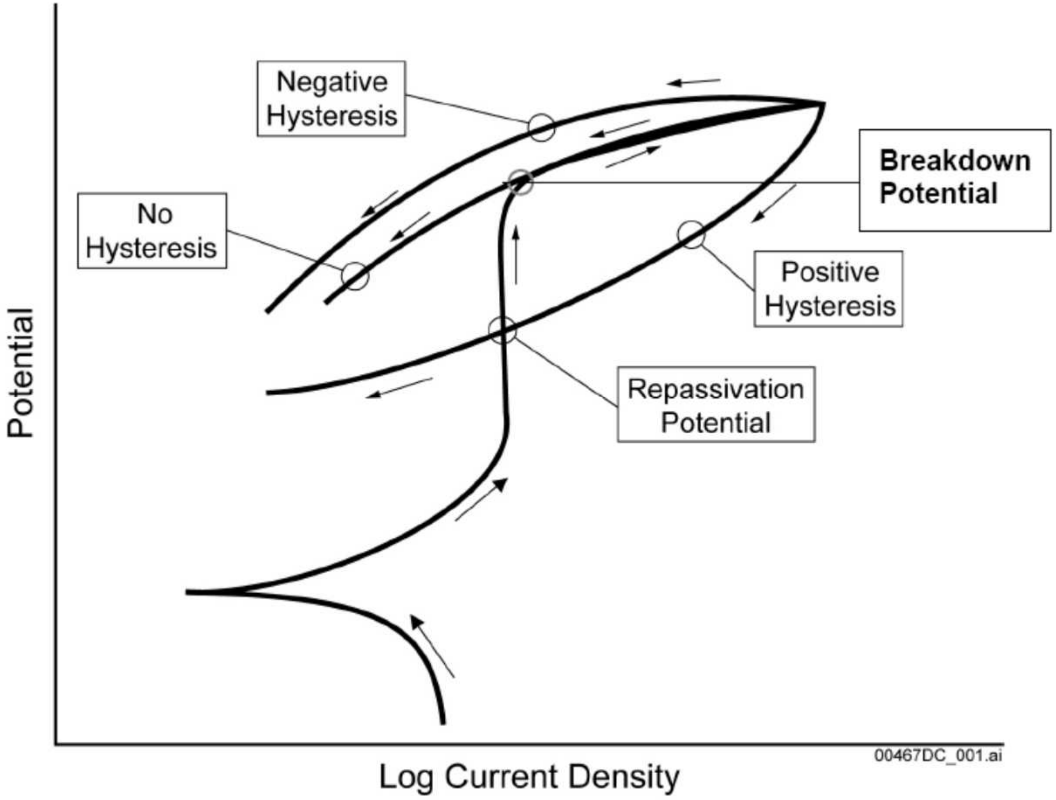

Finish of back side of crevice coupons

Localized Corrosion of Alloy 22 Under Seepage Conditions

- TSPA Implementation
  - Localized corrosion initiates when a critical potential criterion is met (a function of electrolyte composition and temperature)
  - Once initiated, localized corrosion penetrates the material at a high rate until breach occurs
  - Localized corrosion only occurs for seepage contacting the waste package
  - If RH < 70% and seepage contacts the waste package then localized corrosion is assumed to initiate due to salt separation
- Experimental Program
  - Short term electrochemical tests used to measure repassivation potential
  - Long-term measurements used to measure open circuit potential
  - Validate predictions against observations following long-term exposures

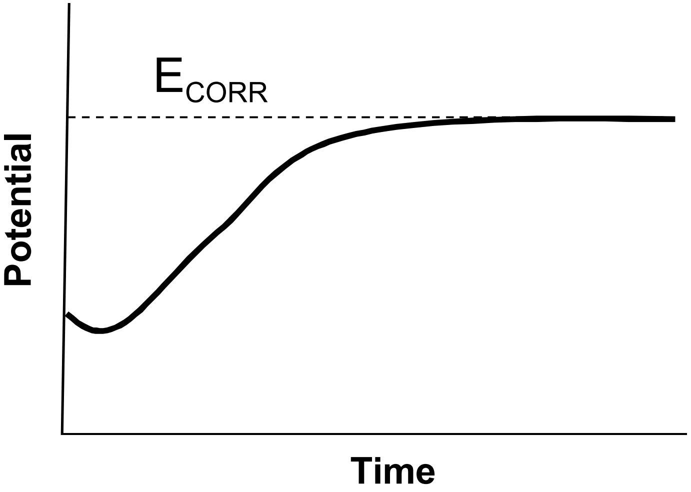
Localized Corrosion is Modeled to Initiate When A Critical Potential Criterion is Met

If $\Delta E \leq 0$, initiate localized corrosion
$\Delta E = E_{RCREV} - E_{CORR}$



E_{RCREV} = crevice repassivation potential: the potential below which a propagating crevice will repassivate

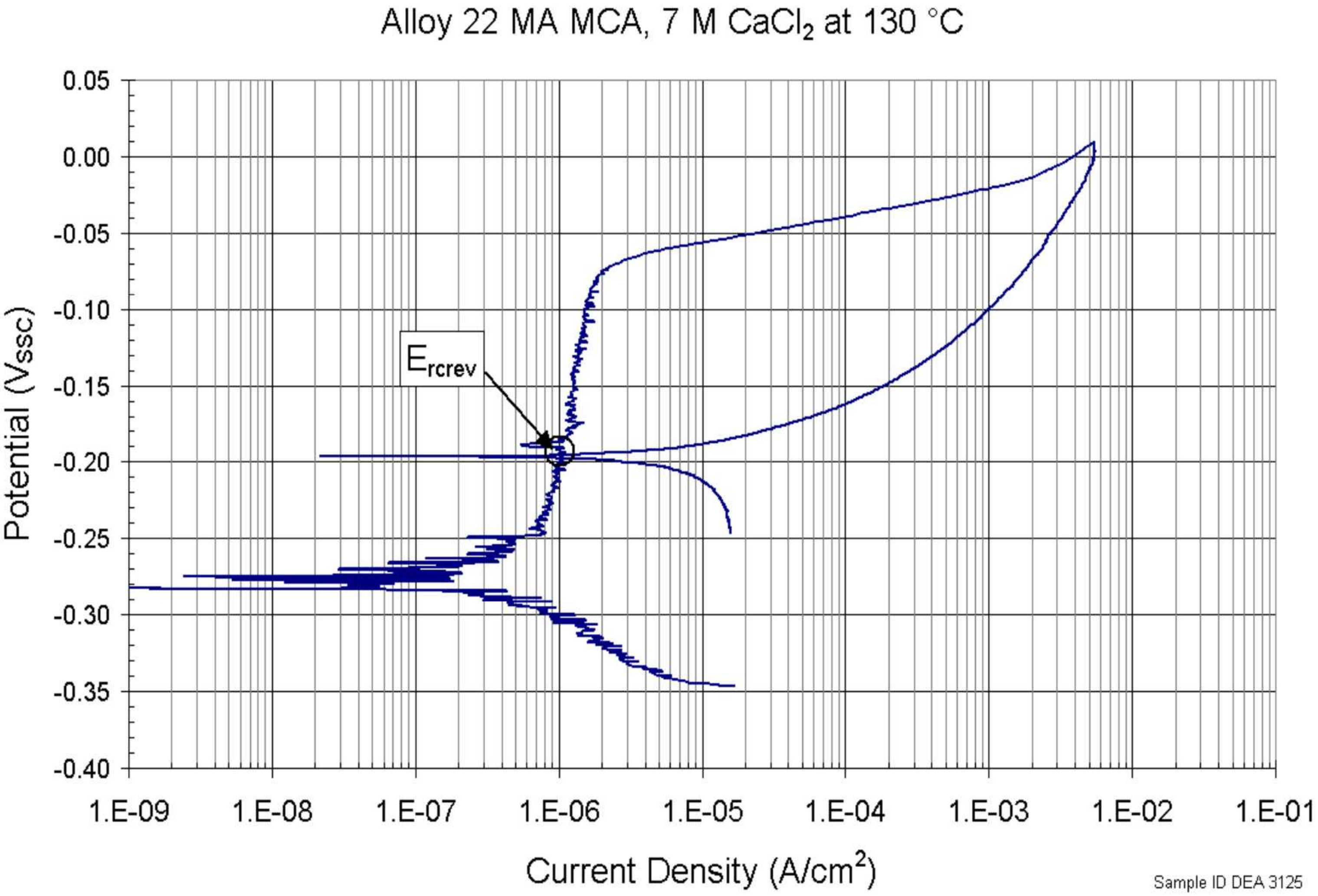
E_{CORR} = corrosion potential: the potential recorded for Alloy 22 following a long-term exposure to an electrolyte



Cyclic Polarization Testing is Used to Measure Repassivation Potential

- Sample exposed at open circuit conditions for 24 hours
- Potential ramped from -150 mV vs. E_{CORR} at +0.167mV/s until a critical current density is reached
- Scan reversed and potential ramped back to starting potential
- Sample examined for evidence of localized corrosion
  - If no LC observed, then no E_{RCREV} value input into the model
  - If LC is observed then E_{RCREV} is defined as:
    - If there was a positive hysteresis, then E_{RCREV} is taken as the potential where the reverse scan crosses the forward scan
    - If there was a negative or zero hysteresis, then E_{RCREV} is assigned the value of +600mV vs SSC

Example: Cyclic Polarization Test on Alloy 22



Crevice Repassivation Potential is Modeled to Depend on [Cl$^-$], [NO$_3^-$], and Temperature

$$E_{RCREV} = a_0 + a_1 T + a_2 \ln[Cl^-] + a_3 \frac{[NO_3^-]}{[Cl^-]} + a_4 T \cdot [Cl^-] + \varepsilon^0_{RCREV}$$

$a_0 = 183.686$

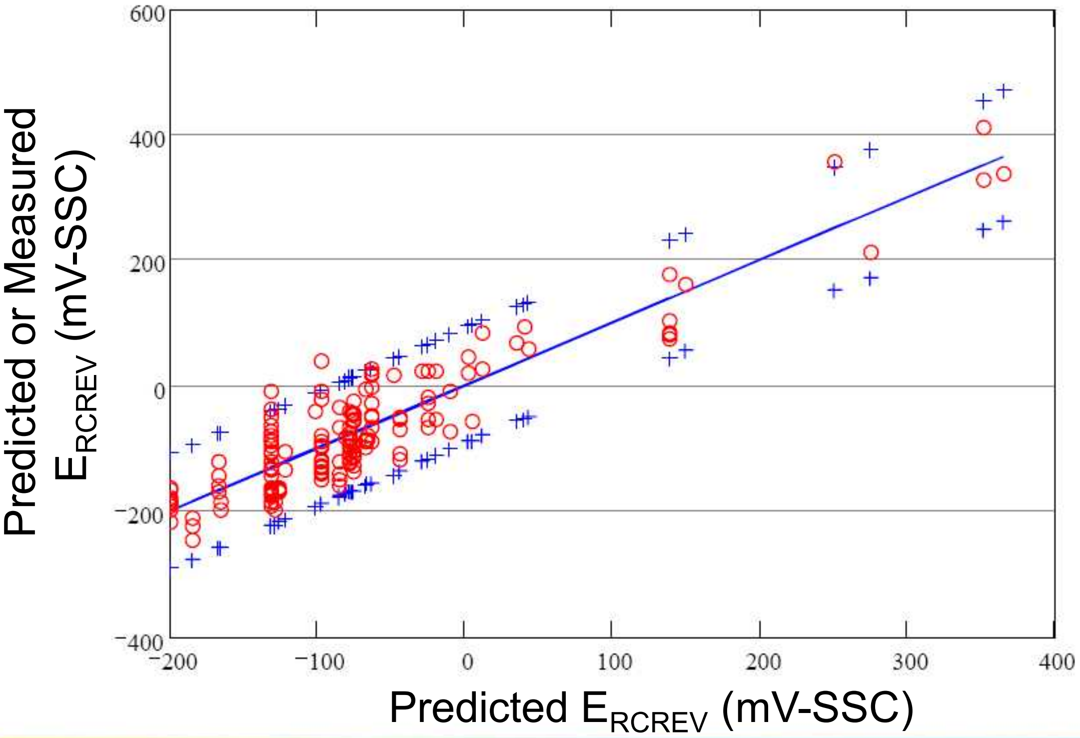
$a_1 = -2.919$

$a_2 = -46.109$

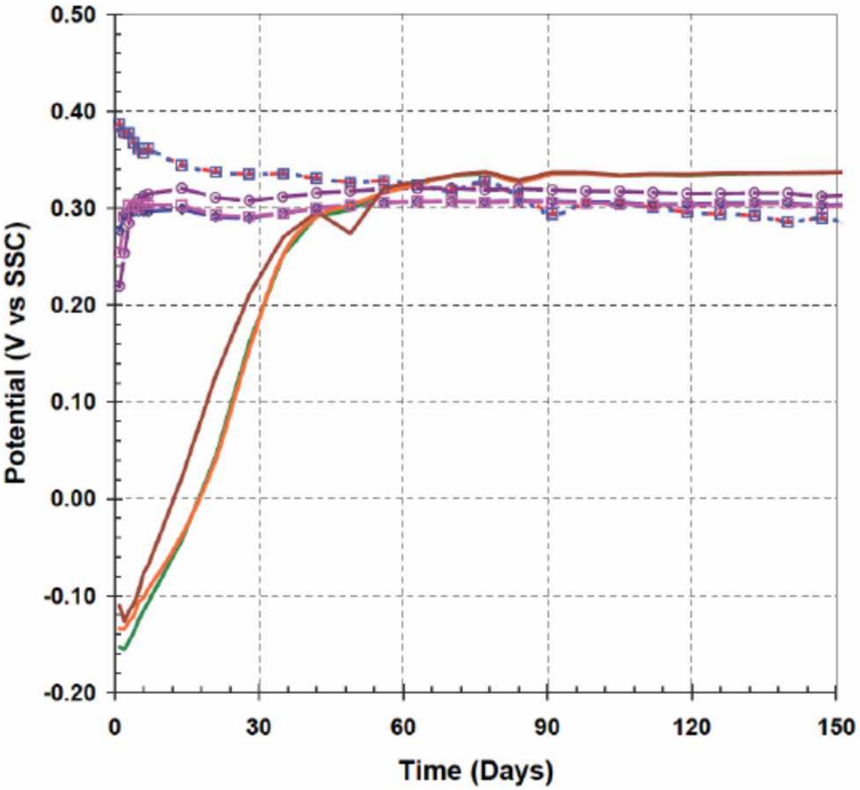
$a_3 = 580.849$

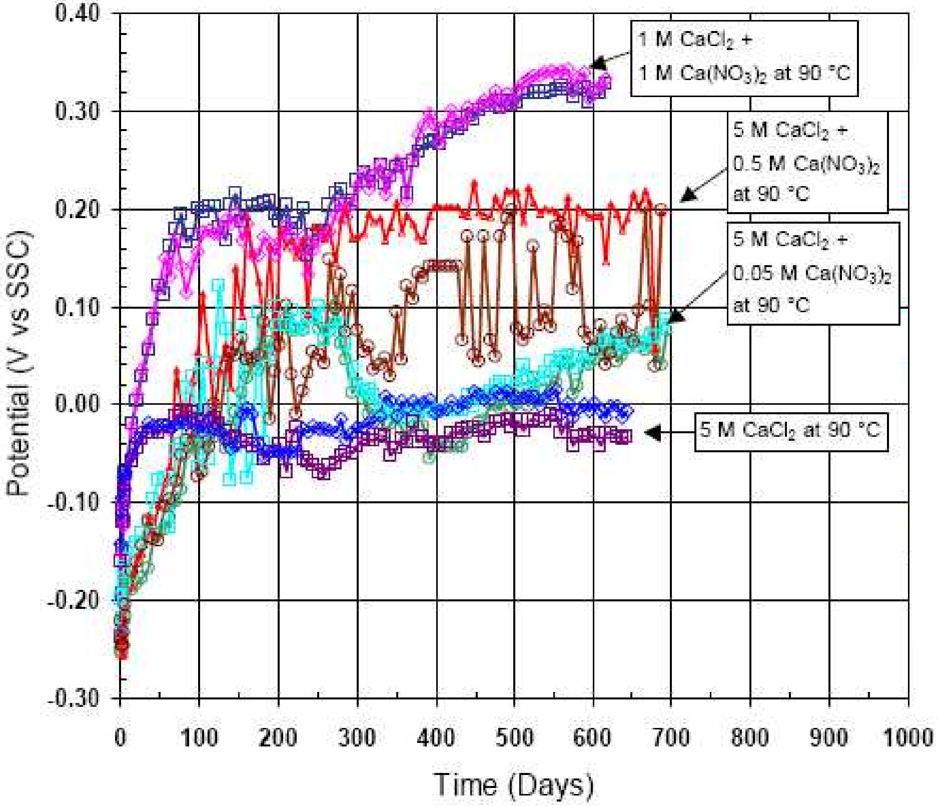
$a_4 = 0.057$

ε^0_{RCREV}: error term representing data variance not explained by the other terms in the model. Normally distributed with a mean of zero and a standard deviation of 52.993 mV



Open Circuit Potential is Measured After at a Minimum of 250 Days of Exposure





Open Circuit Potential is Modeled to Depend on pH, [Cl⁻], [NO$_3^-$], and Temperature

$$E_{CORR} = c_0 + c_1 T + c_2 pH + c_3 \frac{[NO_3^-]}{[Cl^-]} + c_4 T \frac{[NO_3^-]}{[Cl^-]} + c_5 pH \frac{[NO_3^-]}{[Cl^-]} + c_6 pH \ln[Cl^-] + \varepsilon_{CORR}$$

$c_0 = 1051.219$

$c_1 = -3.024$

$c_2 = -155.976$

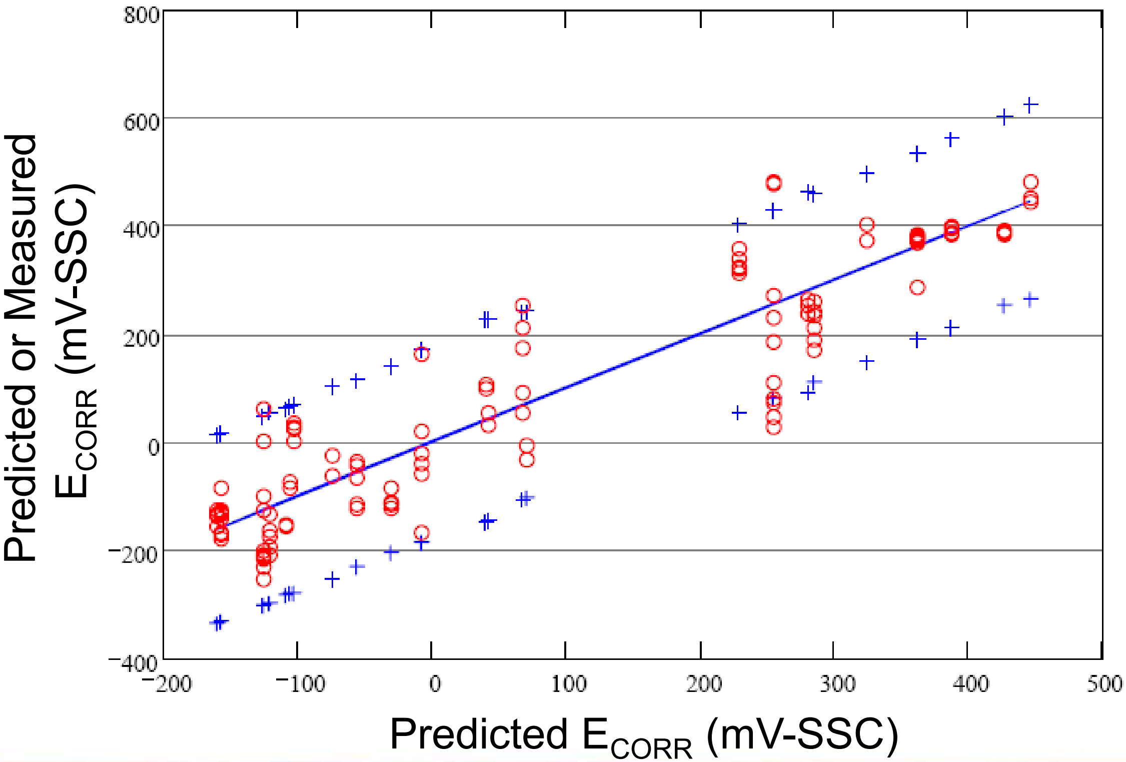
$c_3 = -1{,}352.040$

$c_4 = 10.875$

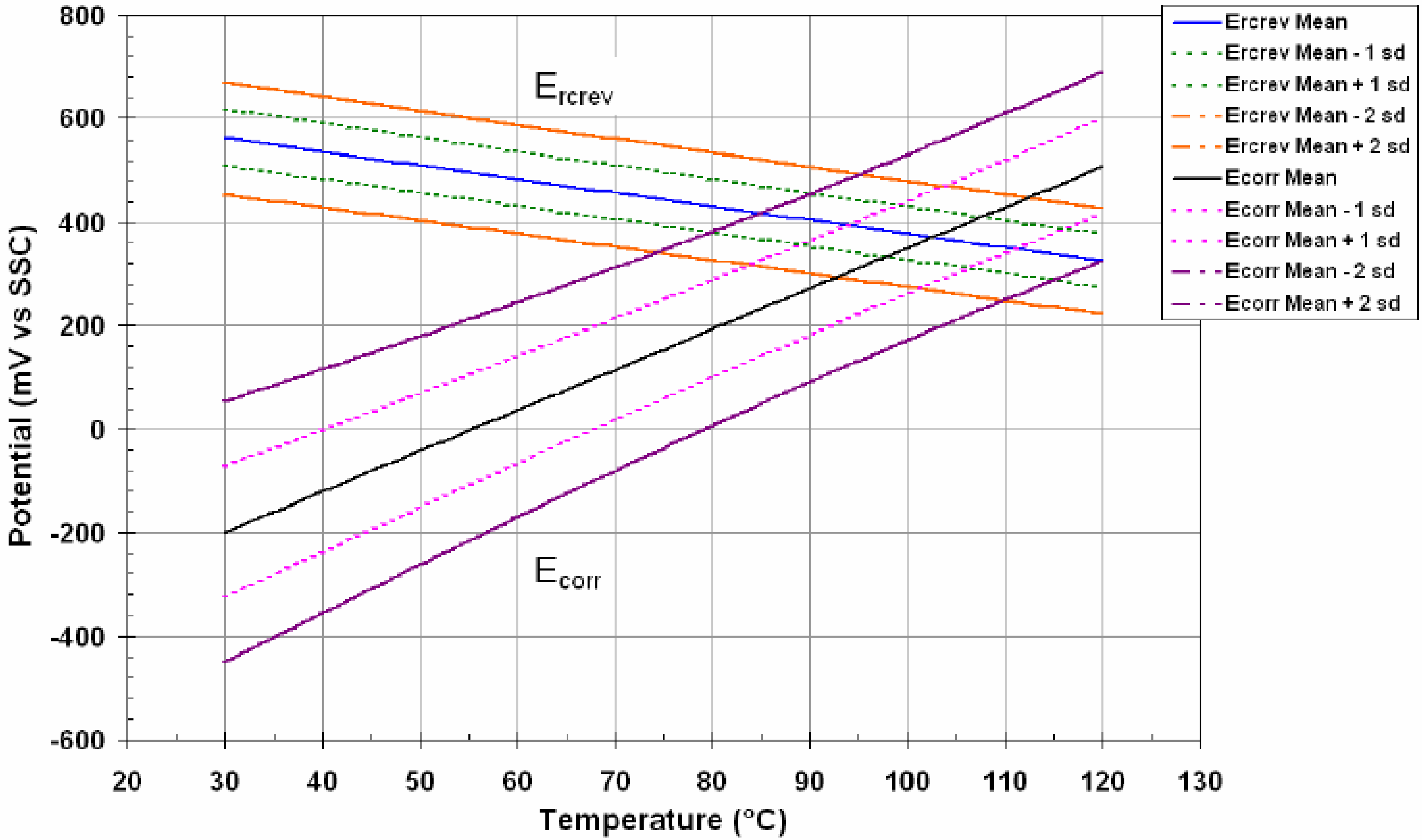
$c_5 = 137.856$

$c_6 = -8.498$

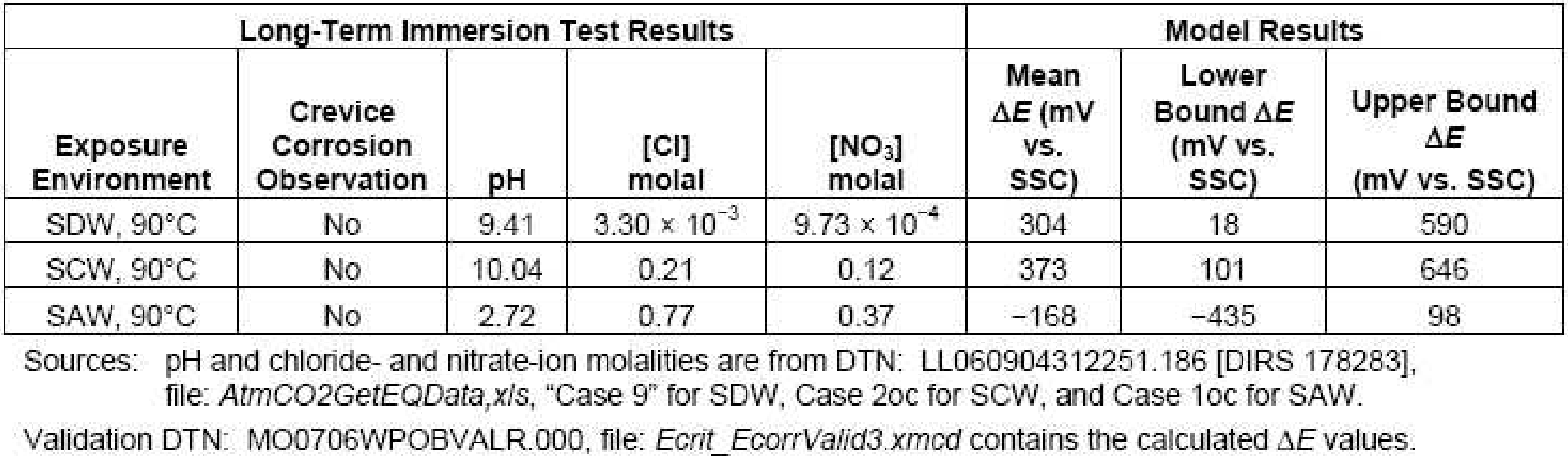
ε_{CORR}: error term representing data variance not explained by the other terms in the model. Normally distributed with a mean of zero and a standard deviation of 85.265 mV



The Localized Corrosion Model Predicts an Increased Probability of Initiation with Increasing Temperature



The Localized Corrosion Model Does not Underestimate Frequency of Corrosion for 5-Year Exposures



Long-Term Immersion Test Results					Model Results		
Exposure Environment	Crevice Corrosion Observation	pH	[Cl] molal	$[NO_3]$ molal	Mean ΔE (mV vs. SSC)	Lower Bound ΔE (mV vs. SSC)	Upper Bound ΔE (mV vs. SSC)
SDW, 90°C	No	9.41	3.30×10^{-3}	9.73×10^{-4}	304	18	590
SCW, 90°C	No	10.04	0.21	0.12	373	101	646
SAW, 90°C	No	2.72	0.77	0.37	−168	−435	98

Sources: pH and chloride- and nitrate-ion molalities are from DTN: LL060904312251.186 [DIRS 178283], file: *AtmCO2GetEQData,xls*, "Case 9" for SDW, Case 2oc for SCW, and Case 1oc for SAW.

Validation DTN: MO0706WPOBVALR.000, file: *Ecrit_EcorrValid3.xmcd* contains the calculated ΔE values.

SDW	No LC Observed	Predicted P(LC) = 0
SCW	No LC Observed	Predicted P(LC) = 0
SAW	No LC Observed	Predicted P(LC) > 0

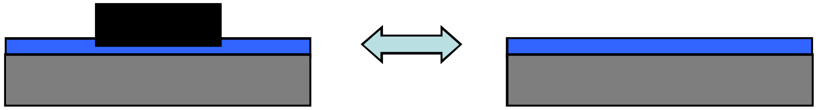
Localized Corrosion Model Predictions are Consistent With Data From Intermediate-Duration Open Circuit Testing

Solution	Immersion Days	Cell #	T(°C)	Creviced Geometry	CC	Rod Geometry	PC	Modeled ΔE		
								Lower Bound	Mean	Upper Bound
5 m $CaCl_2$ + 5 m $Ca(NO_3)_2$	723	33	120	4	0	2	0	−398	−116	166
5 m $CaCl_2$ + 5 m $Ca(NO_3)_2$	729	32	100	4	0	2	0	−184	93	370
3.5 m NaCl + 0.175 m KNO_3 + 0.7 m $MgSO_4$	735	31	80	4	2	2	0	−227	38	303
1 M NaCl + 0.15 M KNO_3	741	30	90	4	0	2	0	−202	62	325
1 M NaCl + 0.15 M KNO_3	749	29	75	4	0	2	0	−185	80	344
5 M $CaCl_2$	650	28	90	4	4	2	0	−466	−201	63
3.5 m NaCl + 0.175 m KNO_3	252	25	100	4	0	0	0	−225	39	304
3.5 m NaCl + 0.525 m KNO_3	256	24	100	4	0	0	0	−223	41	305
6 m NaCl + 0.9 m KNO_3	265	23	100	4	2	0	0	−236	28	291
6 m NaCl + 0.3 m KNO_3	280	22	100	4	0	0	0	−239	26	290
5 M $CaCl_2$ + 0.5 M $Ca(NO_3)_2$	463	21	90	6	6	6	0	−597	−332	-66
5 M $CaCl_2$	497	20	120	6	6	6	0	−462	−191	79

.
.
.

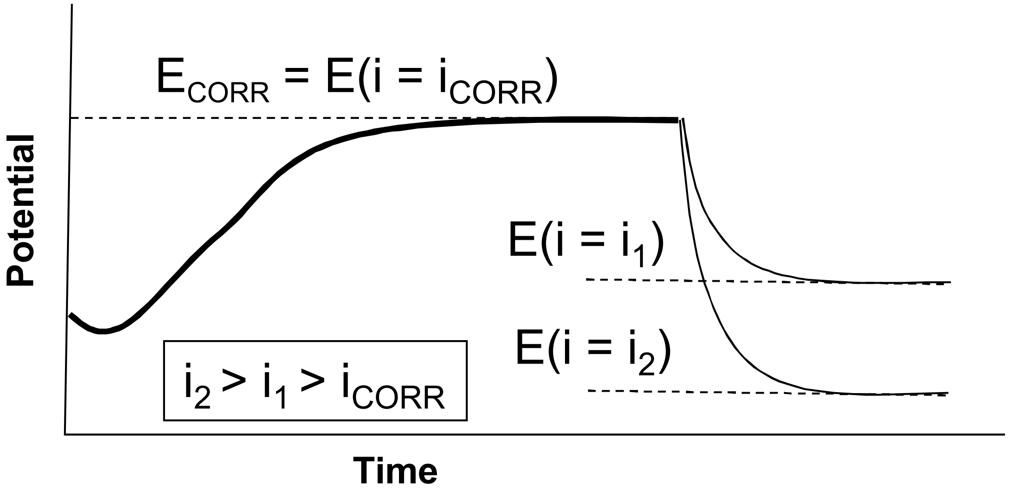
The Corrosion Model is Expected to Overestimate the Frequency and Extent of Localized Corrosion

- Crevice former not needed for initiation
- No stifling or arrest; no time dependent growth law
- Potential of metal is independent of cathodic current density
    - Cathodic current density required to maintain an LC site increases with decrease in wetted area



$$D = k \cdot t^{n}$$

- Theoretical value for n = 0.5
- Experimental values typically less than 0.5



Key Points

- General corrosion is modeled as a continuous process, independent of waste package environment
  - The highest measured rate distribution is used as input to the model
  - Corrosion rate is assumed to be independent of time

- Localized corrosion is modeled to initiate when $E_{RCREV} \leq E_{CORR}$
  - E_{RCREV} and E_{CORR} are functions of electrolyte composition and temperature
  - Localized corrosion does not stifle or arrest
  - Localized corrosion does not require geometric constraint

- The TSPA implementation is designed to avoid underestimating the frequency or extent of corrosion damage