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NM5507

**OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT  
ANALYSIS/MODEL COVER SHEET**

1. QA: QA

Page: 1 of 30

*Complete Only Applicable Items*

2.  Analysis Check all that apply

Type of Analysis	<input type="checkbox"/> Engineering
	<input checked="" type="checkbox"/> Performance Assessment
	<input type="checkbox"/> Scientific
Intended Use of Analysis	<input type="checkbox"/> Input to Calculation
	<input type="checkbox"/> Input to another Analysis or Model
	<input checked="" type="checkbox"/> Input to Technical Document
	<input checked="" type="checkbox"/> Input to other Technical Products

Describe use:

The results of this AMR serve as inputs to the Waste Package Degradation AMR analyses of localized corrosion of the Alloy 22 waste package outer barrier and Titanium grade 7 drip shield

3.  Model Check all that apply

Type of Model	<input type="checkbox"/> Conceptual Model	<input checked="" type="checkbox"/> Abstraction Model
	<input type="checkbox"/> Mathematical Model	<input type="checkbox"/> System Model
	<input type="checkbox"/> Process Model	
Intended Use of Model	<input type="checkbox"/> Input to Calculation	
	<input type="checkbox"/> Input to another Model or Analysis	
	<input checked="" type="checkbox"/> Input to Technical Document	
	<input checked="" type="checkbox"/> Input to other Technical Products	

Describe use:

The results of this AMR serve as inputs to the Waste Package Degradation AMR models of localized corrosion of the Alloy 22 waste package outer barrier and Titanium grade 7 drip shield

4. Title:  
Abstraction of Models for Pitting and Crevice Corrosion of Drip Shield and Waste Package Outer Barrier

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OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

ANALYSIS/MODEL REVISION RECORD

*Complete Only Applicable Items*

1. Page: 2 of 30

2. Analysis or Model Title:

Abstraction of Models for Pitting and Crevice Corrosion of Drip Shield and Waste Package Outer Barrier

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Initial Issue

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## 1. PURPOSE

This analyses and models report (AMR) was conducted in response to written work direction (CRWMS M&O 1999a). The purpose and scope of this AMR is to review and analyze upstream process-level models (CRWMS M&O 2000a and CRWMS M&O 2000b) and information relevant to pitting and crevice corrosion degradation of waste package outer barrier (Alloy 22) and drip shield (Titanium Grade 7) materials, and to develop abstractions of the important processes in a form that is suitable for input to the WAPDEG analysis for long-term degradation of waste package outer barrier and drip shield in the repository. The abstraction is developed in a manner that ensures consistency with the process-level models and information and captures the essential behavior of the processes represented. Also considered in the model abstraction are the probable range of exposure conditions in emplacement drifts and local exposure conditions on drip shield and waste package surfaces. The approach, method, and assumptions that are employed in the model abstraction are documented and justified.

Important processes and parameters that are considered in the abstraction are:

- 1) initiation thresholds for pitting and crevice corrosion both in the presence and absence of dripping water and their uncertainty and variability under repository conditions and,
- 2) penetration rates as a function of time, temperature, and other exposure conditions both in the presence and absence of dripping water, and uncertainty and variability of the penetration rate under repository conditions.

The abstraction analyses are compared to the upstream process-level models, which the abstractions were based upon. The abstractions are tested with the full range of the input parameter values (especially the tails of the parameter ranges) and examined for any abnormal responses. Also, the abstractions are tested for the probable ranges of exposure conditions in emplacement drifts and local exposure conditions on drip shield and waste package surfaces, for which full-scale WAPDEG analyses will be conducted. The validation and testing of the abstraction analyses are documented.

The Nuclear Regulatory Commission (NRC) Issue Resolution Status Report (IRSR) on Container Lifetime and Source Term (NRC 1999) is used as criteria for this analysis. Specific acceptance criteria used are the general acceptance criteria and those applicable to Subissues 1 and 2.

The abstracted models documented in this technical product are potentially important to the evaluation of principle factors for the post-closure safety case, particularly those related to performance of the drip shield and waste package barriers. This analysis is limited to the use of Titanium grade 7 as the material composing the drip shield, and Alloy 22, a nickel-based superalloy, as the material composing the waste package outer barrier. This analysis supports Performance Assessment Department (PAD) and its Engineered Barrier Performance Section in modeling waste package degradation.

## 2. QUALITY ASSURANCE

This analyses and models report (AMR) was prepared in accordance with the Civilian Radioactive Waste Management system (CRWMS) Management and Operating Contractor (M&O) Quality Assurance (QA) program. The information provided in this analysis will be used for evaluating the post-closure performance of the Monitored Geologic Repository (MGR) waste package and engineered barrier segment. The Performance Assessment Operations (PAO) responsible manager has evaluated the technical document development activity in accordance with QAP-2-0, *Conduct of Activities*. The QAP-2-0 activity evaluation (CRWMS M&O 1999b) has determined that the preparation and review of this technical document is subject to *Quality Assurance Requirements and Description* (DOE 2000) requirements. In accordance with AP-2.13Q, *Technical Product Development Plan*, a work plan was developed, issued, and utilized in the preparation of this document (CRWMS M&O 1999a). The documentation of this analysis is in accordance with the directions found in AP-3.10Q, *Analyses and Models*. There is no determination of importance evaluation developed in accordance with NLP-2-0, *Determination of Importance Evaluations*, since the analysis does not involve any field activity.

## 3. COMPUTER SOFTWARE AND MODEL USAGE

### 3.1 COMPUTER SOFTWARE

A software routine, BBreg Version 1.0, is implemented in Mathcad 2000 Professional (see Attachment I for documentation and verification that the software routine provides correct results over the range of input parameters considered in this AMR). Mathcad 2000 Professional is commercially available software. This software is appropriate for this application as it offers all of the mathematical and graphical functionality necessary to perform and document the numerical manipulations used in this AMR. Mathcad 2000 Professional was executed on a DELL PowerEdge 2200 Workstation equipped with two Pentium II 266 MHz processors (CRWMS M&O tag 112371) in the Windows NT 4.0 operating system. Details of the Mathcad 2000 Professional numerical manipulations performed in support of this AMR are discussed throughout this analysis and included in Attachment I.

SigmaPlot 4.00 is commercially available software used in this AMR. This software is graphing and visual display software and is thus exempt from the AP-SI.1Q *Software Management* procedure (Section 2.1). This software is appropriate for this application as it offers all of the graphical functionality necessary to document this analysis. No macros were used and no numerical manipulations were implemented within SigmaPlot 4.00, thus there is no need to conduct software validation exercises. SigmaPlot 4.00 was executed on a DELL PowerEdge 2200 Workstation equipped with two Pentium II 266 MHz processors (CRWMS M&O tag 112371) in the Windows NT 4.0 operating system. SigmaPlot 4.00 was used only for presentation of graphical results and was not used to perform any numerical calculations in support of this AMR.

### 3.2 MODELS USED

No pre-existing models were used in this analyses and models report (AMR). The Alloy 22 Potential-Based Localized Corrosion Initiation Threshold Model is developed in this AMR (see

Section 6.3). The Titanium Grade 7 Potential-Based Localized Corrosion Initiation Threshold Model is developed in this AMR (see Section 6.4).

## 4. INPUTS

### 4.1 DATA AND PARAMETERS

Table 1 summarizes the input data used in this analysis, their data tracking numbers (DTNs), and the Table numbers in this report in which the input data is listed. Corrosion and critical electrochemical potential measurements for Alloy 22 (Table 2) (DTN: LL990610205924.075, LL000112105924.111) (CRWMS M&O 2000a) and Titanium grade 7 (Table 3) (DTN: LL000209105924.127) (CRWMS M&O 2000b) were obtained at temperatures ranging from 30 to 120°C, chloride ion concentrations between 67 and 154,000 mg/L, and pH values between 2.7 and 13 (Table 4) (DTN: LL000320405924.146). The solution compositions are abbreviated as SDW (Simulated Dilute Water), SCW (Simulated Concentrated Water), SAW (Simulated Acidified Water), SSW (Simulated Saturated Water), and (BSW) Basic Saturated Water. These data are documented in Analysis Model Reports (AMRs) which serve as primary input to this AMR (CRWMS M&O 2000a and CRWMS M&O 2000b). These data are qualified.

Table 1. Data and Parameters and Their DTNs

Parameter	DTN	Where Documented in this Document
Corrosion potential and Critical potential measurements of Alloy 22 in SDW, SCW, SAW, and SSW.	LL990610205924.075 s99347_002 DATA REPORT	Table 2
Corrosion potential and Critical potential measurements of Alloy 22 in BSW.	LL000112105924.111 S00040_001 DATA REPORT	Table 2
Corrosion potential and Critical potential measurements of Titanium grade 7 in SAW and SSW.	LL000209105924.127 s00129_002 DATA REPORT	Table 3
Corrosion potential and Critical potential measurements of Titanium grade 7 in SDW and SCW.	LL000209105924.127 s00129_001 DATA REPORT	Table 3
SDW, SCW, SAW, SSW, and BSW Cl <sup>-1</sup> concentration and pH	LL000320405924.146	Table 4

Table 2. Corrosion Potential Measurements of Alloy 22 (DTN: LL990610205924.075, LL000112105924.111) in Solutions of Various Composition (shown in Table 4 of this AMR).

Solution	T (°C)	E <sub>corr</sub> (mV Ag/AgCl)	E <sub>crit1</sub> (mV Ag/AgCl)
SDW	30	-55	466
SDW	30	-65	436
SDW	30	-93	420
SDW	60	-137	317
SDW	60	-174	282
SDW	60	-161	290
SDW	90	-191	192
SDW	90	-162	185
SDW	90	-158	169
SCW	30	-57	169
SCW	30	-188	341
SCW	60	-240	234
SCW	60	-231	226
SCW	60	-226	238
SCW	90	-136	206
SCW	90	-237	199
SAW	30	-42	663
SAW	60	-118	575
SAW	90	-176	555
SAW	60	-115	613
SAW	90	-171	595
SAW	60	-102	605
SAW	90	-150	600
SSW	100	-234	234
SSW	120	-320	171
<b>SSW</b>	<b>120</b>	<b>-253</b>	<b>664</b>
BSW	110	-233	418
BSW	110	-257	419
BSW	110	-345	394
BSW	110	-372	361

Note: The italicized and bold-faced data was not used in generating the results of this AMR (see Assumption 5.2).

Note: BSW is synonymous with BSW-13 (see Assumption 5.7)

Table 3. Corrosion Potential Measurements of Titanium grade 7 (DTN: LL000209105924.127) in Solutions of Various Composition (shown in Table 4 of this AMR).

Solution	T (°C)	E <sub>corr</sub> (mV Ag/AgCl)	E <sub>crit1</sub> (mV Ag/AgCl)
SDW	30	-145	1070
SDW	30	-99	1000
SDW	30	-125	1030
SDW	60	-212	947
SDW	60	-114	912
SDW	60	-214	874
SDW	90	-305	808
SDW	90	-305	752
SCW	30	-37	958
SCW	30	-187	968
SCW	30	-233	1020
SCW	60	-331	880
SCW	60	-364	796
SCW	60	-351	849
SCW	90	-480	849
SCW	90	-506	654
SCW	90	-516	772
SAW	30	-153	1450
SAW	30	-187	1430
SAW	30	-284	1420
SAW	30	-176	1440
SAW	30	-145	1230
SAW	60	-99	1390
SAW	60	-125	1420
SAW	90	-187	1300
SAW	90	-187	1340
SAW	90	-176	1330
SSW	100	-211	921
SSW	120	-336	813

The “target compositions” of the aqueous solutions used for corrosion testing are presented in Table 4. According to the discussion accompanying Table 1 in DTN: LL000320405924.146, actual compositions may vary significantly because of other experimental factors and pH values are estimates and will vary depending on other experimental conditions. For this reason, the solution compositions are referred to as “target compositions.”

Table 4. Target Compositions of Solutions in which Corrosion Potential Measurements of Alloy 22 were made (DTN: LL000320405924.146).

Solution	T (°C)	Cl <sup>-</sup> mg/L	pH
SDW	60, 90	67	9.8 – 10.2
SCW	60, 90	6700	9.8 – 10.2
SAW	60, 90	24250	2.7
SSW	100	128000	5.5 – 7
SSW	120	154000	5.5 – 7
BSW-13	25	130830	13

Note: The chloride ions and pH values for BSW-13 are determined to be measured at room temperature based on statements in the AMR entitled *General Corrosion and Localized Corrosion of the Waste Package Outer Barrier* (CRWMS M&O 2000a, paragraph 1, p. 101).

Note: These data have changed relative to previous revisions of this document due to changes in source data.

## 4.2 CRITERIA

This section provides a summary of the NRC acceptance criteria outlined in the Issue Resolution Status Report (IRSR) that applies to the Container Life and Source Term Key Technical Issues (KTIs) (NRC 1999). The following six sub-issues are identified in the IRSR (NRC 1999, Section 2.2).

- (1) The effects of corrosion processes on the lifetime of the containers.
- (2) The effects of phase instability of materials and initial defects on the mechanical failure and lifetime of the containers.
- (3) The rate at which radionuclides in spent nuclear fuel (SNF) are released from the Engineered Barrier System (EBS) through the oxidation and dissolution of spent fuel.
- (4) The rate at which radionuclides in high-level waste (HLW) glass are leached and released from the EBS.
- (5) The effect of in-package criticality on waste package (WP) and EBS performance.
- (6) The effects of alternate EBS design features on container lifetime and radionuclide release from the EBS.

Of these sub-issues, only sub-issues (1) and (2) are relevant to this analysis.

### 4.2.1 Acceptance Criteria Applicable To All Six Sub-Issues

- (1) The collection and documentation of data, as well as development and documentation of analyses, methods, models, and codes, shall be accomplished under approved quality assurance and control procedures and standards (NRC 1999, Section 4.0).
- (2) Expert elicitations, when used, shall be conducted and documented in accordance with the guidance provided in NUREG-1563 (Kotra, et al., 1996) or other acceptable approaches (NRC 1999, Section 4.0).

- (3) Sufficient data (field, laboratory, and natural analog) shall be obtained to adequately define relevant parameters for the models used to evaluate performance aspects of the sub-issues (NRC 1999, Section 4.0).
- (4) Sensitivity and uncertainty analyses (including consideration of alternative conceptual models) will be used to determine whether additional data would be needed to better define ranges of input parameters (NRC 1999, Section 4.0).
- (5) Parameter values, assumed ranges, test data, probability distributions, and bounding assumptions used in the models shall be technically defensible and can reasonably account for known uncertainties (NRC 1999, Section 4.0).
- (6) Mathematical model limitations and uncertainties in modeling shall be defined and documented (NRC 1999, Section 4.0).
- (7) Primary and alternative modeling approaches consistent with available data and current scientific understanding shall be investigated and their results and limitations considered in evaluating the sub-issue (NRC 1999, Section 4.0).
- (8) Model outputs shall be validated through comparisons with outputs of detailed process models, empirical observations, or both (NRC 1999, Section 4.0).
- (9) The structure and organization of process and abstracted models shall adequately incorporate important design features, physical phenomena, and coupled processes (NRC 1999, Section 4.0).

#### **4.2.2 Acceptance Criteria For Sub-Issue 1**

- (1) The Department of Energy (DOE) shall identify and consider likely modes of corrosion for container materials, including dry-air oxidation, humid-air corrosion, and aqueous corrosion processes, such as general corrosion, localized corrosion, microbial-induced corrosion (MIC), stress corrosion cracking (SCC), and hydrogen embrittlement, as well as the effect of galvanic coupling (NRC 1999, Section 4.1.1).
- (2) The DOE shall identify the broad range of environmental conditions within the WP emplacement drifts that may promote the corrosion processes listed previously, taking into account the possibility of irregular wet and dry cycles that may enhance the rate of container degradation (NRC 1999, Section 4.1.1).
- (3) The DOE shall demonstrate that the numerical corrosion models used are adequate representations, taking into consideration associated uncertainties, of the expected long-term behaviors and are not likely to underestimate the actual degradation of the containers as a result of corrosion in the repository environment (NRC 1999, Section 4.1.1).
- (4) The DOE shall consider the compatibility of container materials, the range of material conditions, and the variability in container fabrication processes, including welding, in assessing the performance expected in the container's intended waste isolation function (NRC 1999, Section 4.1.1).
- (5) The DOE shall justify the use of data collected in corrosion tests not specifically designed or performed for the Yucca Mountain repository program for the environmental conditions expected to prevail at the Yucca Mountain site (NRC 1999, Section 4.1.1).

- (6) The DOE shall conduct a consistent, sufficient, and suitable corrosion testing program at the time of the LA submittal. In addition, DOE shall identify specific plans for further testing to reduce any significant area(s) of uncertainty as part of the performance confirmation program (NRC 1999, Section 4.1.1).
- (7) The DOE shall establish a defensible program of corrosion monitoring and testing of the engineered subsystems components during the performance confirmation period to assure they are functioning as intended and anticipated (NRC 1999, Section 4.1.1).

#### **4.2.3 Acceptance Criteria for Sub-Issue 2**

- (1) The DOE shall identify and consider the relevant mechanical failure processes that may affect the performance of the proposed container materials (NRC 1999, Section 4.2.1).
- (2) The DOE shall identify and consider the effect of material stability on mechanical failure processes for the various container materials as a result of prolonged exposure to the expected range of temperatures and stresses, including the effects of chemical composition, microstructure, thermal treatments, and fabrication processes (NRC 1999, Section 4.2.1).
- (3) The DOE shall demonstrate that the numerical models used for container materials stability and mechanical failures are effective representations, taking into consideration associated uncertainties, of the expected materials behavior and are not likely to underestimate the actual rate of failure in the repository environment (NRC 1999, Section 4.2.1).
- (4) The DOE shall consider the compatibility of container materials and the variability in container manufacturing processes, including welding, in its WP failure analyses and in the evaluation of radionuclide release (NRC 1999, Section 4.2.1).
- (5) The DOE shall identify the most appropriate methods for nondestructive examination of fabricated containers to detect and evaluate fabrication defects in general and, particularly, in seam and closure welds (NRC 1999, Section 4.2.1).
- (6) The DOE shall justify the use of material test results not specifically designed or performed for the Yucca Mountain repository program for environmental conditions (i.e., temperature, stress, and time) expected to prevail at the proposed Yucca Mountain repository (NRC 1999, Section 4.2.1).
- (7) The DOE shall conduct a consistent, sufficient, and suitable materials testing program at the time of the License Application submittal. In addition, DOE has identified specific plans for further testing to reduce any significant area(s) of uncertainty as part of the performance confirmation program (NRC 1999, Section 4.2.1).
- (8) The DOE shall establish a defensible program of monitoring and mechanical testing of the engineered subsystems components, during the performance confirmation period, to assure they are functioning as intended and anticipated, in the presence of thermal and stress perturbations (NRC 1999, Section 4.2.1).

### 4.3 CODES AND STANDARDS

No codes or standards were used to perform the analysis for this AMR.

### 5. ASSUMPTIONS

The assumptions used in this analysis are listed in this Section. These assumptions document accepted scientific practices and are consistent with the supporting AMRs. For this reason, none of the following assumptions require confirmation prior to the use of the parameters developed in this document.

- 5.1 *Ecrit1* (referred to as "Threshold Potential 1" in the source analyses and models reports (AMRs) (CRWMS M&O 2000a, Section 6.4.2) (CRWMS M&O 2000b, Tables 4a and 4b)) was used as the critical or threshold potential above which localized corrosion can initiate. The basis of this assumption is that the use of Threshold Potential 1 as the localized corrosion initiation threshold potential is conservative as Threshold Potential 1 was always observed to be lower than other possible localized corrosion initiation threshold potentials such as "Threshold Potential 2" and/or the various "Repasivation Potentials" (defined in the source AMRs (CRWMS M&O 2000a, Section 6.4.2) (CRWMS M&O 2000b, Tables 4a and 4b)). This assumption is used throughout Attachment I.
- 5.2 One experimentally observed data point in Table 2 (for Alloy 22 in an SSW solution with  $E_{corr} = -253$  mV and  $E_{crit1} = 664$  mV Ag/AgCl) was not part of the data set used in Attachment I to derive the Alloy 22 crevice corrosion initiation criteria. This data point was considered an outlier. The basis for this assumption is that this data point is an outlier as  $\Delta E = (E_{crit1} - E_{corr})$  for this data point is 917 mV, a value almost twice that for any other data point obtained in the same solution. This assumption is used in Attachment I in specifying the input data to the model fitting procedure (the Dat matrix for Alloy 22) (Attachment I, page I-1).
- 5.3 For Alloy 22, it is assumed that the difference ( $\Delta E$ ) between *Ecrit1* and the corrosion potential, *Ecorr*, can be modeled to vary linearly (i.e., linear in the coefficients used in the regression equation) with temperature (in Kelvin), the logarithm in base 10 of the chloride concentration in mol/L, the *pH*, and the  $pH^2$  of the solution in which the potentials were measured. For Titanium Grade 7, it is assumed that the difference ( $\Delta E$ ) between *Ecrit1* and the corrosion potential, *Ecorr*, can be modeled to vary linearly with temperature (in Kelvin), the logarithm in base 10 of the chloride concentration in mol/L, and the *pH* of the solution in which the potentials were measured. These assumptions are based (in part) on assumptions used in the source AMRs (CRWMS M&O 2000a, Section 6.4.3) (CRWMS M&O 2000b, Section 6.4.3) where *Ecrit* and *Ecorr* are represented by linear regression equations based on the exposure temperature. Similar linear regression equations are assumed based on the assumed temperature dependence. This assumption was used throughout Attachment I.
- 5.4 The error terms and model coefficients (the  $b_i$ 's) for all regression models derived in Attachment I are assumed to be normally distributed. The basis for this assumption is the

Central Limit Theorem (Stedinger, et al. 1993, p. 18.11), which states that “. . . if a random variable  $X$  is the sum of  $n$  independent and identically distributed random variables with finite variance, then with increasing  $n$  the distribution of  $X$  becomes normal regardless of the distribution of the original random variables.” It is not unreasonable to assume that the fitting coefficients and error variance arise from a sum of many independent and (at least nearly) identically distributed random processes with finite variances. This assumption is used in Section 6.3.1 and 6.4.1 and in Attachment I on the bottom of pages I-3, I-6, I-8, and I-11 in formulating the EE, EE1, EE2, and EE3 functions.

- 5.5 Chloride ion concentrations and  $pH$  values are supplied in Table 4 for SDW, SCW, and SAW solutions at 60 and 90°C.  $E_{crit1}$  and  $E_{corr}$  values are supplied at 30, 60, and 90°C in Table 2. It is assumed that the chloride ion concentrations and  $pH$  values at 60 and 90°C are appropriate for use at 30°C as well. The basis of this assumption is that it is reasonable and is expected to have little impact on the analysis results. This assumption is used throughout Attachment I.
- 5.6 The  $pH$  values of SDW, SCW, and SSW solutions are provided as ranges in Table 4. It is assumed that the median value of each  $pH$  value range is representative of the solution  $pH$  value. The basis of this assumption is that it is reasonable and is expected to have little impact on the analysis results. This assumption is used throughout Attachment I.
- 5.7 It is assumed that the electrochemical polarization measurements in BSW solution reported in Table 2 (obtained from DTN: LL000112105924.111) were obtained in a solution that is referred to as BSW-13 in Table 4 (obtained from DTN: LL000320405924.146). The basis for this assumption is that the electrochemical polarization curve presented in Figure 46 of the AMR entitled *General Corrosion and Localized Corrosion of the Waste Package Outer Barrier* (CRWMS M&O 2000a, p. 102) has an internal legend identifying the solution chemistry as BSW and an external caption identifying the solution chemistry as BSW-13. Therefore, for the purposes of determination of the solution chemistry in which electrochemical polarization curves were measured, BSW is synonymous with BSW-13. This assumption is used throughout Attachment I.
- 5.8 It is assumed that the  $pH$  value presented in Table 4 for BSW-13 at 25°C is also applicable at a solution temperature of 110°C (the temperature at which the electrochemical potentials reported in Table 2 were made). The basis of this assumption is that it is reasonable and is expected to have little impact on the analysis results. This assumption is used throughout Attachment I.

## 6. ANALYSIS/MODEL

### 6.1 LOCALIZED CORROSION

Localized corrosion (pitting and crevice corrosion) is induced by local variations in electrochemical potential on a micro-scale. The variations in electrochemical potential may result from local perturbations in the structure and composition of usually protective passive

films on metal surfaces and also in the electrolyte composition of the solution that contacts the metal (Kain 1978 and Asphahani and Silence 1978). An excellent summary of the Project's current state of knowledge on localized corrosion is presented in a recent analyses and models report (AMR) entitled *General and Localized Corrosion of Waste Package Outer Barrier* (CRWMS M&O 2000a, Section 6.6). A more general summary of the field is presented here.

Pitting corrosion is one of the most severe types of corrosion attack. For a given alloy, pit growth rates are generally much faster than general corrosion rates. Pitting attack begins by the localized breakdown of passivity on the metal surface. An electrolytic cell is formed in which the anode is the small area of active metal exposed by the breakdown of the passive film, and the cathode is the remaining much larger area of still passive metal. The large potential difference between the passive and active regions, as well as the large difference in their areas, causes rapid corrosion at the small anode and rapid pit growth (Asphahani and Silence 1978, p. 113).

Scale deposits formed on the waste package surface, as well as waste package contact points with the support pedestals, could create occluded regions (crevices) leading to variations in solution chemistry and electrochemical potential inside and outside of the creviced regions. These conditions could induce "crevice corrosion" of the metal underneath the scale deposits. Crevice corrosion refers to the development of localized solution environments whose composition may differ greatly from the bulk solution chemistry outside the crevice. Metallurgical, geometrical, and environmental factors can affect both crevice corrosion initiation and propagation processes. The release of metal ions (particularly chromium) in the creviced region, due to corrosion, can result in acidic crevice solution chemistries through a series of hydrolysis reactions. The excess hydrogen ions produced can lead to chloride ion migration to and concentration in the creviced region. The increased acidity and chloride concentration in the creviced region can lead to breakdown of the passive film and crevice corrosion initiation and propagation (Kain 1978, p. 110).

The complex electrochemical processes summarized above strongly influence pit and crevice initiation and growth processes. In general, localized corrosion appears to be a random process (except where local microstructural differences exist, i.e., fabrication defects, impact damage, etc.). As a result, stochastic approaches are typically applied to represent and quantify localized corrosion processes.

## 6.2 CONCEPTUAL MODEL

The conceptual model used for localized corrosion initiation and propagation to be used in Total System Performance Assessment - Site Recommendation (TSPA-SR) analysis is documented in the analyses and models reports (AMRs) which serve as primary input to this AMR (CRWMS M&O 2000a, Section 6.10 and CRWMS M&O 2000b, Section 6.10). In summary, if aqueous phase corrosion can occur, the corrosion and critical potentials are used to determine whether the mode of attack is general corrosion only or general and localized corrosion together, i.e., only if the corrosion potential ( $E_{corr}$ ) exceeds the critical potential for localized corrosion initiation ( $E_{crit1}$ ) can localized corrosion initiate. The distribution of localized corrosion rates presented in Table 22 of the AMR entitled *General Corrosion and Localized Corrosion of Waste Package Outer Barrier* (CRWMS M&O 2000a, Section 6.6.6) will be used for Alloy 22 localized corrosion modeling and those presented in Table 16 of the AMR entitled *General Corrosion and*

Localized Corrosion of the Drip Shield (CRWMS M&O 2000b, Section 6.7) will be used for Titanium grade 7 localized corrosion modeling.

### 6.3 ALLOY 22 POTENTIAL-BASED LOCALIZED CORROSION INITIATION THRESHOLD MODEL

#### 6.3.1 Alloy 22 Localized Corrosion Initiation Threshold Model Formulation

In the source analyses and model reports (AMRs) (CRWMS M&O 2000a, Section 6.4.3) (CRWMS M&O 2000b, Section 6.4.3), the corrosion and threshold potential data were separately fit to linear functions of exposure temperature only. This approach does not consider possible dependencies on other exposure parameters and the fact that one corrosion and threshold potential pair was measured from each sample. In the present AMR, the potential difference between the critical potential for localized corrosion initiation,  $E_{crit1}$ , and the corrosion potential,  $E_{corr}$ , (i.e.,  $\Delta E$ ) was determined for each sample from which data was collected.  $\Delta E$  was then fit to a function of several exposure parameters such as absolute temperature,  $T$ , the base 10 logarithm of the chloride ion concentration (in mol/L), and solution  $pH$ .

In particular, the data presented in Table 2 for Alloy 22 was used to fit  $\Delta E$  to a function of absolute temperature, the base 10 logarithm of the chloride ion concentration, solution  $pH$ , and solution  $pH^2$ , i.e.,

$$\Delta E = b_0 + b_1 \cdot T + b_2 \cdot \log(Cl^-) + b_3 \cdot pH + b_4 \cdot pH^2 + \varepsilon \quad (\text{Eq. 1})$$

where  $b_0$ ,  $b_1$ ,  $b_2$ ,  $b_3$ , and  $b_4$  are constants determined from fitting to Equation 1 to the collected potential difference data (Table 2). This exercise is documented in detail in Attachment I, pages I-1 to I-5. As discussed in Assumption 5.2, one experimentally observed data point in Table 2 was not part of the data set used as it was considered to be an outlier.  $\varepsilon$  (referred to as the "error" variance or "residual" variance) is a term representing data variance not explained by the fitting procedure and has a normal distribution with a mean of zero (see Assumption 5.4). Linear regression gives the following estimates for the parameters in Equation 1:  $b_0 = 1260$ ,  $b_1 = -0.313$ ,  $b_2 = 8.15$ ,  $b_3 = -188$ , and  $b_4 = 11.8$ . The covariance matrix resulting from the fitting procedure was determined to be:

$$s = \begin{bmatrix} 42400 & -107 & 711 & -1860 & 133 \\ -107 & 0.305 & -3.30 & 0.697 & -0.0905 \\ 711 & -3.30 & 206 & 188 & -11.5 \\ -1860 & 0.697 & 188 & 614 & -40.4 \\ 133 & -0.0905 & -11.5 & -40.4 & 2.74 \end{bmatrix} \quad (\text{Eq. 2})$$

and the variance of  $\varepsilon$  determined from the linear regression fitting procedure is 4970. The coefficient of multiple determination ( $R^2$ ) for the fit is 0.819.

$R^2$  is the ratio of the measures of variation explained by the regression model to the total variation present in the output variable under consideration. Values of  $R^2$  will vary between 0 (no variation explained and a very poor regression model) to 1 (perfect explanation of the model

variation by the regression model). An  $R^2$  value of 0.819 is close to 1, therefore the regression model fits the experimental data relatively well.

As outlined in Section 6.2, localized corrosion can initiate when  $E_{corr}$  exceeds  $E_{crit1}$ . This is equivalent to the condition that  $\Delta E$  is less than zero.

Figure 1 shows a plot of how the median potential difference ( $\Delta E$ ) (the top surface) varies with  $pH$  and absolute temperature at a chloride ion concentration of 3 mol/L. This represents the median behavior in that the error,  $\epsilon$ , in Equation 1 is set to zero and no use is made of the covariance matrix,  $s$ . Also shown in Figure 1 is the  $-4\sigma$  confidence interval surface (the bottom surface). Note that the  $-4\sigma$  confidence interval surface incorporates contributions from the median potential difference, the covariance of the regression coefficients, and the error variance term (see the EE function used in Attachment I, p. I-3).

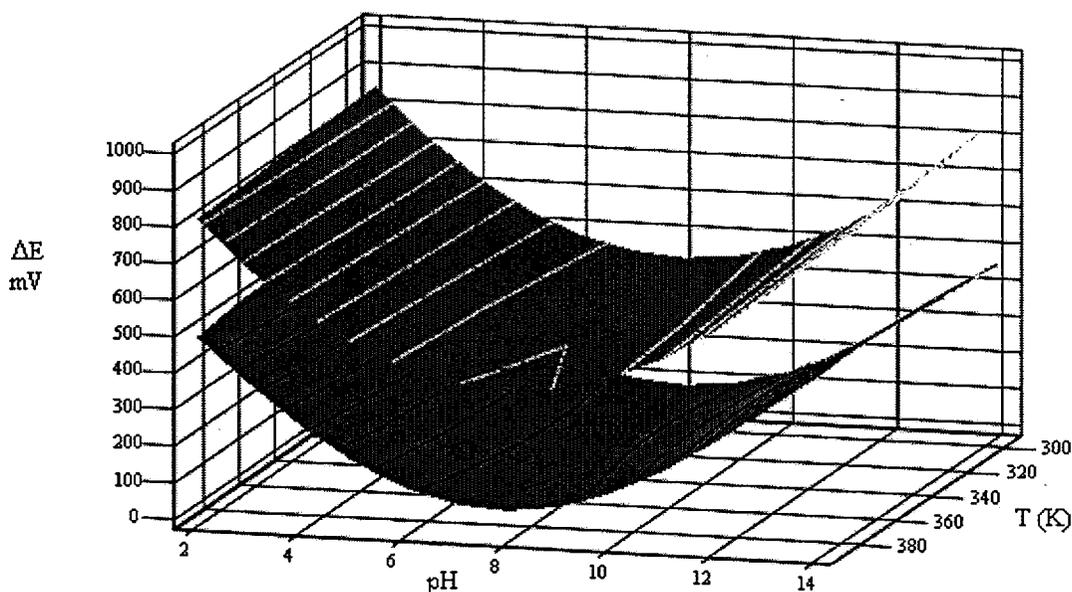


Figure 1. Plot of the median  $\Delta E$  and  $-4\sigma$  confidence interval surface versus  $pH$  and absolute temperature for Alloy 22 from Equation 1 and using a chloride ion concentration of 3 mol/L

Figure 2 shows a plot of how the median potential difference ( $\Delta E$ ) (the top surface) varies with  $pH$  and base 10 logarithm of chloride concentration at an absolute temperature of 380 K. This represents the median behavior in that the error,  $\epsilon$ , in Equation 1 is set to zero and no use is made of the covariance matrix,  $s$ . Also shown in Figure 2 is the  $-4\sigma$  confidence interval surface (the bottom surface).

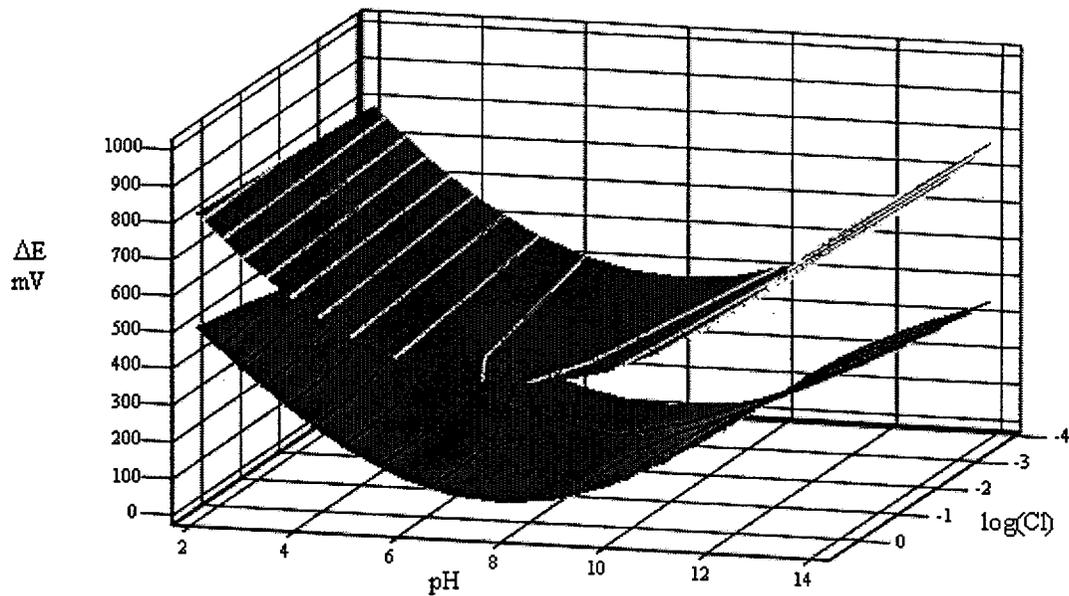


Figure 2. Plot of the median  $\Delta E$  and  $-4\sigma$  confidence interval surface versus  $pH$  and base 10 logarithm of chloride ion concentration for Alloy 22 from Equation 1 using an absolute temperature of 380 K

In Figure 1 and Figure 2,  $\Delta E$  is greater than zero over all ranges of  $pH$ , absolute temperature, and chloride concentration displayed (based on experimental data extrapolation).  $\Delta E$  values decrease as chloride concentration and absolute temperature increases.  $\Delta E$  has a parabolic dependence on  $pH$ , with a minimum at a  $pH$  value of approximately 8. Furthermore,  $\Delta E$  is only weakly dependent on absolute temperature or chloride ion concentration at a given value of  $pH$  for the conditions evaluated. Thus, the salient features of the functional dependence of  $\Delta E$  on the exposure parameters considered (over the ranges considered) are embodied within its dependence on  $pH$ .

The data presented in Table 2 for Alloy 22 were then used to fit a function of solution  $pH$ , i.e.

$$\Delta E = c_0 + c_1 \cdot pH + c_2 \cdot pH^2 + \varepsilon \quad (\text{Eq. 3})$$

where  $c_0$ ,  $c_1$ , and  $c_2$  are constants determined from fitting to Equation 3 to the collected potential difference data (Table 2). This exercise is documented in detail in Attachment I, pages I-6 to I-7. Linear regression gives the following estimates for the parameters in Equation 3:  $c_0 = 1160$ ,  $c_1 = -193$  and  $c_2 = 12.0$ . The covariance matrix ( $s$ ) and correlation matrix ( $C$ ) resulting from the fitting procedure were determined to be:

$$s = \begin{bmatrix} 3530 & -1040 & 64.4 \\ -1040 & 364 & -24.4 \\ 64.4 & -24.4 & 1.69 \end{bmatrix} \quad C = \begin{bmatrix} 1 & -0.915 & 0.835 \\ -0.915 & 1 & -0.982 \\ 0.835 & -0.982 & 1 \end{bmatrix} \quad (\text{Eq. 4})$$

and the variance of  $\varepsilon$  determined from the linear regression fitting procedure is 4670. The coefficient of multiple determination ( $R^2$ ) for the fit is 0.816 which indicates that the regression fits the data relatively well. This  $R^2$  value is very close to that obtained when temperature and chloride ion concentration are included in the regression function.

Figure 3 shows a plot of how the median potential difference  $\Delta E$  given by Equation 3 varies with  $pH$ . Also shown are the  $\pm 3\sigma$  and  $\pm 4\sigma$  confidence intervals.

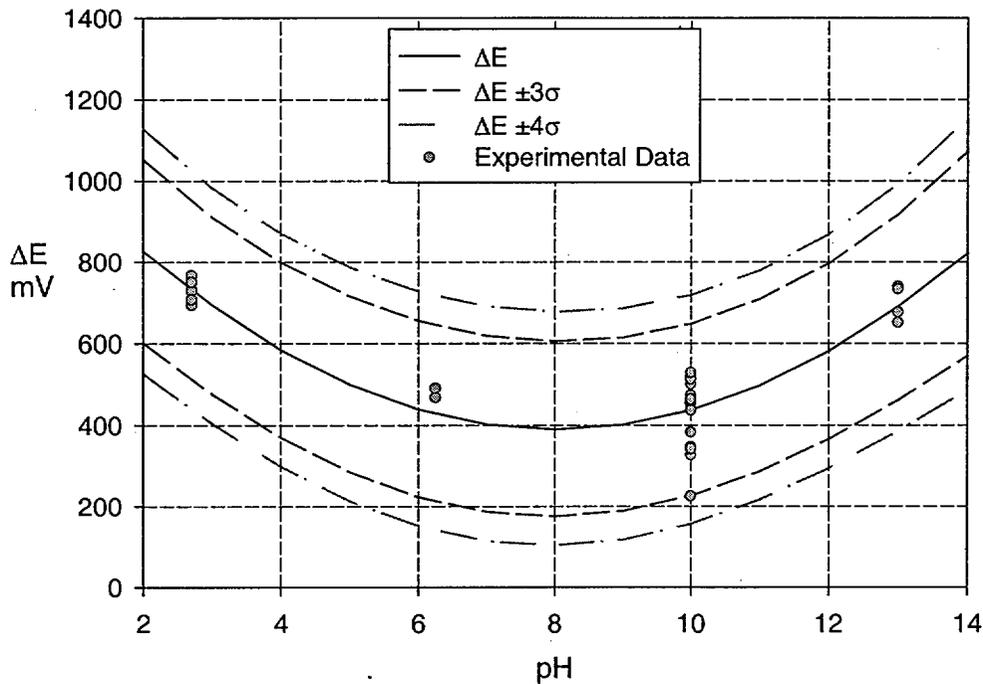


Figure 3. Plot of  $\Delta E$  vs.  $pH$  for Alloy 22 from Equation 3 showing the  $\pm 3\sigma$  and  $\pm 4\sigma$  confidence intervals and the experimental data in Table 2

Figure 3 shows that localized corrosion of Alloy 22 can not initiate at any  $pH$  based on the  $4\sigma$  confidence interval based on extrapolation of the repository-relevant experimental data used in this analysis.

### 6.3.2 Alloy 22 Localized Corrosion Initiation Threshold Model Validation

The model validation criteria used in this section are based on comparison of the model results to collected experimental data to gain an appropriate level of confidence in the model. The primary method used to conduct the model validation is graphing of model results and experimental data for use in visual comparison. By far the strongest argument for the validity of the Alloy 22 Localized Corrosion Initiation Threshold (ALCIT) Model is the fact that it is based on fitting a surface (through linear regression techniques) to the experimental data presented in Table 2. The  $R^2$  value of the regression fit was found to be 0.816, therefore the regression model fits the

experimental data relatively well. Figure 3 shows that most of the experimental data presented in Table 2 falls within the  $\pm 3\sigma$  confidence interval of the model and all of the experimental data falls within the  $\pm 4\sigma$  confidence interval of the model.

Other relevant experimental data against which the model may be compared was presented by the Nuclear Regulatory Commission's Gruss, et al. (1998) and is reproduced in Table 5 (Columns 1 through 4).

Table 5. Repassivation Potentials of Alloy 22 from Gruss et al. (1998) (Column 4) at various chloride ion concentrations (Column 2) and temperatures (Column 3).

Specimen Number	[Cl] mol/L	T °C	Repassivation Potential (mV vs. SCE)	Repassivation Potential (mV vs. Ag/AgCl)	$\Delta E$ (mV)
C22-1	4.0	95	916	962	1004
C22-2	4.0	95	911	957	999
C22-3	4.0	95	900	946	988
C22-4	4.0	60	911	957	999
C22-5	1.0	95	829	875	917
C22-6	1.0	60	986	1032	1074
C22-7	0.028	95	854	900	942

All of Gruss, et al.'s repassivation potential measurements were made in a solution of  $pH$  2.5. As discussed in Assumption 5.1, the repassivation potential is another candidate for use as the localized corrosion initiation threshold potential. Column 4 in Table 5 is the measured repassivation potential relative to the saturated calomel reference electrode while the electrochemical potentials presented in Table 2 are reported relative to the Silver/Silver Chloride (Ag/AgCl) reference electrode. The saturated calomel reference electrode (SCE) potential is approximately 46 mV higher than the Ag/AgCl reference electrode potential (Uhlig and Revie 1985, pp. 32-33). Gruss, et al.'s repassivation potentials rescaled (46 mV added) to the Ag/AgCl reference electrode potential are presented in Column 5 of Table 5. The corrosion potentials corresponding to the repassivation potentials presented in Column 5 of Table 5 were not reported in Gruss et al. (1998). The highest measured corrosion potential,  $E_{corr}$ , reported in Table 2 is  $-42$  mV relative to the Ag/AgCl reference electrode potential. In column 6 of Table 5, an approximate  $\Delta E$  based on the potential difference between Gruss, et al.'s repassivation potentials and an assumed  $-42$  mV corrosion potential is presented. A graphical comparison of Gruss, et al.'s data with the ALCIT Model is shown in Figure 4. As can be seen in Figure 4, use of the ALCIT Model is conservative relative to the use of an approximate  $\Delta E$  based on the potential difference between Gruss, et al.'s repassivation potentials and an assumed  $-42$  mV (vs. Ag/AgCl) corrosion potential.

Based on the graphical comparisons presented in Figure 3 and Figure 4, the ALCIT Model appropriately represents the data it was based upon (Table 2), and it is also conservative relative to data presented by the Nuclear Regulatory Commission's Gruss, et al. (1998). It is concluded that the ALCIT Model is validated.

The ALCIT Model is based on qualified data, however, the validation of the ALCIT Model is based on a combination of qualified and unqualified data. The use of unqualified data to validate

the ALCIT Model has no impact on the validity or appropriateness of the ALCIT Model. The unqualified data is used only for comparison purposes and does not directly contribute to results obtained from the use of the ALCIT Model.

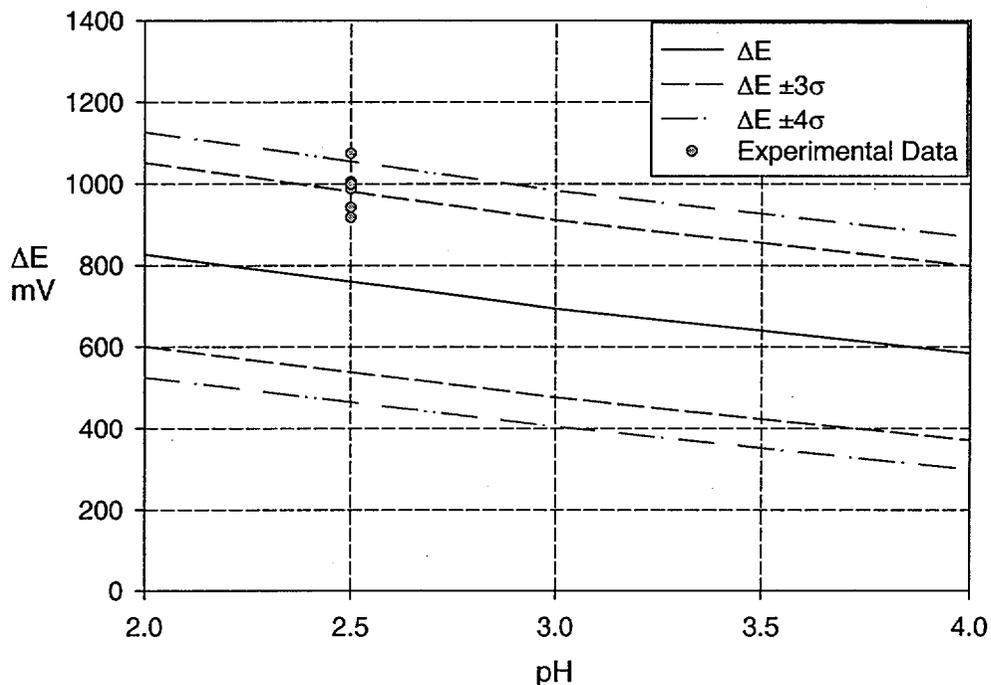


Figure 4. Comparison of Alloy 22 Localized Corrosion Initiation Model with data presented in Gruss, et al. (1998). Note that the “experimental data” for  $\Delta E$  is based on the difference between the repassivation potential from Gruss, et al. (1998) as the critical potential (rescaled from the SCE reference electrode to the Ag/AgCl reference electrode) and the maximum corrosion potential from the data in Table 2.

## 6.4 TITANIUM GRADE 7 POTENTIAL-BASED LOCALIZED CORROSION INITIATION THRESHOLD MODEL

### 6.4.1 Titanium Grade 7 Localized Corrosion Initiation Threshold Model Formulation

The data presented in Table 3 for Titanium grade 7 was used to fit a function of absolute temperature,  $T$ , solution  $pH$ , and the base 10 logarithm of the chloride ion concentration to the potential difference ( $\Delta E$ ) between the critical potential for localized corrosion initiation,  $E_{crit1}$ , and the corrosion potential,  $E_{corr}$ , i.e.,

$$\Delta E = d_0 + d_1 \cdot T + d_2 \cdot \log(Cl^-) + d_3 \cdot pH + \varepsilon \quad (\text{Eq. 5})$$

where  $d_0$ ,  $d_1$ ,  $d_2$ , and  $d_3$  are constants determined from fitting to Equation 5 to the collected potential difference data (Table 3). This exercise is documented in detail in Attachment I, pages I-8 to I-11.  $\varepsilon$  is a term representing data variance not explained by the fitting procedure and has a normal distribution with a mean of zero (see Assumption 5.4). In contrast to Equation 1 (used to fit the Alloy 22 potential difference data), Equation 5 makes no use of a  $pH^2$  term. A  $pH^2$  term was not included in the Titanium grade 7 potential difference fitting exercise as it was felt the experimental data showed no clear indication of a quadratic dependence on  $pH$  (see Figure 7). Linear regression gives the following estimates for the parameters in Equation 5:  $d_0 = 2050$ ,  $d_1 = -1.17$ ,  $d_2 = 14.1$ , and  $d_3 = -48.9$ . The covariance matrix resulting from the fitting procedure was determined to be:

$$s = \begin{bmatrix} 56100 & -165 & 1150 & 66.1 \\ -165 & 0.506 & -4.36 & -1.07 \\ 1150 & -4.36 & 535 & 116 \\ 66.1 & -1.07 & 116 & 56.1 \end{bmatrix} \quad (\text{Eq. 6})$$

and the variance of  $\varepsilon$  determined from the linear regression fitting procedure is 10500. The coefficient of multiple determination ( $R^2$ ) for the fit is 0.784 which indicates that the regression fits the data relatively well.

As outlined in Section 6.2, localized corrosion can initiate when  $E_{corr}$  exceeds  $E_{crit1}$ . This is equivalent to the condition that  $\Delta E$  is less than zero.

Figure 5 shows a plot of how the median potential difference  $\Delta E$  (and the  $-4\sigma$  confidence interval surface) varies with  $pH$  and absolute temperature at a chloride ion concentration of 3 mol/L. This represents the median behavior in that the error,  $\varepsilon$ , in Equation 5 is set to zero and no use is made of the covariance matrix,  $s$ .

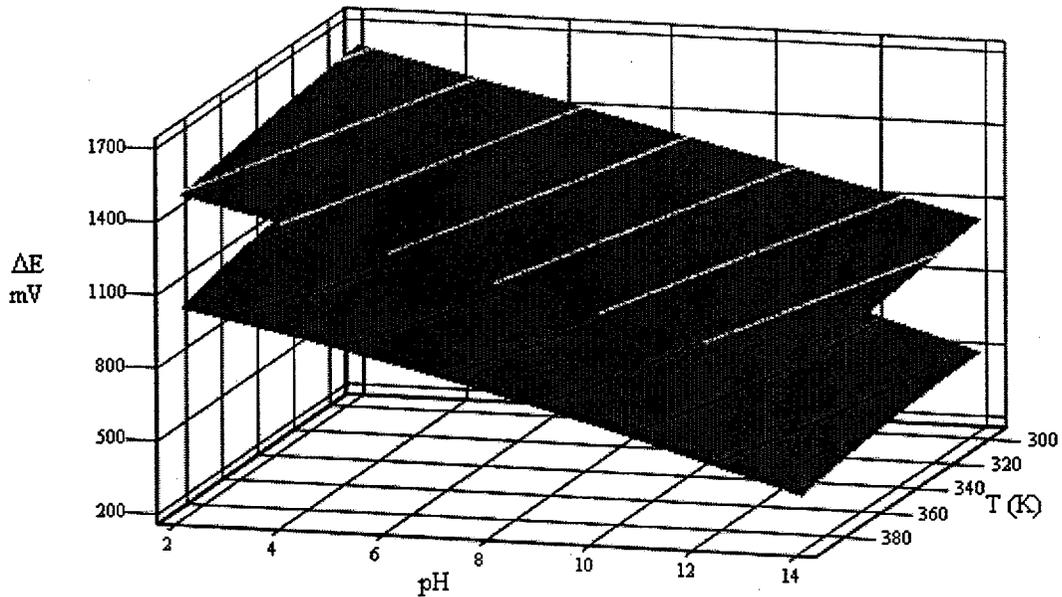


Figure 5. Plot of the median  $\Delta E$  and  $-4\sigma$  confidence interval surface versus  $pH$  and absolute temperature for Titanium grade 7 from Equation 5 using a chloride ion concentration of 3 mol/L

Figure 6 shows a plot of how the median potential difference  $\Delta E$  (and the  $-4\sigma$  confidence interval surface) varies with  $pH$  and base 10 logarithm of chloride concentration at an absolute temperature of 380 K. This represents the median behavior in that the error,  $\epsilon$ , in Equation 5 is set to zero and no use is made of the covariance matrix,  $s$ .

As can be seen from Figure 5 and Figure 6,  $\Delta E$  is greater than zero over all ranges of  $pH$ , absolute temperature, and chloride concentration displayed.  $\Delta E$  values decrease as  $pH$  and absolute temperature increase, and increase as chloride concentration increases. Furthermore,  $\Delta E$  is only weakly dependent on absolute temperature or chloride ion concentration at a given value of  $pH$ , for the conditions evaluated. Thus, the salient features of the functional dependence of  $\Delta E$  on the exposure parameters considered are embodied within its dependence on  $pH$ .

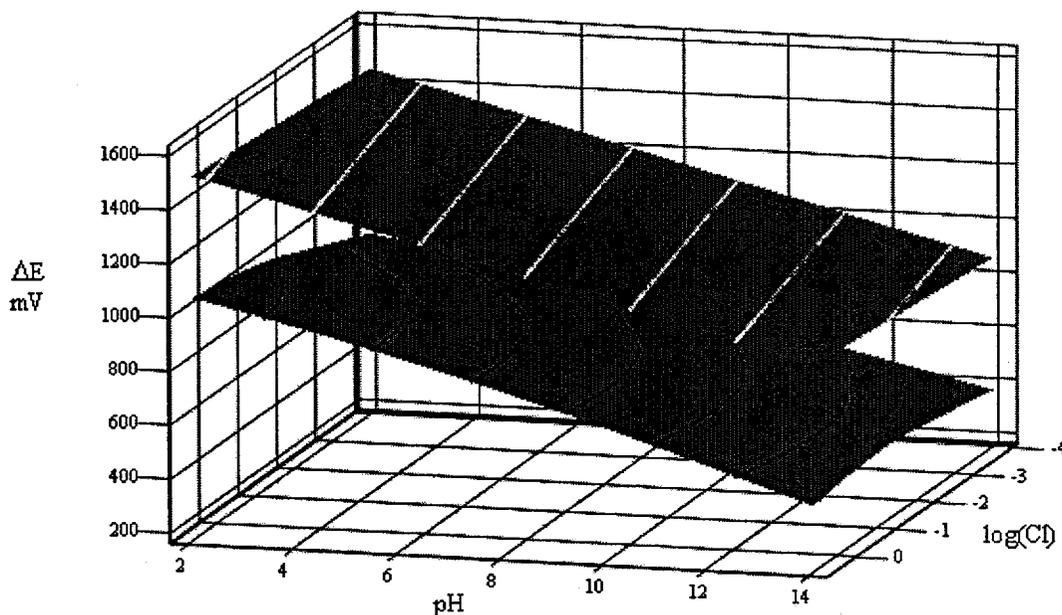


Figure 6. Plot of the median  $\Delta E$  and  $-4\sigma$  confidence interval surface versus  $pH$  and base 10 logarithm of chloride ion concentration for Titanium grade 7 from Equation 5 using an absolute temperature of 380 K

The data presented in Table 3 for Titanium grade 7 was then used to fit a function of solution  $pH$ , i.e.

$$\Delta E = f_0 + f_1 \cdot pH + \varepsilon \quad (\text{Eq. 7})$$

where  $f_0$  and  $f_1$  are constants determined from fitting to Equation 7 to the collected potential difference data (Table 3). This exercise is documented in detail in Attachment I, pages I-12 to I-13. Linear regression gives the following estimates for the parameters in Equation 7:  $f_0 = 1670$  and  $f_1 = -52.2$ . The covariance matrix ( $s$ ) and correlation matrix ( $C$ ) resulting from the fitting procedure was determined to be:

$$s = \begin{bmatrix} 2040 & -230 \\ -230 & 31.9 \end{bmatrix} \quad C = \begin{bmatrix} 1 & -0.904 \\ -0.904 & 1 \end{bmatrix} \quad (\text{Eq. 8})$$

and the variance of  $\varepsilon$  determined from the linear regression fitting procedure is 1080. The coefficient of multiple determination ( $R^2$ ) for the fit is 0.760 which indicates that the regression fits the data relatively well.

Figure 7 shows a plot of how the median potential difference  $\Delta E$  given by Equation 7 varies with  $pH$ . Also shown are the  $\pm 3\sigma$  and  $\pm 4\sigma$  confidence intervals.

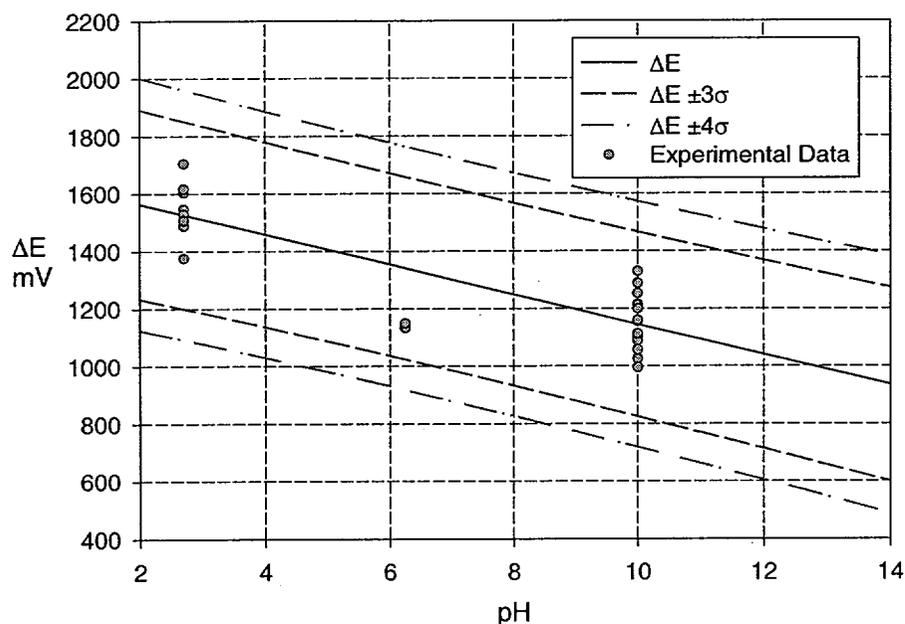


Figure 7. Plot of  $\Delta E$  versus  $pH$  for Titanium grade 7 from Equation 7 showing the  $\pm 3\sigma$  and  $\pm 4\sigma$  confidence intervals and the experimental data from Table 3

Figure 7 shows that localized corrosion of Titanium grade 7 can not initiate even at a  $pH$  of 14 based on the  $3\sigma$  and  $4\sigma$  confidence intervals based on extrapolation of the repository-relevant experimental data used in this analysis.

#### 6.4.2 Titanium Grade 7 Localized Corrosion Initiation Threshold Model Validation

The model validation criteria used in this section are based on comparison of the model results to collected experimental data to gain an appropriate level of confidence in the model. The primary method used to conduct the model validation is graphing of model results and experimental data for use in visual comparison. By far the strongest argument for the validity of the Titanium grade 7 Localized Corrosion Initiation Threshold (TLCIT) Model is the fact that it is based on fitting a surface (through linear regression techniques) to the experimental data presented in Table 3. The  $R^2$  value of the regression fit was found to be 0.760, therefore the regression model fits the experimental data relatively well. Figure 7 shows that the experimental data presented in Table 3 falls within the  $\pm 3\sigma$  confidence interval of the model.

Other relevant experimental data against which the model may be compared has been presented by Schutz and Thomas (1987) and is reproduced in Table 6.

Table 6. Pitting Potentials of Titanium Grade 7 from Schutz and Thomas (1987, p. 688 Table 23) in Saturated NaCl Solutions at Various Temperatures and *pH* Values.

Alloy	Solution	<i>pH</i>	Temperature °C	Pitting Potential (mV vs. Ag/AgCl)
Ti grade 7	Saturated NaCl	1, 7	25	9600
Ti grade 7	Saturated NaCl	1, 7	95	5200 – 7000

Schutz and Thomas also quote the repassivation potential of Titanium grade 7 as 5600 mV relative to the Ag/AgCl reference electrode (Schutz and Thomas 1987, p. 688 Table 24). Given that the highest corrosion potential, *E<sub>corr</sub>*, reported in Table 3 is – 37 mV relative to the Ag/AgCl reference electrode, any approximate  $\Delta E$  based on the potential difference between either the pitting potentials reported in Table 6 or the above mentioned repassivation potential would exceed 4500 mV, a value well outside (above) even the  $4\sigma$  confidence interval of the TLCIT Model at any *pH* value greater than 2. This serves as conclusive evidence that the TLCIT Model is conservative relative to the data considered.

Based on the graphical comparison presented in Figure 7 and the discussion presented in this section, the TLCIT Model appropriately represents the data it was based upon (Table 3), and is conservative relative to data presented by Schutz and Thomas (1987). It is concluded that the TLCIT Model is validated.

The TLCIT Model is based on qualified data, however, the validation of the TLCIT Model is based on a combination of qualified and accepted data. The use of accepted data to validate the TLCIT Model has no impact on the validity or appropriateness of the TLCIT Model. The accepted data is used only for comparison purposes and does not directly contribute to results obtained from the use of the TLCIT Model.

## 7. CONCLUSIONS

### 7.1 GENERAL ANALYSIS CONCLUSIONS

In this document, localized corrosion of the waste package outer barrier (Alloy 22) and drip shield (Titanium grade 7) materials is analyzed. A general discussion of localized corrosion processes was presented along with references to other documents in which the TSPA-SR conceptual model for localized corrosion initiation and propagation is documented. Potential-based localized corrosion initiation threshold functions for Alloy 22 and Titanium grade 7 were derived from the functional dependence of experimentally obtained electrochemical potential data on absolute temperature, *pH*, and the base 10 logarithm of chloride ion concentration. From the characteristics of these functional forms, it was determined that the salient features of their functional dependence on the exposure parameters considered are embodied within their dependence on *pH*. It was concluded, based on the solutions tested and exposure conditions evaluated, that localized corrosion of Alloy 22 can not initiate at any *pH* based on the  $4\sigma$  confidence interval. It was also concluded, based on the solutions tested and exposure conditions evaluated, that localized corrosion of Titanium grade 7 can not initiate at a *pH* values up to 14 based on the  $3\sigma$  and  $4\sigma$  confidence intervals.

The results of this analysis are based on qualified data inputs (DTN: LL990610205924.075, LL000209105924.127, LL000112105924.111, LL000320405924.146) and thus are also qualified. This analysis does not contain information or assumptions that need to be confirmed prior to the use of the results of this Analyses and Models Report (AMR). The output data of this AMR (i.e., Attachment I) is tracked by DTN: MO0003SPAPCC03.004.

## 8. INPUTS AND REFERENCES

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## 8.3 SOURCE DATA, LISTED BY DATA TRACKING NUMBER

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LL000112105924.111. Corrosion and Potential Data Associated with High pH Saturated Water. Submittal date: 01/25/2000.

LL000209105924.127. General Corrosion and Localized Corrosion of the Drip Shield. Submittal date: 02/29/2000.

LL000320405924.146. Target Compositions Of Aqueous Solutions Used For Corrosion Testing. Submittal date: 03/22/2000.

## 9. ATTACHMENTS

### I Alloy 22 and Titanium Grade 7 Potential Difference Analysis

## Attachment I - Alloy 22 and Titanium Grade 7 Potential Difference Analysis

Software Routine: BBreg Version 1.0

Critical and Corrosion Potentials for Alloy 22 in Long-Term Corrosion Test Facility Solutions

Cl<sup>-</sup> in mg/L converted to Cl<sup>-</sup> in mol/L by division by 35.453 g/mol (35,453 mg/mol) (Sargent-Welch Scientific Company 1979).

The following table contains data that are tracked by DTN: LL990610205924.075, LL000112105924.111, LL000209105924.127, and LL000320405924.146.

Dat :=

	Solution	T °C	E <sub>corr</sub> mV vs. Ag/AgCl	E <sub>crit1</sub>	Cl <sup>-</sup> mg/L	Cl <sup>-</sup> mol/L	pH
1	SDW	30	-55	466	67	1.89E-03	10.00
2	SDW	30	-65	436	67	1.89E-03	10.00
3	SDW	30	-93	420	67	1.89E-03	10.00
4	SDW	60	-137	317	67	1.89E-03	10.00
5	SDW	60	-174	282	67	1.89E-03	10.00
6	SDW	60	-161	290	67	1.89E-03	10.00
7	SDW	90	-191	192	67	1.89E-03	10.00
8	SDW	90	-162	185	67	1.89E-03	10.00
9	SDW	90	-158	169	67	1.89E-03	10.00
10	SCW	30	-57	169	6700	1.89E-01	10.00
11	SCW	30	-188	341	6700	1.89E-01	10.00
12	SCW	60	-240	234	6700	1.89E-01	10.00
13	SCW	60	-231	226	6700	1.89E-01	10.00
14	SCW	60	-226	238	6700	1.89E-01	10.00
15	SCW	90	-136	206	6700	1.89E-01	10.00
16	SCW	90	-237	199	6700	1.89E-01	10.00
17	SAW	30	-42	663	24250	6.84E-01	2.70
18	SAW	60	-118	575	24250	6.84E-01	2.70
19	SAW	90	-176	555	24250	6.84E-01	2.70
20	SAW	60	-115	613	24250	6.84E-01	2.70
21	SAW	90	-171	595	24250	6.84E-01	2.70
22	SAW	60	-102	605	24250	6.84E-01	2.70
23	SAW	90	-150	600	24250	6.84E-01	2.70
24	SSW	100	-234	234	128000	3.61E+00	6.25
25	SSW	120	-320	171	154000	4.34E+00	6.25
26	BSW	110	-233	418	130830	3.69E+00	13
27	BSW	110	-257	419	130830	3.69E+00	13
28	BSW	110	-345	394	130830	3.69E+00	13
29	BSW	110	-372	361	130830	3.69E+00	13

• This function fills a matrix, M, with r rows and c columns with a constant value, v. Note that matrix indices begin at zero and not one.

The field below allows for visual verification that the cmatrix(r,c,v) function provides correct results and is therefore verified.

$$\text{cmatrix}(r,c,v) := \begin{cases} \text{for } i \in 0..r-1 \\ \text{for } j \in 0..c-1 \\ M_{i,j} \leftarrow v \end{cases}$$

M

$$\text{cmatrix}(3,1,1) = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$$

Linear regression function:

$$\text{BBreg}(rX, rY) := \left( \begin{array}{l}
 \text{invrXX} \leftarrow (rX^T \cdot rX)^{-1} \\
 rb \leftarrow \text{invrXX} \cdot rX^T \cdot rY \\
 r\sigma\epsilon^2 \leftarrow \frac{\left( rY^T \cdot rY - rb^T \cdot rX^T \cdot rY \right)}{\left( \text{length}(rY) - \text{cols}(rX) \right)} \\
 r\Sigma \leftarrow r\sigma\epsilon^2 \cdot \text{invrXX} \\
 \text{len} \leftarrow \text{length}(rY) - 1 \\
 \text{SS}_{\text{tot}} \leftarrow \sum_{i=0}^{\text{len}} (rY_i - \text{mean}(rY))^2 \\
 \text{SS}_{\text{res}} \leftarrow \sum_{i=0}^{\text{len}} [rY_i - (rX \cdot rb)_i]^2 \\
 \text{SS}_{\text{reg}} \leftarrow \sum_{i=0}^{\text{len}} [(rX \cdot rb)_i - \text{mean}(rY)]^2 \\
 \text{Rsquared} \leftarrow \frac{\text{SS}_{\text{reg}}}{\text{SS}_{\text{tot}}} \\
 \text{SS} \leftarrow (r\sigma\epsilon^2 \quad \text{Rsquared} \quad \text{SS}_{\text{tot}} \quad \text{SS}_{\text{res}} \quad \text{SS}_{\text{reg}}) \\
 (rb \quad r\Sigma \quad \text{SS}^T)
 \end{array} \right)$$

- Regression coefficients (rb<sub>i</sub>)
- Residual or error variance (rσϵ<sup>2</sup>)
- Covariance matrix (rΣ)
- Sum of Squares total
- Sum of Squares residual
- Sum of Squares regression
- R Squared
- Output Values

Here, for Alloy 22,  $\Delta E = (E_{crit1} - E_{corr})$  is fit to a linear function of Temperature (K),  $\log(\text{Cl})$ , pH, and  $\text{pH}^2$  i.e.,

$$\Delta E = (E_{crit1} - E_{corr}) = b_0 + b_1 \cdot T + b_2 \cdot \log(\text{Cl}) + b_3 \cdot \text{pH} + b_4 \cdot \text{pH}^2$$

$$rY := \text{Dat}^{(2)} - \text{Dat}^{(1)} \quad \Delta E$$

$$rX^{(0)} := \text{cmatrix}(\text{length}(rY), 1, 1) \quad \text{This is a vector of ones. Used to calculate the intercept of the model}$$

$$rX^{(1)} := \text{Dat}^{(0)} + 273.15 \quad \text{Temperature in Kelvin}$$

$$rX^{(2)} := \overrightarrow{\log(\text{Dat}^{(4)})} \quad \text{Logarithm (base 10) of chloride concentration.}$$

$$rX^{(3)} := \text{Dat}^{(5)} \quad \text{pH}$$

$$rX^{(4)} := (\text{Dat}^{(5)})^2 \quad \text{pH}^2$$

Multiple linear regression is performed  $(b \ s \ SS) := \text{BBreg}(rX, rY)$

$\text{conde}(rX^T \cdot rX) = 3.162 \times 10^7$  This is the Euclidean norm of the matrix that is inverted in the first line of function BBreg.

These are the results of the regression operation.

• Regression coefficients ( $b_i$ )

• Covariance matrix,  $s$

$$(b \ s) = \left[ \begin{array}{c} \left( \begin{array}{c} 1.26 \times 10^3 \\ -3.13 \times 10^{-1} \\ 8.15 \times 10^0 \\ -1.88 \times 10^2 \\ 1.18 \times 10^1 \end{array} \right) \\ \left( \begin{array}{cccccc} 4.24 \times 10^4 & -1.07 \times 10^2 & 7.11 \times 10^2 & -1.86 \times 10^3 & 1.33 \times 10^2 \\ -1.07 \times 10^2 & 3.05 \times 10^{-1} & -3.30 \times 10^0 & 6.97 \times 10^{-1} & -9.05 \times 10^{-2} \\ 7.11 \times 10^2 & -3.30 \times 10^0 & 2.06 \times 10^2 & 1.88 \times 10^2 & -1.15 \times 10^1 \\ -1.86 \times 10^3 & 6.97 \times 10^{-1} & 1.88 \times 10^2 & 6.14 \times 10^2 & -4.04 \times 10^1 \\ 1.33 \times 10^2 & -9.05 \times 10^{-2} & -1.15 \times 10^1 & -4.04 \times 10^1 & 2.74 \times 10^0 \end{array} \right) \end{array} \right]$$

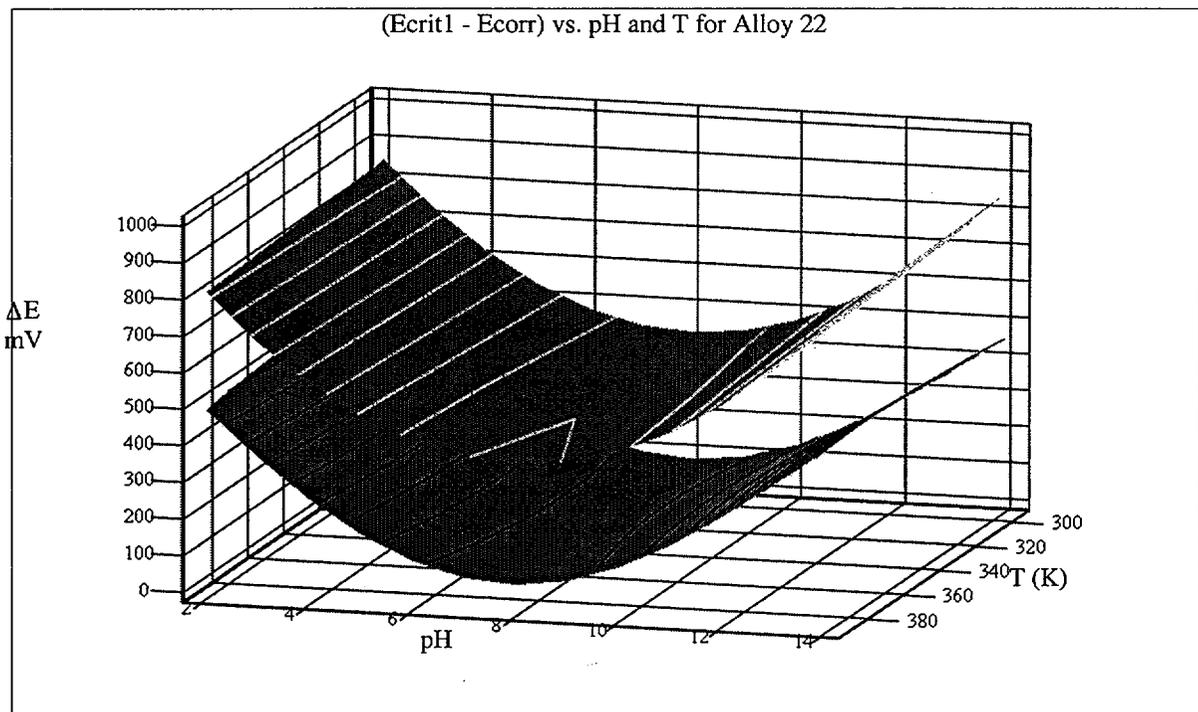
$$SS = \left( \begin{array}{c} 4.97 \times 10^3 \\ 8.19 \times 10^{-1} \\ 6.59 \times 10^5 \\ 1.19 \times 10^5 \\ 5.39 \times 10^5 \end{array} \right) \quad \begin{array}{l} \bullet \text{ Residual variance (} r\sigma\epsilon^2 \text{)} \\ \bullet \text{ R squared} \\ \bullet \text{ Sum of Squares total} \\ \bullet \text{ Sum of Squares residual} \\ \bullet \text{ Sum of Squares regression} \end{array}$$

$EE(T, \text{Cl}, \text{pH}, z)$  is a function that evaluates  $\Delta E$  using the median surface,  $X_0 \cdot b$ , a given  $z$ -value (number of standard deviations away from the median values), the residual variance,  $SS_0$ , and the covariance matrix,  $s$ .

$$EE(T, \text{Cl}, \text{pH}, z) := \left| \begin{array}{l} X_0 \leftarrow \left( 1 \quad T \quad \log(\text{Cl}) \quad \text{pH} \quad \text{pH}^2 \right) \\ \left( X_0 \cdot b + z \cdot \sqrt{SS_0 + X_0 \cdot s \cdot (X_0)^T} \right)_0 \end{array} \right|$$

The following steps evaluate EE at various values of T and pH for a constant chloride ion concentration of 3 mol/L.

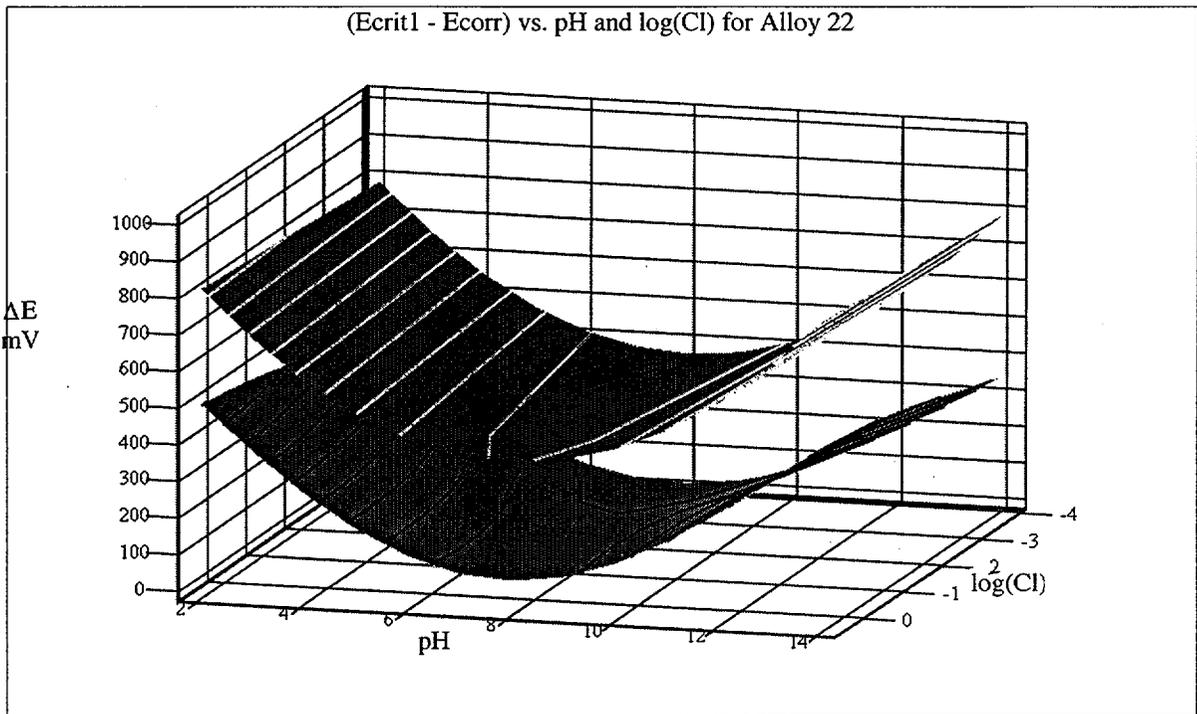
$T := 20..120 \quad ^\circ\text{C}$                        $\text{pH} := 2..14$   
 $x1_{T-20, \text{pH}-2} := T + 273.15$                $y1_{T-20, \text{pH}-2} := \text{pH}$   
 $Z := \overrightarrow{\text{EE}(x1, 3, y1, 0)}$                       Z is the median surface  
 $Zm4 := \overrightarrow{\text{EE}(x1, 3, y1, -4)}$                       Zm4 is the  $-4\sigma$  confidence surface



$(x1, y1, Z), (x1, y1, Zm4)$

The following steps evaluate EE at various values of chloride concentration and pH for a constant temperature of 380 K.

$\text{minCl} := 10^{-4}$                $\text{maxCl} := 4$                $N := 200$                $i := 0..N$   
 $i\text{Cl}_{i, \text{pH}-2} := \text{minCl} + \frac{i}{N} \cdot (\text{maxCl} - \text{minCl})$                $i\text{pH}_{i, \text{pH}-2} := \text{pH}$   
 $Z2 := \overrightarrow{\text{EE}(380, i\text{Cl}, i\text{pH}, 0)}$                       Z2 is the median surface  
 $Z2m4 := \overrightarrow{\text{EE}(380, i\text{Cl}, i\text{pH}, -4)}$                       Z2m4 is the  $-4\sigma$  confidence surface



$(\overrightarrow{\log(iCl)}, ipH, Z2), (\overrightarrow{\log(iCl)}, ipH, Z2m4)$

Here, for Alloy 22,  $\Delta E$  is fit to a function of pH only, i.e.,

$$\Delta E = c_0 + c_1 \cdot pH + c_2 \cdot pH^2$$

$rY := \text{Dat}^{(2)} - \text{Dat}^{(1)}$   $\Delta E$

$rX1^{(0)} := \text{cmatrix}(\text{length}(rY), 1, 1)$  Vector of ones

$rX1^{(1)} := \text{Dat}^{(s)}$  pH

$rX1^{(2)} := (\text{Dat}^{(s)})^2$  pH<sup>2</sup>

Multiple linear regression is performed  $(c \ s \ SS) := \text{BBreg}(rX1, rY)$

$\text{conde}(rX1^T \cdot rX1) = 2.303 \times 10^5$  This is the Euclidean norm of the matrix that is inverted in the first line of function BBreg.

These are the results of the regression operation.

- Regression coefficients ( $c_i$ )
- Covariance matrix,  $s$

- Residual variance ( $r\sigma^2$ )
- R squared
- Sum of Squares total
- Sum of Squares residual
- Sum of Squares regression

$$(c \ s \ SS) = \left[ \begin{array}{c} \left( \begin{array}{c} 1.16 \times 10^3 \\ -1.93 \times 10^2 \\ 1.20 \times 10^1 \end{array} \right) \left( \begin{array}{ccc} 3.53 \times 10^3 & -1.04 \times 10^3 & 6.44 \times 10^1 \\ -1.04 \times 10^3 & 3.64 \times 10^2 & -2.44 \times 10^1 \\ 6.44 \times 10^1 & -2.44 \times 10^1 & 1.69 \end{array} \right) \left( \begin{array}{c} 4.67 \times 10^3 \\ 8.16 \times 10^{-1} \\ 6.59 \times 10^5 \\ 1.21 \times 10^5 \\ 5.37 \times 10^5 \end{array} \right) \end{array} \right]$$

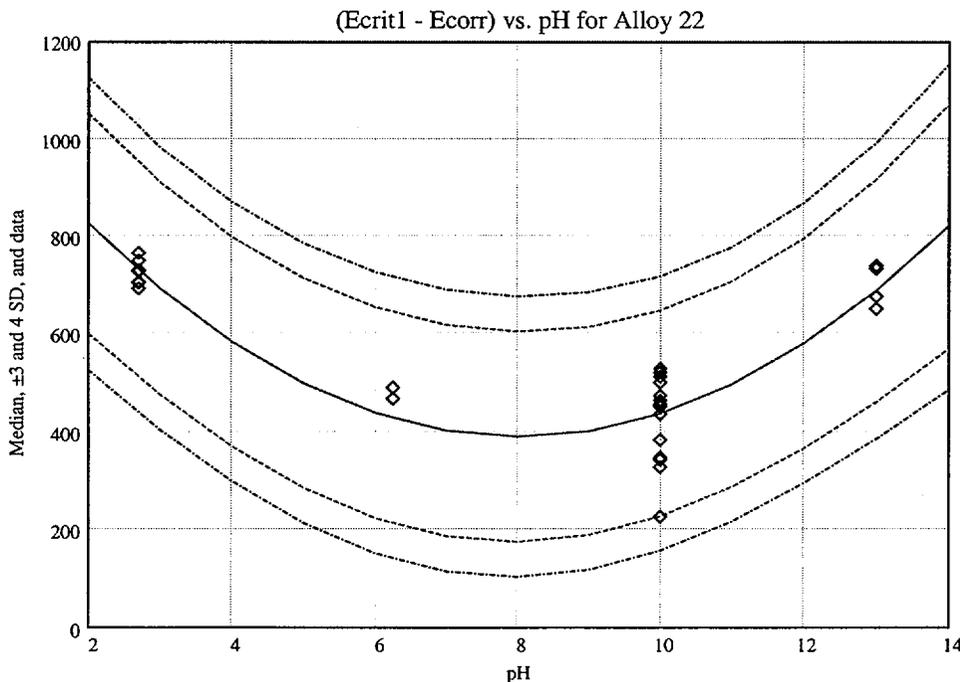
The correlation matrix (Corr(i,j)) is determined from the covariance matrix:

$$i := 0..2 \quad j := 0..2 \quad \text{Corr}_{i,j} := \frac{s_{j,i}}{\sqrt{s_{j,j}} \sqrt{s_{i,i}}} \quad \text{Corr} = \begin{pmatrix} 1 & -0.915 & 0.835 \\ -0.915 & 1 & -0.982 \\ 0.835 & -0.982 & 1 \end{pmatrix}$$

EE(pH,z) is a function that evaluates  $\Delta E$  using the median surface,  $X_{0-c}$ , a given z-value (number of standard deviations away from the median value), the residual variance ( $SS_0$ ), and the covariance matrix,  $s$ .

$$\text{EE2}(\text{pH}, z) := \begin{cases} X_0 \leftarrow \begin{pmatrix} 1 & \text{pH} & \text{pH}^2 \end{pmatrix} \\ \left( X_0 \cdot c + z \cdot \sqrt{SS_0 + X_0 \cdot s \cdot (X_0)^T} \right)_0 \end{cases} \quad \text{pH1} := 2..14$$

The results of the software routine documented in this Attachment are verified by visual comparison of model outputs to model inputs. The graph below shows that the computer outputs are acceptable for the current application and that the software routine is properly operating for the specified input parameters.



Critical and Corrosion Potentials for **Titanium Grade 7** in Long-Term Corrosion Test Facility Solutions

mV vs. Ag/AgCl      mol/L

Dat :=

	Solution	T	E <sub>corr</sub>	E <sub>crit1</sub>	Cl <sup>-</sup>	Cl <sup>-</sup>	pH
		°C	mV vs. Ag/AgCl		mg/L	mol/L	
1	SDW	30	-145	1070	67	1.89E-03	10.00
2	SDW	30	-99	1000	67	1.89E-03	10.00
3	SDW	30	-125	1030	67	1.89E-03	10.00
4	SDW	60	-212	947	67	1.89E-03	10.00
5	SDW	60	-114	912	67	1.89E-03	10.00
6	SDW	60	-214	874	67	1.89E-03	10.00
7	SDW	90	-305	808	67	1.89E-03	10.00
8	SDW	90	-305	752	67	1.89E-03	10.00
9	SCW	30	-37	958	6700	1.89E-01	10.00
10	SCW	30	-187	968	6700	1.89E-01	10.00
11	SCW	30	-233	1020	6700	1.89E-01	10.00
12	SCW	60	-331	880	6700	1.89E-01	10.00
13	SCW	60	-364	796	6700	1.89E-01	10.00
14	SCW	60	-351	849	6700	1.89E-01	10.00
15	SCW	90	-480	849	6700	1.89E-01	10.00
16	SCW	90	-506	654	6700	1.89E-01	10.00
17	SCW	90	-516	772	6700	1.89E-01	10.00
18	SAW	30	-153	1450	24250	6.84E-01	2.70
19	SAW	30	-187	1430	24250	6.84E-01	2.70
20	SAW	30	-284	1420	24250	6.84E-01	2.70
21	SAW	30	-176	1440	24250	6.84E-01	2.70
22	SAW	30	-145	1230	24250	6.84E-01	2.70
23	SAW	60	-99	1390	24250	6.84E-01	2.70
24	SAW	60	-125	1420	24250	6.84E-01	2.70
25	SAW	90	-187	1300	24250	6.84E-01	2.70
26	SAW	90	-187	1340	24250	6.84E-01	2.70
27	SAW	90	-176	1330	24250	6.84E-01	2.70
28	SSW	100	-211	921	128000	3.61E+00	6.25
29	SSW	120	-336	813	154000	4.34E+00	6.25

Here, for Titanium grade 7,  $\Delta E = (E_{crit1} - E_{corr})$  is fit to a linear function of Temperature (K),  $\log(Cl)$ , and pH, i.e.,

$$\Delta E = (E_{crit1} - E_{corr}) = d_0 + d_1 \cdot T + d_2 \cdot \log(Cl) + d_3 \cdot pH$$

$$rY := Dat^{(2)} - Dat^{(1)}$$

This is  $\Delta E$

$$rX2^{(0)} := cmatrix(\text{length}(rY), 1, 1)$$

This is a vector of ones. Used to calculate the intercept of the model

$$rX2^{(1)} := Dat^{(0)} + 273.15$$

Temperature in Kelvin

$$rX2^{(2)} := \overrightarrow{\log(Dat^{(4)})}$$

Logarithm (base 10) of chloride concentration.

$$rX2^{(3)} := Dat^{(5)}$$

pH

Multiple linear regression is performed

$$(d \ s \ SS) := BBreg(rX2, rY)$$

$$\text{conde}(rX2^T \cdot rX2) = 1.742 \times 10^7$$

This is the Euclidean norm of the matrix that is inverted in the first line of function BBreg.

These are the results of the regression operation.

• Regression coefficients ( $c_i$ )

• Covariance matrix, s

$$(d \ s) = \begin{bmatrix} \begin{pmatrix} 2.05 \times 10^3 \\ -1.17 \times 10^0 \\ 1.41 \times 10^1 \\ -4.89 \times 10^1 \end{pmatrix} & \begin{pmatrix} 5.61 \times 10^4 & -1.65 \times 10^2 & 1.15 \times 10^3 & 6.61 \times 10^1 \\ -1.65 \times 10^2 & 5.06 \times 10^{-1} & -4.36 \times 10^0 & -1.07 \times 10^0 \\ 1.15 \times 10^3 & -4.36 \times 10^0 & 5.35 \times 10^2 & 1.16 \times 10^2 \\ 6.61 \times 10^1 & -1.07 \times 10^0 & 1.16 \times 10^2 & 5.61 \times 10^1 \end{pmatrix} \end{bmatrix}$$

$$SS = \begin{pmatrix} 1.05 \times 10^4 \\ 7.84 \times 10^{-1} \\ 1.21 \times 10^6 \\ 2.62 \times 10^5 \\ 9.49 \times 10^5 \end{pmatrix}$$

• Residual variance ( $r\sigma^2$ )  
 • R squared  
 • Sum of Squares total  
 • Sum of Squares residual  
 • Sum of Squares regression

$EE2(T, Cl, pH, z)$  is a function that evaluates  $\Delta E$  using the median surface,  $X_0 \cdot d$ , a given z-value (number of standard deviations away from the median values), the residual variance ( $SS_0$ ), and the covariance matrix, s.

$$EE2(T, Cl, pH, z) := \begin{cases} X_0 \leftarrow (1 \ T \ \log(Cl) \ pH) \\ \left( X_0 \cdot d + z \cdot \sqrt{SS_0 + X_0 \cdot s \cdot (X_0)^T} \right)_0 \end{cases}$$

The following steps evaluate EE2 at various values of T and pH for a constant chloride ion concentration of 3 mol/L.

$$T := 20..120 \quad ^\circ\text{C}$$

$$\text{pH} := 2..14$$

$$x3_{T-20,\text{pH}-2} := T + 273.15$$

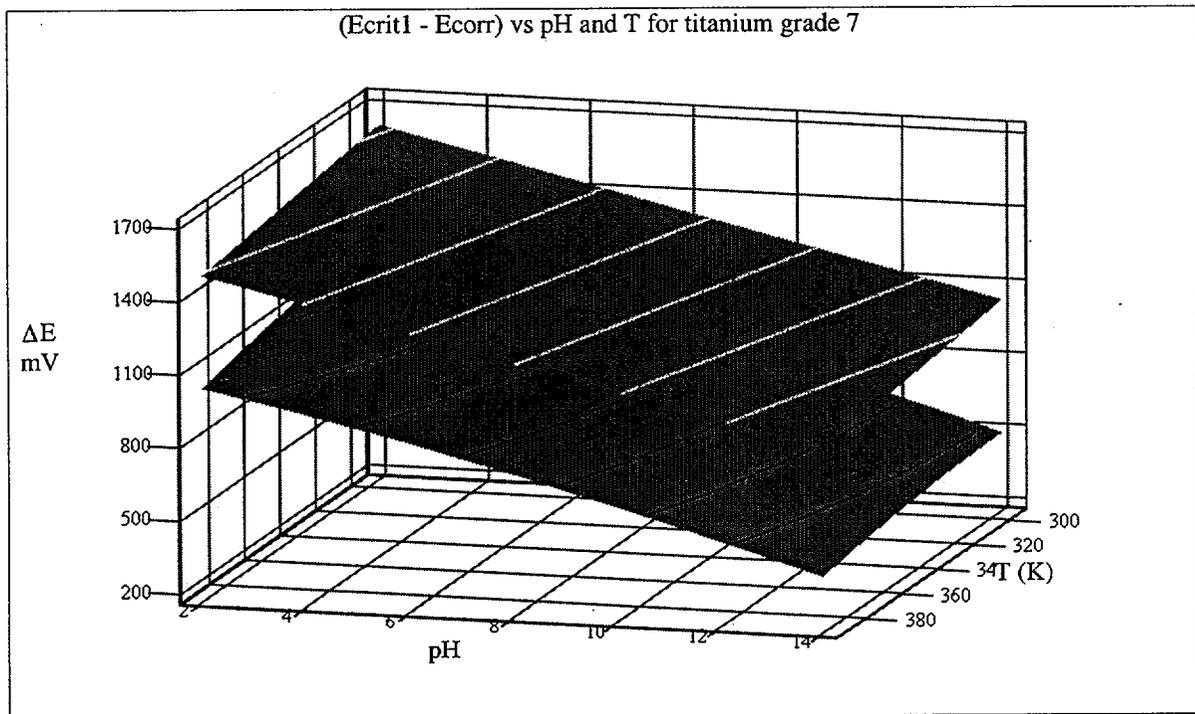
$$y3_{T-20,\text{pH}-2} := \text{pH}$$

$$Z3 := \overrightarrow{\text{EE2}(x3, 3, y3, 0)}$$

Z3 is the median surface

$$Z3m4 := \overrightarrow{\text{EE2}(x3, 3, y3, -4)}$$

Z3m4 is the  $-4\sigma$  confidence surface



$(x3, y3, Z3), (x3, y3, Z3m4)$

The following steps evaluate EE2 at various values of chloride concentration and pH for a constant temperature of 380 K.

$$\text{minCl} := 10^{-4}$$

$$\text{maxCl} := 4$$

$$N := 200$$

$$i := 0..N$$

$$iCl_{i,\text{pH}-2} := \text{minCl} + \frac{i}{N} \cdot (\text{maxCl} - \text{minCl})$$

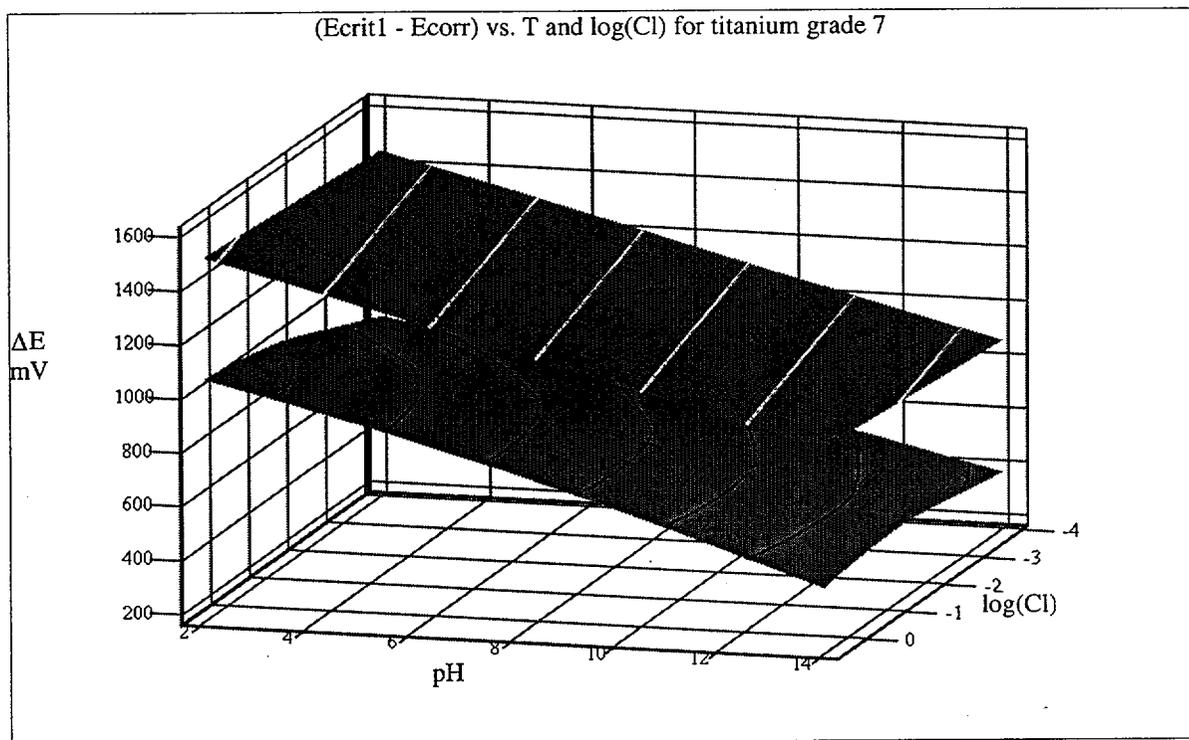
$$ipH_{i,\text{pH}-2} := \text{pH}$$

$$Z4 := \overrightarrow{\text{EE2}(380, iCl, ipH, 0)}$$

Z4 is the median surface

$$Z4m4 := \overrightarrow{\text{EE2}(380, iCl, ipH, -4)}$$

Z4m4 is the  $-4\sigma$  confidence surface



$(\overrightarrow{\log(i\text{Cl}), ipH, Z4}), (\overrightarrow{\log(i\text{Cl}), ipH, Z4m4})$

Here, for Titanium grade 7,  $\Delta E$  is fit to a linear function of pH only, i.e.,

$$\Delta E = f_0 + f_1 \cdot \text{pH}$$

$$rY := \text{Dat}^{(2)} - \text{Dat}^{(1)} \quad \Delta E$$

$$rX3^{(0)} := \text{cmatrix}(\text{length}(rY), 1, 1) \quad \text{Vector of ones}$$

$$rX3^{(1)} := \text{Dat}^{(5)} \quad \text{pH}$$

Multiple linear regression is performed  $(f \ s \ SS) := \text{BBreg}(rX3, rY)$

$$\text{conde}(rX3^T \cdot rX3) = 359.05$$

This is the Euclidean norm of the matrix that is inverted in the first line of function BBreg.

These are the results of the regression operation.

• Regression coefficients ( $f_i$ )

• Covariance matrix, s

• Residual variance ( $r\sigma E2$ )

• R squared

• Sum of Squares total

• Sum of Squares residual

• Sum of Squares regression

$$(f \ s \ SS) = \begin{bmatrix} \begin{pmatrix} 1.67 \times 10^3 \\ -5.22 \times 10^1 \end{pmatrix} & \begin{pmatrix} 2.04 \times 10^3 & -2.30 \times 10^2 \\ -2.30 \times 10^2 & 3.19 \times 10^1 \end{pmatrix} & \begin{pmatrix} 1.08 \times 10^4 \\ 7.60 \times 10^{-1} \\ 1.21 \times 10^6 \\ 2.91 \times 10^5 \\ 9.20 \times 10^5 \end{pmatrix} \end{bmatrix}$$

The correlation matrix ( $\text{Corr}(i,j)$ ) is determined from the covariance matrix:

$$i := 0..1 \quad j := 0..1 \quad \text{Corr2}_{i,j} := \frac{s_{j,i}}{\sqrt{s_{j,j}} \cdot \sqrt{s_{i,i}}} \quad \text{Corr2} = \begin{pmatrix} 1 & -0.904 \\ -0.904 & 1 \end{pmatrix}$$

EE3(pH,z) is a function that evaluates  $\Delta E$  using the median value,  $X_0 \cdot f$ , a given z-value (number of standard deviations away from the median value), the residual variance ( $SS_0$ ), and the covariance matrix, s.

$$\text{EE3}(\text{pH}, z) := \begin{bmatrix} X_0 \leftarrow (1 \ \text{pH}) \\ \left( X_0 \cdot f + z \cdot \sqrt{SS_0 + X_0 \cdot s \cdot (X_0)^T} \right)_0 \end{bmatrix}$$

$$\text{pH1} := 2..14$$

$\Delta E$  vs. pH for Titanium grade 7

