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# Environmental Effects on Corrosion Properties of Alloy 22

K. S. Raja

*University of Nevada, Las Vegas*

L. G. McMillion

*University of Nevada, Reno*

Shantanu A. Namjoshi

Paige Russel

Raymond E. Keeler

*Cooperative Agreement Project Director*

*See next page for additional authors*

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**Authors**

K. S. Raja, L. G. McMillion, Shantanu A. Namjoshi, Paige Russel, Raymond E. Keeler, and Amy J. Smiecinski



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(DCN)

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DCN No. 1 to Document No. SIP-UNR-036, Revision 0, Effective Date: 11/10/04.

Document Title: Environmental Effects on Corrosion Properties of Alloy 22

**Identify applicable affected page, section, paragraph, attachment, exhibit, table, figure, or other:**

1) **Add to Section 1.0.3.1:** Redesign of working electrode mounting method using Micro Stop stop-off lacquer or a similar approach to mitigate localized corrosion will proceed coincident with the following electrochemical test series.

2) **Delete from Section 1.0.3.1:** Objectives 4, 5, 6 and 8.

3) **Delete from Section 1.0.3.3.1:** Experimental plans for Phase III and Phase IV.

4) **Modify first sentence in 3. in experimental plan in Section 1.0.3.3.1 to Read:** pH will be monitored throughout each experiment using a calibrated glass electrode and pH meter. pH will be adjusted using HCl for acid pH solutions and NaOH for basic pH solutions; no buffer systems will be used for acid and basic pH solutions.

5) **Add the following Note to Tables 1, 2, & 3:** Note that these values are nominal and may be changed if experimental results or other considerations indicate the need.

6) **Add to end of point 10. in experimental plan in Section 1.0.3.3.1 :** or a characteristic time interval has passed.

7) **Delete Sections 1.0.3.3.3 and 1.0.3.3.4**

8) **Modify Section 1.0.4 to Read:**

- Phase I anodic experimentation will be performed during Years 2, 3 and 4.
- Phase I cathodic experimentation will begin during Year 3.
- Phase II anodic experimentation will be performed during Years 3, 4 and 5.
- Phase II cathodic experimentation will be performed during Years 4 and 5.

9) **Modify Section 1.1.4 to Read:**

The following represents the proposed schedule for this subtask (Note: Recruiting of students and research associates will also have a significant impact on schedules.)

Year 1: Literature review and background data developed.

Year 2: Continue literature review and background data development. Initial development of a basic physical model for electrochemical conditions at the interface between metal and hygroscopic dust and particulate deposits using first principles for steady state conditions.

Year 3: Extension of the above model will to consider hygroscopic salt deposits for different humidity levels and oxygen and carbon dioxide diffusion conditions. Development of the thermodynamic/kinetic/transport parameters needed for the model. Development of the physical model to calculate the under-deposit corrosion rates under steady state conditions.

Year 4: Extension of steady state physical and numerical models to dynamic conditions. The model will be validated using the existing qualified data developed through the subtask 3. Variation of ionic concentration, pH, and temperature with exposure time will be incorporated in the dynamic model.

Year 5: Model calibration by comparison of qualified data (generated by subtask 3) at limiting boundary conditions.

Improvement of the model of under-deposit corrosion rates at different times and distances from the crevice mouth into the crevice will be completed based on the validation with qualified experimental data.

10) **Delete from Section 1.2.3.1:**

- Materials and Heat Treatment: **Multi-Pass Welded Coupons**,
- Test Environments: Perched Water, Pore Water, Simulated Concentrated Water (SCW), Simulated Saturated Water (SSW)

11) **Modify Section 1.2.4 to Read:**

The following represents the proposed schedule for this subtask (Note: Receiving and calibrating new and updated equipment, receiving qualified weld specimens, and recruiting of students and research associates will also have a significant impact on schedules):

- Year 1: SIP Preparation and approval, design and fabrication of electrochemical cells, IP development initiation,

and initiation of experimental work.

- Year 2: Immersed heated electrode tests of Alloy-22 solution annealed and aged in dilute and concentrated water. Development of IPs for Welding of Alloy-22 plates using Gas Tungsten Arc Welding Process. Initiation of Liquid drop-on heated electrode testing and Determination and Calibration of Ionic Strength of Electrolyte in the Heated Electrode Cell.
- Year 3: Immersed heated electrode tests of Ti Gr 7 in dilute and concentrated waters, Continuation of immersed heated electrode tests and initiation of liquid drop-on heated electrode tests of Alloy-22 solution annealed and aged in concentrated waters. Initiation of Alloy-22 as-weld specimens. User calibration of Transmission Electron Microscopy (TEM) and Electron Energy Loss Spectroscopy (EELS) and study of the surface films of the corroded surface using these analytical instruments
- Year 4: Initiate heated electrode corrosion testing on Alloy-22 AWSP and AWSPWA specimens. Initiate corrosion testing on Alloy-22 AWSPSA specimens. Continuation of immersed heated electrode tests of Ti Gr 7 in dilute and concentrated waters. Continuation of liquid drop-on heated electrode tests of Alloy-22 aged specimens in concentrated waters. Initiate Transmission Electron Microscopy and Electron Energy Loss Spectroscopy study of the surface films of the corroded surface
- Year 5: Complete testing on Alloy-22 AWSP and AWSPWA specimens. Complete testing on Alloy-22 AWSPSA specimens. Continue Transmission Electron Microscopy and Electron Energy Loss Spectroscopy study of the surface films of the corroded surface

[Note: AW = as weld, SP = single pass, SA = solution annealed, WA = weld + aged]

- Delete the Test Matrix from this section

**12) Modify the Electrochemical Cell Section in 1.3.4.1 to read:** 5 necked ASTM G-5 type electrochemical cell.

**13) Modify Section 1.3.4.3 to Read:** TEM studies will be carried out to characterize the passive film and to understand the hydrogen diffusion behavior in the film. The variation of metal/film interface structure after hydrogen charging will be studied and evaluated.


**14) Modify Section 1.3.5 to read:**

The following represents the proposed schedule for this subtask (Note: Receiving and calibrating new and updated equipment, and recruiting of students and research associates will also have a significant impact on schedules):

- Year 1: SIP Preparation and approval, design and fabrication of electrochemical cells, IP development initiation, and initiation of experimental work.
- Year 2: Initiation of development of IP's for Gas Tungsten Arc Welding of Alloy-22 plates, Heat treatment of Alloy-22, Hydrogen Permeation studies, Electrochemical impedance and Mott-Schottky Measurements, User calibration of EDAX analyzer etc.
- Year 3: Completion of above IPs. Continued experimental work for the determination of the diffusivities of hydrogen in Alloy-22 at different microstructural conditions. Continued work on the calculations of the activation energies through evaluation of diffusion coefficients at different temperatures. Initiation of experimental work for the determination of the change in electronic properties of the passive film of Alloy-22 in the presence of hydrogen.
- Year 4: Continued experimental work for the determination of the change in electronic properties of the passive film of Alloy-22 in the presence of hydrogen. Initiation of Transmission Electron Microscopy studies on the solution annealed specimens to investigate the interface between passive film/metal with and without hydrogen charging after polarization in pitting environments.
- Year 5: Transmission Electron Microscopy and Electron Energy Loss Spectroscopy studies on the aged Alloy 22 specimens to investigate the interface between passive film/metal with and without hydrogen charging after polarization in pitting environments.

Additional testing with different aging conditions and different electrochemical cells may be carried out as budget and time constraints allow. These include different surface conditions and use of Devanathan and Stachurski type electrochemical cells.

This DCN may be cancelled to restore original scope to the SIP.


Approved by: 

PI: 

Date: 03/15/05

(Signature)

Print name: Shantanu Namjoshi

QA Manager:  Date: 3-28-05  
(Signature)

Print name: Amy J. Smiecinski

QA Manager evaluated acceptability, that it does not violate quality requirements, and for impacts to other procedures; signature above documents this evaluation as successfully completed.

Send electronic version of this DCN to Webmaster.

Attach this DCN as first page of hard copies of document, if any.



*University and Community College System of Nevada (UCCSN)*

**SCIENTIFIC INVESTIGATION PLAN (SIP)**

Task title: **Environmental Effects on Corrosion Properties of Alloy 22**

Task Number: **ORD-FY04-014**

Document Number: **SIP-UNR-036**

Revision: **0**

Effective Date: **November 10, 2004**

Authors: [Redacted] 9/23/04  
K. S. Raja L. Glen McMillion Date

Approvals: [Redacted] 9/23/04  
Principal Investigator (Technical Reviewer) Date  
Shantanu A. Namjoshi

[Redacted] 10/6/04  
Technical Task Representative Date  
Paige Russell

[Redacted] 10/11/2004  
Project Director Date  
R.E. Keeler

[Redacted] 11-10-04  
QA Manager Date  
A. J. Smiecinski

**REVISION HISTORY**

<b><u>Revision Number</u></b>	<b><u>Effective Date</u></b>	<b><u>Description and Reason for Change</u></b>
0	11/10/2004	Initial Issue

**Document Format:**

This Scientific Investigation Plan presents detailed plans for four Subtasks that will be conducted independently. All four Subtasks investigate environmental effects on corrosion properties of Alloy 22. The four Subtasks are:

Subtask 1: Experimental Determination of Parameters for the General Corrosion Model.

Subtask 2: Corrosion under Dust Deposits Containing Hygroscopic Salts.

Subtask 3: Heated Electrode Approach for the Study of Corrosion Under Aggressive Conditions.

Subtask 4: Effect of Hydrogen Permeation on the Stability of the Passive Film of Alloy 22.

**1.0 Subtask 1: Experimental Determination of Parameters for the General Corrosion Model**

**1.0.1 Introduction**

During the regulatory life of the Yucca Mountain High Level Nuclear Waste (HLNW) repository the primary engineered barrier that is to prevent release of radioactive material into the environment is proposed to be a Corrosion-Resistant Material (CRM) outer shell covering the Waste Package (WP) container. The current selection for the CRM is Alloy 22 (UNS N06022), a Ni-Cr-Mo-W-Fe alloy. Alloy 22 forms a defective chromic oxide passive film which results in excellent corrosion resistance; the presence of molybdenum in Alloy 22 offers corrosion resistance in reducing environments as well as oxidizing environments.

Yucca Mountain is composed of fractured volcanic tuff and rhyolite. The fractured nature of the mountain results in the air in the repository drifts being in equilibrium with the external atmospheric pressure. Considering the different ground waters present (well water, perched water, pore water), the conditions are such that relatively concentrated aerated brine solutions of near-neutral to basic pH and a wide range of ionic compositions may be present on the WP containers resulting in a variety of corrosive environments<sup>1</sup>.

Because of the need to isolate high-level nuclear waste for the regulatory life of the YM-HLNW repository, and the very low corrosion rates of Alloy 22 and other candidate CRM's, WP container integrity in the face of general and localized corrosion should be assured on the basis of model predictions in addition to direct measurements of corrosion rates, which may be subject to large experimental uncertainty because of relatively short test periods. These models should be deterministic, relying upon time- and space-invariant natural laws in order to yield accurate predictions over the very long time scale



of the regulatory life of the repository. To accurately predict corrosion of all kinds DOE has developed the General Corrosion Model (GCM), which will be used as part of the regulatory task of designing the WP container and drip shield. As part of the General Corrosion Model (GCM) for overall corrosion performance prediction modeling, the Point Defect Model (PDM) of passive film growth and breakdown on metals, developed by Dr. Digby D. Macdonald<sup>2</sup>, will be used to model anodic processes; cathodic processes will be modeled using the exchange current density and the modified Butler-Volmer equation.

### **1.0.2 Scope and Objectives**

The objective of the proposed investigation of Task ORD-FY04-014, “Environmental Effects on Corrosion Properties of Alloy 22,” Subtask 1, “Experimental Determination of Parameters for the General Corrosion Model,” is to obtain very high-accuracy experimental data which will be used to determine model parameters that will provide accurate general corrosion modeling over the full range of temperature, pH, ionic composition, and potential anticipated over the lifetime of the repository. To model general corrosion of Alloy 22 over the repository lifetime, during which many significantly different temperatures and solution compositions will occur, fundamental mechanistic parameters used by the models must be known for all of the conditions expected to be encountered. Development of the PDM or GCM may be indicated to account for the complex ionic compositions of Yucca Mountain ground waters and the solutions that may result from deposition of airborne salt particles. More accurate modeling of general corrosion will allow cost reduction by improving the level of confidence in the design thickness of the Alloy 22 corrosion resistant barrier and reducing the degree of over design required to compensate for uncertainties in corrosion rates determined from weight loss measurements.

This work is subject to University and Community College System of Nevada (UCCSN) Quality Assurance Program requirements.

This Scientific Investigation Plan presents an independently derived, unbiased body of scientific data. The data generated are believed to be unique and do not support information previously gathered by the Yucca Mountain Project.

### **1.0.3 Approach**

Knowledge of both anodic and cathodic processes on Alloy 22 is required for successful modeling of corrosion. Anodic processes are characterized by the growth and breakdown of the defective  $\text{Cr}_2\text{O}_3$  passive film that forms on Alloy 22. Kinetic rate constants and other parameters for the Point Defect Model (PDM) of passive films on metals will be extracted from electrochemical impedance spectroscopy (EIS) data and passive current density transients resulting from step changes in potential. Passive current density, which is proportional to passive corrosion rate, can be expressed in the form:

$$i_p = i_p^o [H^+]^p [Cl^-]^q \exp(-E_a/RT) \quad (1)$$

where  $p$  and  $q$  are reaction orders,  $E_a$  is the activation energy, and  $i_p^o$  is a constant. Subtask 1 will make measurements of “steady state” current, current transients, and frequency-dependent impedance. Values for  $p$ ,  $q$ ,  $E_a$ , and  $i_p^o$  will be determined by a global fit of Equation 1 to these experimental data. The data will be collected at “steady state” under the conditions summarized in Tables 1, 2, and 3.

Kinetic rate constants and other parameters in the Point Defect Model are extracted by a multivariate best fit method for a set of equations that is too complex to present here; please refer to Macdonald and Sun<sup>3</sup> for a complete description.

Kinetic parameters for the cathodic processes of hydrogen evolution and oxygen reduction are also required for the General Corrosion Model. The two parameters of interest are the exchange current density and the Tafel constant ( $\beta_c$ ). The exchange current density can be expressed in terms of the reactant and product concentrations as:

$$i_o = i_o^o [H_2 \text{ or } O_2]^m [H^+]^n \exp(-E_a / RT) \quad (2)$$

where  $m$  and  $n$  are the reaction orders,  $E_a$  is the activation energy and  $i_o^o$  is a constant. For this aspect of the model, the objective of the experimental work is to derive values for  $m$ ,  $n$ ,  $E_a$ , and  $i_o^o$  for the hydrogen evolution and oxygen reduction reactions on Alloy 22. The parameter values will be determined by a global fit of Equation 2 to the experimental data. The Tafel constant ( $\beta_c$ ) will be determined from the generalized Butler-Volmer equation:

$$i = \frac{-e^{-(E-E_e)/\beta_c}}{\frac{1}{i_0} - \frac{e^{-(E-E_e)/\beta_c}}{i_L}} \quad (3)$$

where  $E_e$  is the equilibrium potential and  $i_L$  is the limiting current density.

Anodic and cathodic electrochemical testing will be performed under a variety of conditions to simulate the expected range of conditions in the repository. Three types of electrolytes will be used: NaCl brines, NaCl + NO<sub>3</sub> solutions, and simulated Yucca Mountain ground waters concentrated approximately 1,000 fold. The exact composition of concentrated simulated ground waters to be used will be determined in collaboration with scientific investigators at the DOE Office of Repository Development (ORD), Bechtel-SAIC, and Lawrence Livermore National Laboratory (LLNL). Of special importance is the molar ratio of anions, as corrosion processes are quite sensitive to the accelerating or passivating effects of chloride, nitrate, and sulfate, as well as other anions. Three temperatures will be used: 30°, 60°, and 90°C. These temperatures are subject to change based on performance of materials and the tendency for crevice corrosion to increase with increasing temperature.

**1.0.3.1 The proposed work consists of the following tasks:**

1. *Objective:* Experimental studies and data analysis for development of the Point Defect Model for passive films on Alloy 22 will be conducted. Experiments conducted under idealized laboratory conditions will yield fundamental information about reaction mechanisms and reaction rate constants. This will improve understanding of the underlying surface science of corrosion on metals displaying passivity, and on Alloy 22 in the HLNW repository environment in particular. Experimental data collected under conditions simulating the YM repository service conditions will be used to derive model parameters that will be used to model corrosion into the far future of the regulatory life of the repository.
2. Collection of EIS and  $I_p$  data for solution-annealed Alloy 22 in 0.1 M NaCl solutions at pH 2, 6, and 10, all at 30°, 60°, and 90°C. This is considered to be a complete set of data for determining fundamental parameters for the PDM including standard kinetic rate constants for the controlling reaction mechanism. Validation of the PDM will be performed with these data.
3. Collection of EIS and  $I_p$  data for solution-annealed Alloy 22 in solutions containing nitrate anions. Tests will be conducted in solutions having a 1-to-1 ratio of chloride to nitrate such as 0.05M  $Cl^-$  + 0.05M  $NO_3^-$ . Three pH values and three temperatures will be tested. Other total concentrations and chloride/nitrate ratios may be considered. Nitrate is known to further passivate Alloy 22 in brine solutions and decrease the aggressive effect of chloride. It is believed that nitrate adsorbs to the chromic oxide passive film surface occupying oxygen sites and suppressing the annihilation of oxygen defects at the surface thereby decreasing the associated rate constants. The EIS/ $I_p$  results will be analyzed to verify the mechanism of nitrate addition and, if necessary, to further develop the PDM reaction mechanism to account for the action of nitrate. These data will be used to validate the PDM for Alloy 22 in chloride- and nitrate-containing solutions.
4. Collection of EIS and  $I_p$  data for solution-annealed Alloy 22 in solutions of concentrated Yucca Mountain ground waters, which contain nitrate and chloride. Once the PDM has been validated for Alloy 22 in chloride- and nitrate-containing solutions, model parameters directly representing repository service conditions will be developed.
5. Redesign of working electrode mounting method and determination of the highest chloride concentration that does not lead to crevice corrosion in this test system. High chloride concentrations may be subsequently investigated to allow the PDM to account for concentration effects on chloride chemical activity.
6. Collection of EIS and  $I_p$  data for solution-annealed Alloy 22 in a solution of the highest chloride concentration found to be usable without resulting in failure by crevice corrosion.
7. Experimental investigation of the influence on electrochemical behavior, including PDM parameters, of Alloy 22 that has a porous black oxide film resulting from solution annealing in air followed by water quench. This is the process that will be used in manufacturing the WP container shells and results in a porous black oxide layer on the surface of the metal. This will be the condition of Alloy 22 in service in the repository and therefore is of great practical importance.

8. Variability of as-received Alloy 22:
  1. Acquire six different heats of Alloy 22 from two different suppliers representing limits of chemical composition specified in ASTM B-575 and including trace elements unique to different suppliers.
  2. Perform a literature search on the on the available heat compositions of Alloy 22 (and perhaps Alloy 276) from Haynes, Inco, Allegheny-Ludlum, and any other commercial suppliers of Alloy 22 and compare their heat chemistries. This is a paper study only.
  3. Evaluate variability of electrochemical behavior (corrosion potential, polarization resistance, and cyclic polarization) and microstructure of as-received, mill-annealed Alloy 22.
  4. Solution anneal as-received specimens and re-test for corrosion potential, polarization resistance, and cyclic polarization.
  5. Age specimens for 10 hours at 750°C and re-test for corrosion potential, polarization resistance, and cyclic polarization.
  6. Using results developed above, specimens representing limits of electrochemical behavior found in as-received Alloy 22 will be tested to evaluate variability of PDM model parameters due to heat-to-heat variability.
9. Transmission Electron Microscopy may be used to investigate the composition of the defective chromic oxide passive layer to determine if chromium interstitials or oxygen vacancies are the principle defect. If the film is cation-rich the composition is estimated to be  $\text{Cr}_{2.028}\text{O}_3$  close to the film-metal interface, whereas if it is oxygen deficient it is estimated to be  $\text{Cr}_2\text{O}_{2.981}$  at the same location. Learning the identity of the principle defect will improve our understanding of the fundamental reaction mechanisms and is of practical importance because it will improve our understanding of the role of nitrate in improving passivation of Alloy 22 in the repository environment. TEM may also be used to investigate chromium depletion profiles in the near-surface of passivated Alloy 22 and in Alloy 22 solution annealed in air to form a porous black oxide surface layer. Chromium depletion due to solution annealing in air may affect corrosion properties.
10. Work is continuing on required necessary development of the PDM for the analysis of our data under separate contract to Professor Macdonald from DOE-YMP through IDT Services. Collaboration with Professor Macdonald will result in greater value from both the work proposed by UNR and the Dr. Macdonald's work through IDT Services.

### ***1.0.3.2 Specimen Preparation:***

Alloy 22 specimens for this project will be obtained from commercial suppliers Haynes International and Inco. The material will be qualified for use under the control of the University and Community College System of Nevada (UCCSN) Quality Assurance (QA) Program. The Alloy 22 will be sampled and tested by a testing laboratory on the DOE Qualified Suppliers List (QSL) to ensure it meets the ASTM standards for Alloy 22. UNR has a plate of Alloy 22 that has been qualified for use under the UCCSN QA Program and this material will be used for the initial proposed work; new material will be acquired and qualified as needed.

As shown from previous results, as-received, mill-annealed Alloy 22 displays significant variability in microstructure and electrochemical behavior that makes it unsuitable for use in this program. All specimens to be tested here will be subjected to metallographic analysis and solution heat treatment before being used. Specimens will be prepared as follows:

1. Alloy 22 plate or rod stock will be cut into 2 ½ inch long x 5/8 inch diameter cylinders.
2. Each specimen will be mounted in epoxy for metallographic analysis.
3. The mounted specimens will be polished to a mirror finish with successively finer polishing media. Experience has found that the sequence: 240 grit Silica carbide paper, 400 grit SiC paper, 600 grit SiC paper, 1.0 μm Al<sub>2</sub>O<sub>3</sub> suspension, 0.3 μm Al<sub>2</sub>O<sub>3</sub> suspension and 0.05 μm Al<sub>2</sub>O<sub>3</sub> suspension yields a suitable surface for microstructure analysis.
4. The specimen will be etched using the best available etching method.
5. Examination of the microstructure using optical microscopy and Scanning Electron Microscopy will be performed. Photographs will be made to record the microstructure. The Metallurgical and Materials Science Engineering Department at UNR has an Olympus metallographic optical microscope and a Hitachi SEM that will be used for this task.
6. After examination of the mill-annealed condition, each specimen will be solution heat treated in a tube furnace at 1200°C for two and one half hours. This heat treatment was determined experimentally at UNR using recommendations from Haynes International; Alloy 22 specimens with obvious precipitates were examined before and after this heat treatment, and this time and temperature treatment was found to be effective.
7. After solution heat treatment, the specimens will be remounted, repolished and examined to verify the microstructure.
8. The specimens are acceptable for electrochemical testing at this point.

### ***1.0.3.3 Test Plan:***

#### ***1.0.3.3.1 Anodic Measurements:***

Experiments will be performed in aqueous solutions of sodium chloride and concentrated, simulated Yucca Mountain waters at various temperatures and pH in two phases, which will be conducted sequentially. To collect data that will yield kinetic parameters for anodic processes on Alloy 22 in deaerated solutions, we will measure “steady state” passive current density ( $i_p$ ) and frequency-dependent impedance under potentiostatic conditions at a suitable number of steps over the full range of potential for which Alloy 22 displays passivity. The passivity range is about 600 mV and 100 mV steps are presently being used. Electrochemical Impedance Spectroscopy (EIS) will be used to measure frequency-dependent impedance. Current transients between potential increments will also be measured. The Point Defect Model predicts that passive current density is independent of potential for n-type passive film as in the case of Alloy 22 and this has been demonstrated to be valid in previous work done at UNR. True steady state

cannot be attained reasonably in the time available during these experiments. We will allow the system to approach true steady state as closely as possible within the time constraints. Our experience has shown that in 4M NaCl solution at 60°C, Alloy 22 initially requires about 150 hours to reach a suitable quasi-steady state and then about 44 hours to return to the steady state current density upon step change in potential. Reverse scanning to examine hysteresis is performed as a check to verify that the system is sufficiently close to steady state to yield experimental data with acceptable accuracy and uncertainty.

The experimental work collecting EIS and  $I_p$  data for the PDM parameter derivation and development will be conducted in several phases:

- Phase I will be long-term testing to collect potentiostatic EIS and passive current density data over the passive range for 0.1M NaCl solutions at three temperatures and three pH values (30°, 60°, and 90°C and pH 3, 6, and 11). Temperatures and pH values may be changed if required.
- Phase II will add nitrate to the test solution. Nitrate and chloride will be present in 1-to-1 molar ratio and the test matrix will use the same pH values and temperatures as Phase I. Phases I and II are idealized laboratory conditions for development of fundamental mechanistic understanding.
- Phase III, which will derive parameters for use in modeling repository service conditions, will use 1000x concentrated simulated Yucca Mountain waters at the same pH and temperatures as Phases I and II. The exact composition of water to be used for Phase III will be determined through consultation with Raul Rebak of LLNL.
- Phase IV will conduct long-term EIS and  $I_p$  data collection at the highest chloride concentration found to be usable without resulting in failure due to crevice corrosion. Tests will be conducted at the same pH and temperatures as Phase I to allow the PDM to account for concentration effects on chloride chemical activity.
- Further Phases of experimental data collection for PDM analysis may include:
  - Alloy 22 with black oxide surface layer formed by solution annealing in air (service condition of surface)
  - specimens representing extremes of Alloy 22 manufacturing variability,
  - concentrated chloride solutions to investigate concentration effects

The experiments will be conducted according to the following plan:

1. Sample coupons will be fabricated from mill annealed Alloy 22 plate or rod stock that has been tested and qualified in accordance with ASTM standards and UCCSN QAP procedures. Sample coupons will be solution heat treated and examined metallographically as described above before use.
2. The values of NaCl molarity, pH, and temperature at which the experiments will be performed for Phase I are given in Table 1. Conditions for Phase II experiments, which add nitrate anion in a solution of NaCl + NaNO<sub>3</sub>, are given in Table 2. Table 3 shows conditions for Phase III, which will measure EIS and passive current density in concentrated simulated Yucca Mountain waters. Phase IV experiments will be conducted

at the same pH and temperature values as shown in Table I, but will use the highest chloride concentration determined to be usable without resulting in failure due to crevice corrosion (see section 1.0.3.3.3 below).

3. pH will be adjusted using HCl for pH 3, a boric acid/ sodium borate buffer system for pH 6, and sodium hydroxide for pH 11. No buffer system will be used for pH 3 or 11. This is not expected to be a concern because electrolyte is constantly replenished so no significant changes in pH can occur during the short residence time of electrolyte in the test cell (6 hours in the WE compartment and 30 minutes in the CE compartment for the present design). Phosphate buffers will be avoided as they are known to significantly modify the electrochemistry of iron and nickel alloys. Organic buffers will be avoided as some are known to oxidize at moderate anodic potentials. Oxidation of acetate in an acetic acid/sodium acetate buffer system was observed at UNR at +400mV vs. Ag/AgCl/4M KCl. Alternative buffer systems may be used if required. pH will be monitored throughout each experiment using a calibrated glass electrode and pH meter.

*Table 1. Test Matrix for Phase I Anodic and Cathodic Measurements in 0.1 Molar Sodium Chloride-Only Solutions*

pH	Temperature °C		
3	30	60	90
6	30	60	90
11	30	60	90

*Table 2. Test Matrix for Phase II Anodic and Cathodic Measurements in 0.05 Molar Sodium Chloride + 0.05 Molar Sodium Nitrate Solutions*

pH	Temperature °C		
3	30	60	90
6	30	60	90
11	30	60	90

*Table 3. Test Matrix for Phase III Anodic and Cathodic Measurements in 1,000x Concentrated Simulated Yucca Mountain Water (SCW ~pH 8-10)*

pH	Temperature °C		
3	30	60	90
6	30	60	90
11	30	60	90

4. The anodic polarization curves for Alloy 22 for each of the conditions for anodic testing in all Phases of the project will be determined potentiodynamically according to ASTM G5-94<sup>4</sup> before beginning the passive current measurements. This will indicate the passive potential range over which the measurements will be made.

5. Steps will be taken to exclude oxygen from the system to avoid oxygen reduction contributions to the measured current. Solutions will be highly deaerated with ultra-high purity or “zero grade” compressed nitrogen gas. Nitrogen delivery tubing and metering components will be copper metal, FEP-lined Tygon® tubing, and glass. Copper metal acts as an oxygen scavenger and is impermeable to oxygen diffusion. FEP-lined Tygon® tubing has the lowest oxygen permeability of all commercially available tubing materials that meet chemical compatibility requirements for these tests and thus will be used to minimize diffusion of oxygen into the system through tubing runs.

6. Electrolyte solutions must not contain any redox species (H<sub>2</sub>, Cr<sup>3+</sup>, CrO<sub>4</sub><sup>2-</sup>, etc.) because they may result in a current that would be added to the passive current. Accordingly, the counter electrode will be housed in a separate compartment that is connected to the working electrode compartment by a glass frit and both electrode compartments will have a continuous flow of fresh electrolyte through them. This will continuously remove any redox species that are evolved. The electrolyte flow system will be constructed from a high-density polyethylene (HDPE) tank, FEP-lined Tygon® tubing, and glass flow meters and bleed valves to minimize diffusion of oxygen into the system through tank walls and tubing runs.

7. The reference electrode will be Ag/AgCl and will be placed inside the test cell next to the working electrode so it is at the same temperature as the WE. All measured potentials will be corrected for temperature and converted to the standard hydrogen scale.

8. Each “steady state” current determination will begin with the imposition of a positive potential step starting from a suitably low (negative) potential in the passive range for the specific conditions (NaCl molarity, pH, temperature) as shown by the anodic polarization curve. The magnitude of the potential steps will be about 100 mV per step. The choice of potential step magnitude will be finalized per experimental conditions to produce acceptable results in a reasonable time frame. The system must be demonstrated to be at “steady state” upon acquisition of final anodic passive current (*i<sub>p</sub>*)



data. Current density vs. time will be plotted on a log-log plot and the slope of the curve approaches zero as the system approaches steady state.

9. When the system has reached “steady state” and the  $i_p$  acquired, the impedance will be measured over the frequency range of 10 kHz to 10 mHz in the high frequency to low frequency direction, with multiple measurements being taken for each decade in frequency. Once the lowest frequency has been reached, the impedance will be re-measured in the low frequency to high frequency direction to test for system stability (hysteresis). Small hysteresis indicates small uncertainty. An excitation voltage of not more than 10 mV peak-to-peak will be used to ensure linearity. The impedance data will be validated by Kramers-Kronig transformation or a similar method.

10. When the impedance data has been collected the system will be stepped to the next (more positive) potential. The resulting current transient will be recorded until the current returns to the measured steady state value.

11. Preferably, at least six transients should be measured in the anodic (positive) direction. Once the transient at the most positive potential has been measured, the experiments will be repeated with cathodic (negative) potential steps back to the initial potential to check for hysteresis. Uncertainty is minimal when hysteresis is minimal. The magnitude of the negative potential steps will be determined based on experimental conditions and time constraints. The sample will not be disturbed between transient experiments for a single run at a single set of NaCl molarity, pH, and temperature conditions.

#### **1.0.3.3.2 Cathodic Measurements:**

12. H<sub>2</sub> evolution and O<sub>2</sub> reduction experiments will be performed after items 4-11 above have been completed. The conditions for which H<sub>2</sub>/O<sub>2</sub> tests will be performed are the same as those shown in Tables 1, 2, and 3.

13. The cathodic H<sub>2</sub>/O<sub>2</sub> reactions should be studied under the highest mass transfer rates possible in order to maximize the potential range over which the reactions are under activation control. Vigorous agitation by rotating disk electrodes will be used to increase mass transfer rates. H<sub>2</sub>/O<sub>2</sub> tests will be performed in different test cells than the anodic tests; cathodic test cells will not require constant replenishment of electrolyte and will require a different design to accommodate rotating disk electrodes. Specimen design will also be different from that used for anodic testing requiring additional machine shop services.

14. For O<sub>2</sub> reduction tests the ultra-high purity nitrogen gas will be replaced with a 21 % O<sub>2</sub>/ 79% N<sub>2</sub> mixture. Other O<sub>2</sub> concentrations may be used as data analysis proceeds and indicates the need. This may necessitate the use of a pressurized system to achieve high oxygen concentrations and to maintain oxygen in solution as the temperature is increased. Oxygen concentration may be varied from 100 ppm down to 1 ppm. Hydrogen peroxide may be added to the system to assist in controlling dissolved oxygen content. For H<sub>2</sub> evolution tests a single hydrogen concentration may be used in order to

establish a well-defined mixed potential. The H<sub>2</sub> concentration will be the equilibrium concentration that is established by replacing the nitrogen purge with 100% H<sub>2</sub>.

15. The new gas mixture (O<sub>2</sub> or H<sub>2</sub>) will be run long enough to reach equilibrium. The current-voltage curves for H<sub>2</sub> evolution and O<sub>2</sub> reduction must be measured under quasi-steady-state conditions starting at the open circuit potential. Once the current and voltage have stabilized under open circuit potential, the potential will be scanned slowly in the negative (cathodic) direction at a rate of about 600 mV/hr. The potential scan rate may be adjusted in order to achieve quasi-steady state. An alternative to slow, continuous potential scanning is to step the potential in the cathodic direction allowing sufficient time between steps for the system to reach quasi-steady state. For O<sub>2</sub> reduction tests, the final potential will be sufficiently negative that the mass transfer limit of O<sub>2</sub> diffusing to the solid electrode surface from solution is achieved.

**1.0.3.3.3 Localized Corrosion:** Localized corrosion has been observed during long-term potentiostatic testing with anodic polarization in pH 6, 4M NaCl solutions. Every specimen tested in 4M NaCl solution has developed localized corrosion within three weeks causing the experiments to be terminated. In order to design a comprehensive experimental matrix that can be used for long-term testing, the threshold values for NaCl concentration and pH below which localized corrosion does not become stable within the test period (75 days at 30°C, 18 days at 90°C) must be determined. This will begin during Phase I while tests are being conducted on 0.1M NaCl solutions, which is believed to be a low enough Cl<sup>-</sup> concentration to ensure no stable localized corrosion development during the test period. Additional localized corrosion studies will be performed on concentrated ground waters during anodic passive current/EIS measurements on NaCl brines to determine if there is a risk of failure for the concentrated ground water tests.

Specimen mounting technique will be developed. Use of different mounting epoxies (such as Loctite Hysol<sup>®</sup> EE4183 filled compound with HD0243 hardener) and use of coatings on the Alloy 22 specimen to retard the onset of crevice corrosion will be investigated. These approaches have been found to be beneficial by investigators at the Pennsylvania State University under the direction of Dr. D.D. Macdonald.

**1.0.3.3.4 Evaluation of Mill-Annealed Variability:** This portion of the proposed investigation will be performed in collaboration with Dr. J. C. Lacombe of UNR, who is also proposing studies on variability of mill-annealed Alloy 22. Dr. Lacombe's proposed investigation deals primarily with phase stability and microstructure whereas the work proposed here deals primarily with electrochemical behavior.

Electrochemical testing in 1 M NaCl and 1 M HCl solutions, and SCW (1000x YM UE-25 J-13 well water) will be performed. These solutions are chosen because much data has been generated by other researchers under these conditions and this project will add significantly to the existing data base. The electrochemical tests to be performed are:

- 24-hour corrosion potential measurement,
- polarization resistance, and
- cyclic polarization.

These tests will be performed sequentially on each specimen without removing it from the test cell. Specimens for these tests will be mounted using the methods developed in section 1.3.3.3 to retard the onset of crevice corrosion.

The proposed variability testing will be performed as follows:

1. Alloy 22 plate stock will be obtained from two suppliers, Haynes International and Inco, Ltd. Three different heats will be purchased from each supplier.
2. Certification sheets for all available heats will be requested from each supplier for choosing the heats to be obtained. It is known that Alloy 22 from Inco contains small amounts of copper, but no cobalt or vanadium, and that Alloy 22 from Haynes contains small amounts of cobalt and vanadium, but no copper. Copper has been observed to decrease transpassive potentials (cathodically) in Alloy 22, and other effects due to copper, cobalt, and vanadium are expected. Heats will be chosen to represent mid, upper and lower limits of chromium, molybdenum, and iron concentrations as specified by ASTM -B575. The following combinations will be chosen:
  - a. High Cr, Low Mo, with Cu (Inco)
  - b. High Cr, low Mo, with Co and V (Haynes)
  - c. Low Cr, high Mo, with Cu (Inco)
  - d. Low Cr, high Mo, with Co and V (Haynes)
  - e. Mid Cr, Mid Mo, low Fe, with Cu (Inco)
  - f. Mid Cr, Mid Mo, low Fe, with Co and V (Haynes)
3. Each plate obtained will be sampled and tested according to ASTM standards for mechanical, properties, chemical analysis, and grain size by a laboratory on the QSL to qualify it for work under the UCCSN QA program.
4. Tests will be performed with the metal in each of three metallurgical states:
  - a. Mill-annealed "as received"
  - b. Solution annealed at 1200°C
  - c. Aged for 10 hours at 750°C
5. Metallography (as described above in "sample preparation") will be performed on all specimens tested.
6. Electrochemical tests will be performed according to ASTM standards test methods.
7. Each test will be performed in triplicate for each heat, i.e., three specimens from each heat will be cut from different locations in the plate and tested.
8. Specimens will be prepared and tested for 24-hour corrosion potential, polarization resistance, and cyclic polarization according to ASTM standards. These tests will be performed sequentially without removing the specimen from the test flask. Three solutions will be used to test specimens from each heat:
  - a. 1 M NaCl at 90°C
  - b. 1 M HCl at 60°C
  - c. SCW at 90°C (1000x concentrated UE-25 J-13 well water)
9. Test results will be collected and analyzed to yield statistical data and increase understanding of mechanisms.

10. The preferred number of tests to be performed is: 3 sol'ns x 3 met. states x 6 heats x 3 repetitions = 162 tests. Three repetitions are desired to evaluate accuracy and reproducibility. However, because of budget shortfalls and schedule delays, the time and equipment required to perform the full test matrix described above may not be available. Availability of a Gamry potentiostat with an 8-channel multiplexer and 8 test cells was assumed when the above test matrix was designed. If this equipment is not available the first alternative is to perform the test matrix as described but to omit the three repetitions of each condition. This will result in 3 sol'ns x 3 met. states x 6 heats = 54 tests, which still covers the complete matrix. If further reduction of effort is imposed by budget and schedule limitations beyond the control of the PI, modification of the test matrix will be considered. It is preferable to retain the complete matrix of Alloy 22 conditions and decrease the number of electrolyte solutions in which they will be tested. Additional alternative test matrixes are 1 or 2 electrolyte solutions x 3 met. states x 6 heats = 18 or 36 tests, respectively.
11. Test results will be examined and upper and lower limits of behavior will be identified. Appropriate samples will be selected for further testing to evaluate the variability of PDM parameters due to material variability. Details for PDM tests will depend upon corrosion potential, polarization resistance, and cyclic polarization results.

**1.0.4 Schedule of Work and Milestones**

- Phase I anodic experimentation will be completed during Year 2 (FY05).
- Determination of threshold NaCl concentration for onset of localized corrosion will be completed by the end of Year 2.
- Phase I cathodic experimentation will begin during Year 3.
- Phase II anodic experimentation will be performed during Years 3 and 4.
- Phase II cathodic experimentation will be performed during Years 3 and 4.
- Phase III anodic tests will be performed during Years 4 and 5.
- Variability of mill-annealed Alloy 22 study will begin during Year2.

Start Date	Completion Date	Description
Sept. 2, 2004	Sept. 17, 2004 for Phase I, pH 11 tests. (Ongoing for duration of anodic tests for Phases I- IV.)	Specimen preparation and characterization for anodic testing (machining and solution annealing; polishing, etching and microscopy to examine microstructure).
Sept. 2, 2004	Sept. 17, 2004	User calibration checks for Gamry potentiostats. Verify calibration for all other M&TE.
Sept. 6, 2004	Dec. 21, 2004	Phase I, pH 11 anodic electrochemical test preparation, execution, and EIS data validity checks using Kramers-Kronig transforms.

Dec. 7, 2004	Dec.14, 2004	End-point calibration checks for M&TE used on Phase I, pH 11 anodic electrochemical tests.
Oct. 15, 2004		Begin collaboration with Dr. J.C. Lacombe to purchase appropriate Alloy 22 heats for variability study.
	Oct. 31, 2004	Acquisition of 8-channel potentiostat multiplexer for controlling test cells for localized corrosion threshold testing.
Oct. 31, 2004	Oct. 30, 2006	Localized corrosion threshold determination/specimen mounting re-design. Acquisition and testing of alternative epoxies and coatings.
Jan. 4, 2005	Jan. 18, 2005	Verify calibration for M&TE to be used on Phase I, pH 6 anodic electrochemical tests.
Jan. 4,2005	Apr. 21, 2005	Phase I, pH 6 anodic electrochemical test preparation , execution, and EIS data validity checks using Kramers-Kronig transforms.
	Feb. 28, 2005	Acquisition of Rotating Disk Electrodes and test cells for cathodic testing.
Mar. 7, 2005	Dec. 23, 2005	Phase I cathodic electrochemical tests.
Apr. 7, 2005	Apr. 14, 2005	End-point calibration checks for M&TE used on Phase I, pH 6 anodic electrochemical tests.
Apr. 18, 2005	May 2, 2005	Verify calibration for M&TE to be used on Phase I, pH 3 anodic electrochemical tests.
Apr. 18, 2005	Aug. 3, 2005	Phase I, pH 3 anodic electrochemical test preparation, execution, and EIS data validity checks using Kramers-Kronig transforms. Phase I data collection is complete at this point.
July 20, 2005	July 27, 2005	End-point calibration checks for M&TE used on Phase I, pH 3 anodic electrochemical tests.
Sept. 5, 2005		Hire graduate student or post-doc associate to work on variability study.
Sept. 5, 2005	Dec. 4, 2007	Variability of Alloy 22 electrochemical tests.
Sept. 5, 2005	Aug. 7, 2006	Phase II (NaCl + NaNO <sub>3</sub> , 3 pH's, 3 temperatures) anodic electrochemical tests.
Jan. 9, 2006	May 29, 2006	Phase II cathodic electrochemical tests.
Jun. 5, 2006	Nov. 6, 2006	Phase III cathodic electrochemical tests.
Sept. 4, 2006	Aug. 6, 2007	Phase III (Conc. UE-25 J-13 water, 3 pH's, 3 temperatures) anodic electrochemical tests.
Dec. 4, 2006	Jun. 4, 2007	Phase IV cathodic electrochemical tests.
Apr. 14, 2007	Apr. 1, 2008	Phase IV (high chloride, 3 pH's, 3 temperatures) anodic electrochemical tests.

## **1.1 Subtask 2: Scientific Investigation Plan: Corrosion under Dust Deposits Containing Hygroscopic Salts**

### **1.1.1 Introduction**

The WP Materials Performance Peer Review Panel has identified three conditions under which the surfaces of Alloy-22 may be subject to corrosion at Yucca Mountain: 1) Accumulated dust and particulate on the metal, 2) deposits and scale on the metal, and 3) tight areas of contact (crevices) between metals. The development of a strong technical basis for materials performance under these conditions was recommended by the panel. Alloy-22, proposed for use as the high-level nuclear waste package (WP) container material at YM, may experience corrosion under a hygroscopic dust deposit due to absorption of moisture from air, moisture diffusion through defects and porosity in the deposits, formation of a solution layer under the deposits, and dissolution of salts in the deposits. Hydration of chloride-containing deposits, including calcium chloride, produces entrapped solutions of reduced pH, which causes crevice type corrosion in many stainless alloys. The diffusion of O<sub>2</sub> into the entrapped solution from ambient air through the mouth at deposit fissures and/or through the porous deposit is expected to accelerate the corrosion by providing local oxygen concentration cells. The transport of O<sub>2</sub> and the hydration of chloride-containing deposits both favor the localized crevice corrosion of Alloy-22. This crevice type corrosion may result in failure of the WP containers much earlier than their projected lifetimes.

### **1.1.2 Scope and Objectives**

The objectives of this subtask are to model and experimentally verify the corrosion of Alloy-22 under an oxygen permeable hygroscopic dust deposit. To determine the feasibility of the projected life of the containers, it is important to quantitatively understand how the O<sub>2</sub> transport and the reduced pH affect the localized corrosion of Alloy-22, a key for a reliable long-term prediction of the container lifetime. Mechanistic modeling of corrosion is one of the methods allowing lifetime predictions under expected conditions. Parameters for use in such a model can be generated experimentally and can also provide verification of the predictions. Initial work of the modeling and experimental verification for corrosion of Alloy-22 will focus on corrosion due to oxygen transport through both the interface of the dust deposit and metal substrate and the thickness of the porous deposit, with considerations of both the passivity and corrosion kinetics of Alloy-22. Further development of the model will include more complex factors such as transport of ionic species, possible chemical reactions in the solution layer, precipitation, corrosion kinetics, and cyclic wet and dry conditions, etc.

The major objectives of the subtask are:

- To conduct extensive literature review on established theories of localized corrosion,

- To compile the thermodynamic/kinetic/transport parameters needed for the model development and their mechanistic correlations with temperature, environment pH, etc.,
- To develop a model to calculate the under-deposit corrosion rates,
- To compare the model results with certain experimental results obtained from subtask 3 : “Heated electrode approach for the study of corrosion under aggressive conditions” and
- To compare the proposed model results with qualified experimental results for similar conditions.

**1.1.2.1 Technical Requirement:**

Developing a mathematical model to calculate the under-deposit corrosion rate and compare with the available experimental results.

No previous work has been done / reported in support of this investigation on Alloy-22.

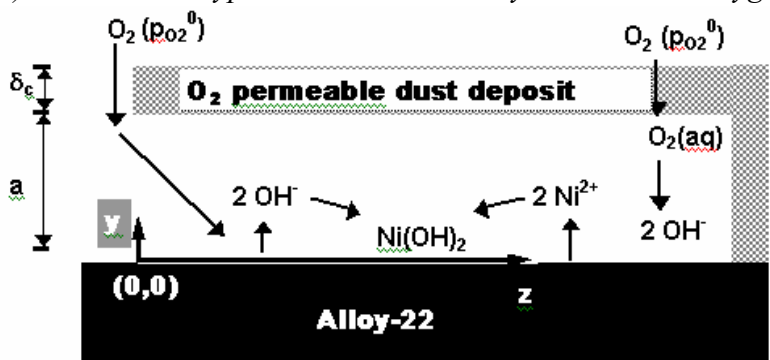
This work is subject to University and Community College System of Nevada (UCCSN) Quality Assurance (QA) Program requirements. A mathematical model will be developed in accordance with QAP-3.3 “Models”.

**1.1.3. Approach**

The approach described here provides a degree of flexibility to allow leeway for improvements as the investigation continues. The work plan essentially consists of the following major parts viz., 1. Literature review for published theories of localized corrosion. 2. Development of a model to calculate under-deposit corrosion rate. 3. Comparison of and model results with the available qualified experimental results (generated through sub-task 3 by following qualified procedures).

**1.1.3.1 Model Development**

(1) *The Crevice Type Corrosion Model System Due To Oxygen Transport* (Figure 2.1):



The crevice type configuration can be assumed to form between the metal surface and a tight but porous dust deposit, having a thin (y) narrow (not shown) deep (z) rectangular geometry. A solution layer exists within the deposit due to moisture absorption by and diffusion through the hygroscopic deposit.

Figure 2.1: Geometry of the crevice corrosion system for Alloy-22.

Corrosion of Alloy-22 occurs mainly due to oxygen transport, as it diffuses into the crevice from its mouth and through the dust deposit wall.

(2) *Steady-state Model Equations:*

For the rectangular crevice with oxygen transport, Laplace's equation governs the alloy electrical potential,  $\psi$ , in the crevice solution:

$$\frac{\partial^2 \psi}{\partial z^2} + \frac{\partial^2 \psi}{\partial y^2} = 0 \quad (2.1)$$

Mass conservation for oxygen can be expressed in its molar concentration in under-deposit solution,  $c_{O_2}$ , by:

$$\frac{\partial^2 c_{O_2}}{\partial z^2} + \frac{\partial^2 c_{O_2}}{\partial y^2} = 0 \quad (2.2)$$

Equations (2.1) and (2.2) can be solved with the necessary boundary conditions.

(3) *Transient Model Equations*

The distribution of electrochemical potential,  $V$ , across a hygroscopic salt deposit on a cylindrical container can be expressed as:

$$\frac{dq}{dt} = \sigma \cdot \left( \frac{\partial^2 V}{\partial r^2} + \frac{1}{r} \frac{\partial V}{\partial r} + \frac{\partial^2 V}{\partial z^2} \right)$$

where,  $\sigma$  = conductivity and  $q$  = charge density.

Similar expressions can be proposed for depicting oxygen concentrations in the hygroscopic salt deposits assuming pure diffusion. Incorporating advective component into the diffusion expression, the oxygen concentration can be expressed as:

$$\frac{dC_{ox}}{dt} = A_1 \cdot \left( \frac{\partial^2 C_{ox}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{ox}}{\partial r} + \frac{\partial^2 C_{ox}}{\partial z^2} \right) + v \frac{\partial C}{\partial z}$$

where,  $C_{ox}$  = molar concentration of oxygen,  $v$  = velocity of air causing advective mass transfer,  $A_1$  = constant.

The potential and oxygen concentration profiles can be substituted into standard Butler-Volmer type expressions to find out the corrosion rates. It will be assumed that oxygen reduction is the cathodic reaction process during the stage of the drying of the container wall surface. The corrosion rate can be calculated from the rate of change of oxygen concentration as:

$$i_{corr} = i_{ox} = 4F \frac{1}{A} \frac{\partial C_{ox}}{\partial t}$$



where,  $i_{\text{corr}}$  = corrosion current density,  $F$  = Faraday's constant,  $A$  = surface area.

### **1.1.3.2 Preliminary Model Performance Check**

The analysis above for crevice corrosion of Alloy-22 is qualitative. A quantitative corrosion profile for Alloy-22 can be obtained when the Tafel parameters and the relation between the passivity and the Tafel parameters are known.

Parameters required for the modeling may be initially obtained from a broad literature survey and through broad correlation of the above parameters with the environmental conditions (temperature, pH, etc.). Validation of the model will be carried out at each stage of development using the qualified experimental data obtained from the subtask 3 of Task ORD-FY04-014.

With the above known model parameters and their correlation with environmental conditions, the model can then be used to approximate the distribution of the alloy potential and corrosion rate within the crevice. The results thus obtained will then be compared with qualified experimental results of subtask 3. Any necessary modifications for the model will be made based on mechanisms resulting in the deviation, if any, between the model results and the available experimental data.

### **1.1.4 Schedules**

Recruiting of students and research associates will also have a significant impact on schedules.

Year 1:

- Literature review and background data will be developed.

Year 2

- A basic physical model for electrochemical conditions at the interface between metal and hygroscopic dust and particulate deposits using first principles will be developed for steady state conditions.
- Extension of the above model will be carried out for hygroscopic salt deposits for different humidity levels and oxygen and carbon dioxide diffusion conditions.
- Development of the thermodynamic/kinetic/transport parameters needed for the model will be carried out.

Year 3

- Development of the physical model to numerical one to calculate the under-deposit corrosion rates under steady state conditions will be carried out.
- The above physical and numerical model for corrosion under hygroscopic deposits on metal substrate under "steady state" conditions will be extended to 'dynamic' conditions.
- The model will be validated using the existing qualified data developed through the subtask 3.

Year 4

- Variation of ionic concentration, pH, and temperature with exposure time will be incorporated in the dynamic model.
- Model calibration will be performed by comparing the qualified data generated through subtask 3 at limiting boundary conditions.

Year 5

- Improvement of the model of under-deposit corrosion rates at different times and distances from the crevice mouth into the crevice will be completed based on the validation with qualified experimental data.

## **1.2 Subtask 3: Heated Electrode Approach for the Study of Corrosion Under Aggressive Conditions**

### **1.2.1. Introduction**

The WP Materials Performance Peer Review Panel has identified three conditions under which the surfaces of Alloy-22 may be subject to corrosion at Yucca Mountain<sup>5</sup>: 1) Accumulated dust and particulate on the metal, 2) deposits and scale on the metal, and 3) tight areas of contact (crevices) between metals. The development of a strong technical basis for materials performance under these conditions was recommended by the panel<sup>5</sup>.

The ground water seeping through the faults of volcanic rocks could contain varying levels of anions such as chloride, nitrate, sulfate and bicarbonate and cations of sodium, potassium, calcium and magnesium. Since the nuclear decay process heats the waste packages, they are always hotter than the surrounding drift walls. Therefore, the ground water with high ionic strength contacting the surface of the WP would evaporate and form concentrated brines. The provision of a drip shield, the surface temperature of which may not be as high as that of WP, surrounding the WP for diverting the potential seepage water and rock-fall impingement has been considered in the design. However, if the drip shield fails, contact of seepage water on the WP surface cannot be prevented. Breaches in the drip shield or waste package can take different forms, ranging from fine cracks caused by stress-corrosion cracking, to patches where general corrosion has penetrated a larger area.

Continued evaporation would result in the formation of a dry-salt deposit on the surface of the WP (or drip shield). Contact of fresh seepage water or a high humidity condition could deliquesce the dry-salt deposit resulting in a thin layer of saturated brine solution, which would evaporate again to form dry-salt deposits. Evaporation of water increases the ionic strength and decreases the thickness of the aqueous layer of the brine solution (in contact with the WP or drip shield) with time. Therefore, the aggressiveness of the environment to corrosion increases during the evaporation process and the corrosion attack would stop if the brine solution were completely dry. The presence of high humidity levels would again make the salt deposits more aggressive.

It is expected that the actual operating environment may alternate between wet and dry environmental conditions. While corrosion studies being carried out on Alloy-22 and Ti-Grade 7 (drip shield material) pertain to aqueous conditions, there isn't a significant amount of work addressing wet-dry environments in detail. Increased corrosion rates and stress corrosion crack growth rates of low alloy steels have been reported in alternate exposure to wet and dry environments as compared to that in continuous exposure to aqueous environments<sup>6</sup>. The passive oxide of the low alloy steel was observed to lose its corrosion resistance due to de-hydration of the outer layer of the passive film during exposure to dry conditions<sup>7</sup>. It is not known how the properties of the passive film of Alloy-22 and Ti-Grade 7 would change with a change in water content in the outer re-precipitated layer of the passive film. Therefore, this subtask proposes to investigate the corrosion behavior of Alloy-22 and Ti-Grade 7 during alternate wet-dry environmental conditions that simulate the repository evaporation-saturation events using a heated electrode approach.

### **1.2.2. Scope and Objective:**

In conventional electrochemical-corrosion tests, a specimen of standard shape and size would be immersed in the electrolyte solution of interest. The electrolyte will be heated to the required temperature. The volume, ionic strength and pH of the electrolyte will be constant throughout the test period. However, this type of standard test may not truly represent the service condition of the repository. Therefore, in this investigation it is proposed to employ a heated electrode testing technique to simulate the predicted repository condition. In this technique, the specimen will be heated instead of the electrolyte and the ionic strength of the electrolyte will be allowed to vary as the water in the aqueous solution evaporates. Corrosion tests will be carried out in simulated repository water environments at different-constant temperatures.

The objectives of this subtask therefore are as follows:

1. To simulate the most aggressive corrosion conditions that could be expected in repository environments and evaluate the corrosion resistance of Alloy-22 using heated electrode approach.
2. To investigate the incubation time required for passive film breakdown at different anion concentrations and pH levels

#### **1.2.2.1 Technical Requirement:**

Simulate the most aggressive corrosion conditions that could be expected in repository environment and evaluate corrosion resistance of alloy 22 at two different operating temperatures of the repository.

No previous work has been done / reported in support of this investigation on Alloy-22.

This work is subject to University and Community College System of Nevada (UCCSN) Quality Assurance (QA) Program requirements.

**1.2.3. Approach:**

The approach described here provides a degree of flexibility to allow leeway for improvements as the investigation continues. The work plan essentially consists of four major parts viz., 1. Material and heat treatment 2. Electrochemical heated electrode corrosion testing 3. Transmission Electron Microscopy studies for characterization of passive film.4. Correlation of electrochemical data to passive film structure.

**1.2.3.1 Materials and Heat Treatment:**

Alloy-22 (wrought)

1. Solution Annealed Condition
2. Aged Condition: *Aged at 600-850°C for 0.1-100 hours*

Ti-Grade 7 (wrought)

Solution Annealed

Alloy-22 welded coupons

Single pass

1. As welded
2. Welded + solution annealed
3. Welded + Aged

Multi-pass welded coupons:

*(to study the effect of thermal cycling on the weld-passes due to subsequent weld-passes)*

1. As welded
2. Welded + solution annealed

*Test Environments:*

Both dilute and concentrated Yucca Mountain waters will be investigated. Heated Electrode corrosion tests will be carried out in the following dilute water environments:

1. UE-25 J-13 Well Water
2. Perched Water
3. Pore water

Typical composition of dilute Yucca Mountain waters is given in Table 3.1.

TABLE 3.1. Composition of dilute Yucca Mountain waters

Ions	UE-25 J-13 Well Water (mg/L)	Perched Water (mg/L)	Pore Water (mg/L)
Na <sup>+</sup>	45.8	36.0	20 to 65
Si(aq)	28.5	37.0	26 to 39
Ca <sup>2+</sup>	13	25.0	43 to 125
K <sup>+</sup>	5.04	1.7	2 to 4
Mg <sup>2+</sup>	2.01	2.2	9 to 24
F <sup>-</sup>	2.18	0.7	1

Cl <sup>-</sup>	7.14	6.3	34 to 170
NO <sub>3</sub> <sup>-</sup>	8.78	4 to 17	2 to 81
SO <sub>4</sub> <sup>2-</sup>	18.4	15.0	48 to 260
HCO <sub>3</sub> <sup>-</sup>	128.9	147.0	74 to 220
pH	7.41	8.1	6.2 to 7.5
Molar Ratio	0.56	0.76	2.3

Heated electrode corrosion tests will also be carried out in the following concentrated water environments (Table 3.2):

1. Simulated Acidified Water (SAW)
2. Simulated Concentrated Water (SCW)
3. Basic Saturated Water (BSW)
4. Simulated Saturated Water (SSW)

*(Note: The heated electrode specimen will not be immersed in the concentrated solution; instead the solution will be dripped on the hot specimen surface at the determined rate in drops per unit time.)*

TABLE 3.2. Composition of concentrated YM Waters

ions	SAW (mg/L)	SCW (mg/L)	BSW (mg/L)	SSW (mg/L)
Na <sup>+</sup>	40900	40900	231224	487000
Si(aq)	27	27	9038	-
Ca <sup>2+</sup>	1000	<1	-	-
K <sup>+</sup>	3400	3400	81480	141600
Mg <sup>2+</sup>	1000	<1	-	-
F <sup>-</sup>	0	1400	1616	-
Cl <sup>-</sup>	24250	6700	169204	128000
NO <sub>3</sub> <sup>-</sup>	23000	6400	177168	1313000
SO <sub>4</sub> <sup>2-</sup>	38600	16700	16907	-
HCO <sub>3</sub> <sup>-</sup>	0	70000	107171	-
pH	2.8	10.3	>12	6.7
Molar Ratio	0.9	0.7	1.6	0.2

*Test Temperature:*

The electrodes (test specimens) will be heated to 80 - 160°C in all tests. In some cases, tests will be carried out at higher temperatures (up to 400° C).

*Electrochemical Heated Electrode Corrosion Test:*

Two types of heated electrode corrosion tests will be carried out viz., 1. fully immersed electrode type and 2. liquid drop on the heated surface type. The tests will be carried out in both open circuit and potentiostatic conditions in fully immersed conditions as shown in Figure 3.1. The liquid drop type test will be carried out in open circuit condition only. All tests will be carried out in a controlled humidity chamber so that they can be continued even after the water in the brine solution has fully evaporated. The data generated after formation of dry-salt (hygroscopic) deposition in high humidity conditions will be used for modeling in another subtask.

In fully-immersed-electrode type tests (Fig. 3.1), the height of the electrolyte solution will decrease with time as the evaporation process continues. Therefore, the ionic strength of the solution, corrosion potential and pH will vary with time. This condition more or less simulates the expected repository environments. In order to characterize the electrochemical conditions more deterministically, calibrations runs will be performed initially. The calibration tests will help determine the variation in ionic strength of the solution with time for a given heating surface area, surface temperature, initial concentration and initial height (volume) of the solution. Characterization / calibration of pH of the environment is more difficult as it will be determined mainly by the hydrolysis of the species and cathodic reactions during corrosion. The pH of the electrolyte will be recorded continuously with time. In open circuit tests, the corrosion potential will be recorded continuously with time. All these values (ionic strength, corrosion potential and pH, (if possible)) will be plotted as a function of electrolyte thickness as a calibration procedure for different temperatures. Linear polarization studies will be carried out at different solution thicknesses (at corresponding ionic strength, pH values) in a standard five neck cell to determine the corrosion rates in addition to the “in-situ” type heated electrode corrosion tests under different potentiostatic conditions.

The heated electrode corrosion tests by liquid drop on heated electrode surfaces as shown in Figure 3.2. Tests will be carried out with and without the application of stress. The number of test solution drops per unit time will be controlled by a timer circuit, which would actuate the solenoid valve. The tests will be carried out in a humidity-controlled chamber. Surface temperature, frequency of liquid drops, applied stress and concentration of the solution will be varied to determine the time to crack initiation and corrosion rate.

#### *Transmission Electron Microscopy Studies*

Characterization of passive film and surface scales is very important to understand the corrosion behavior. As heated electrode corrosion-surface closely simulates the WP container surface in repository conditions, it will be very instructive to study the nature of the surface film formed on the electrodes using high resolution electron microscopes. As the thickness of the passive film /surface film will be in the order of few Angstroms, high resolution microscopy is required. Transmission Electron Microscopy (TEM) studies will help identify the phases present in the passive film and understand the failure (if any) mechanism by evaluating the atomic structure at the metal/film interface. Possible vacancy condensation or elemental segregation at the metal/film interface could be detected if localized corrosion occurred. By carrying out the Electron Energy Loss Spectroscopy (EELS), passive film chemistry / structure could be evaluated. This would

help predict the life of the WP in a more deterministic way and improve the alloy system for corrosion resistance. Extensive TEM and EELS studies will be carried out the heated electrode specimens after corrosion tests to characterize the passive film /surface scale and to evaluate the film/metal interface.

The expected outcomes of the proposed work in this subtask are outlined below:

- During open circuit heated electrode corrosion tests, the corrosion potential will be monitored with time. The change in corrosion potential will be correlated with the change in ionic strength of the electrolyte solution.
- In the presence of localized attack or increased (break-away) corrosion conditions, irregular corrosion potential transients may be expected. The results of this investigation would generate quantitative data to detect such break-away corrosion conditions under a thin layer of electrolyte.
- The heated electrode corrosion tests under potentiostatic control would give corrosion current transient data. For initiation of localized corrosion, the required critical or threshold potential, temperature, ionic strength of environmental species, and pH could be quantitatively determined under transient experimental conditions.
- The change in passivation kinetics, passive film properties, and susceptibility to corrosion under alternate wet and dry test conditions will be quantitatively determined.
- The susceptibility to stress corrosion cracking under alternate wet and dry test conditions will be determined.

All the above data generated for Alloy-22 (both wrought and weld) and Ti-Grade 7 can be effectively used for corrosion modeling in real-life YM repository conditions and for life predictions of the waste package, with a minimum margin of error.

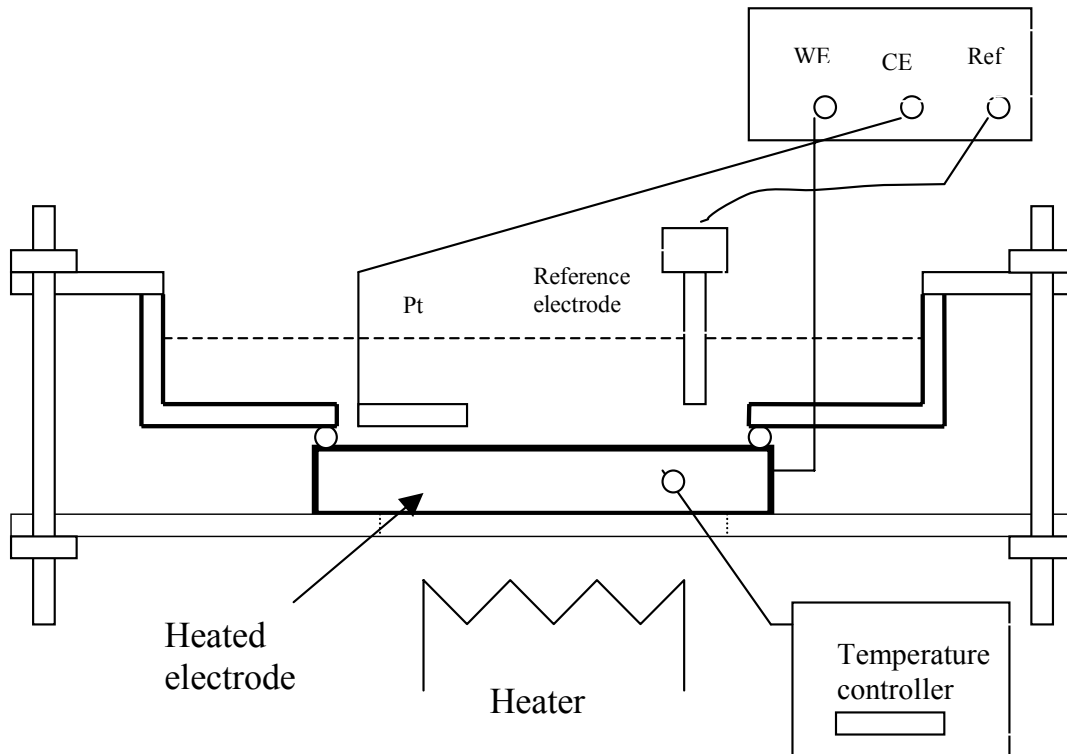


Figure 3.1 Schematic illustration of the heated electrode-cell assembly. The electrolyte covers the surface of the electrode and the level decreases with time while the ionic strength increases.



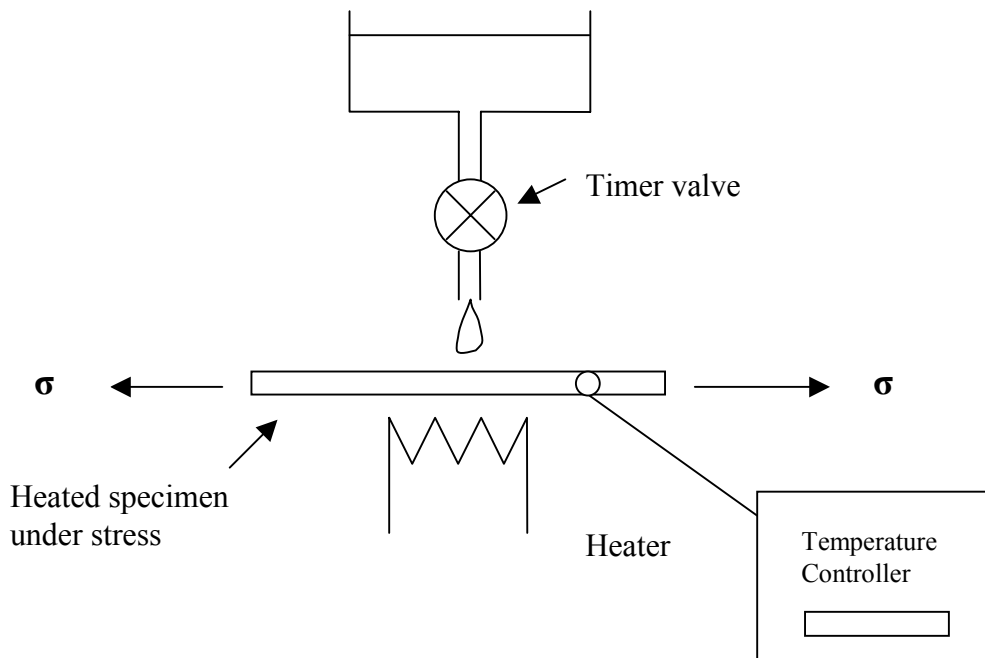


Figure 3.2 Schematic illustration of the heated electrode – liquid drop test with application of stress. The test will be carried out in a humidity controlled chamber.

#### 1.2.4 Schedules

Schedules will be highly dependent on receiving and calibrating new and updated equipment and receiving qualified weld specimens. Recruiting of students and research associates will also have a significant impact on schedules.

The project schedule of the proposed subtask is as follows:

Year 1: (Start Date June 01, 2004)

- Preparation of SIP for this subtask.
- Submission of SIP for technical and QA review for approval
- Design and fabrication of electrochemical cells for immersed and liquid drop-on heated electrode tests
- Development of IP's for the following activities:
  - o Heat treatment of Alloy-22
  - o Immersed Heated Electrode corrosion tests
- Initiation of experimental work on solution annealed specimens

Year 2:

- Immersed heated electrode tests of Alloy-22 solution annealed and aged in dilute and concentrated water
- Development of IPs for Welding of Alloy-22 plates using Gas Tungsten Arc Welding Process, Liquid drop-on heated electrode testing and Determination and Calibration of Ionic Strength of Electrolyte in the Heated Electrode Cell.
- User calibration of Transmission Electron Microscopy (TEM) and Electron Energy Loss Spectroscopy (EELS) and study of the surface films of the corroded surface using these analytical instruments

Year 3:

- Immersed heated electrode tests of Ti Gr 7 in dilute and concentrated waters
- Continuation of immersed heated electrode tests and initiation of liquid drop-on heated electrode tests of Alloy-22 solution annealed and aged in concentrated waters
- Initiation of Alloy-22 as-weld specimens
- Transmission Electron Microscopy and Electron Energy Loss Spectroscopy study of the surface films of the corroded surface

Year 4: (see test matrix above for notation explanation)

- Initiate heated electrode corrosion testing on Alloy-22 AWSP and AWSPWA specimens
- Initiate corrosion testing on Alloy-22 AWMP and AWMPWA specimens
- Initiate corrosion testing on Alloy-22 AWSPSA specimens
- Continuation of immersed heated electrode tests of Ti Gr 7 in dilute and concentrated waters
- Continuation of liquid drop-on heated electrode tests of Alloy-22 aged specimens in concentrated waters
- Transmission Electron Microscopy and Electron Energy Loss Spectroscopy study of the surface films of the corroded surface

Year 5: (see test matrix above for notation explanation)

- Complete testing on Alloy-22 AWSP and AWSPWA specimens
- Complete testing on Alloy-22 AWSPSA specimens
- Complete testing on Alloy-22 AWMP and AWMPWA specimens
- Transmission Electron Microscopy and Electron Energy Loss Spectroscopy study of the surface films of the corroded surface

*Test Matrix:*

Material	Material Condition	Immersed Heated Electrode		Liquid-Drop on Heated Electrode	
		Dilute YM Waters	Concentrated YM waters	Dilute YM Waters	Concentrated YM waters
Alloy-22	Solution Annealed (SA)	Year 1, 2	Year 2, 3	Year 3	Year 3
	Aged	Year 2	Year 2,3	Year 3	Year 4,5

Ti-Grade 7	SA	Year 3	Year 3, 4		
Alloy-22 weld (single pass)	As weld (AWSP)	<b>Years 3-5</b>			
	Weld + SA (AWSPSA)				
	Weld + Aged (AWSPWA)				
Alloy-22 weld (multi pass)	As weld (AWMP)				
	Weld + SA (AWMPSA)				

**1.3 Subtask 4: Effect of Hydrogen Permeation on the Stability of the Passive Film of Alloy-22**

**1.3.1 Scope**

Evolution of hydrogen occurs during corrosion processes, which could result in ingress of hydrogen into the metal. Welding with coated electrodes, cathodic protection, acid pickling, and electroplating also could result in diffusion of hydrogen in to metals. Hydrogen reducing bacteria is reported to be present in the YM repository site. At higher hydrogen fugacity, atomic hydrogen could diffuse into the Alloy-22 WP container wall. It is widely documented that ingress of hydrogen could change the passive film properties of austenitic stainless steels and enhance susceptibility to pitting. Therefore, it is imperative to investigate the effect of hydrogen ingress on the stability of passive film of Alloy-22. In this subtask pitting potentials of Alloy-22 will be evaluated under different hydrogen charged conditions in a chloride-containing environment.

**1.3.2 Background**

It has been reported that the presence of hydrogen enhances the anodic dissolution of austenitic stainless steels<sup>8</sup> and decreases the critical chloride content required for breakdown of the passive film<sup>9</sup>. The diffusivity of hydrogen in passivated iron is reported to be around 12 orders less than that in the metallic iron<sup>10</sup>. Both n-type passive film (on iron) and p-type film (on nickel) were found to be affected by hydrogen in an chloride-containing environment. Most investigations studying the effect of hydrogen were carried out in strong hydrogen charged conditions, such that hydrogen transport occurred due to both a potential and a concentration gradient. Hydrogen generating bacteria present in the soil/ground water could cause ingress of hydrogen in the WP or drip shield. In this condition the hydrogen entry occurs mainly by the concentration gradient. However, the electronic structure of the passive film could be affected by the presence of hydrogen and the electric field within the passive film may be altered to facilitate further transport of the hydrogen. There has not been a significant amount of work done to understand the effect of hydrogen on the electronic structure and the degradation mechanism(s) of the passive film in the presence of hydrogen. Moreover a quantitative analysis of the effect of hydrogen on the degradation of passive films is

required in order to estimate the life prediction of nuclear waste containers. As the pH inside the pits is usually low (acidic); there could be a correlation between pH of the electrolyte inside a growing pit and the critical concentration of hydrogen required inside the passive film to nucleate a pit in a neutral chloride environment.

In preliminary work at UNR on the effects of hydrogen charging on the pitting behavior of mill-annealed Alloy-22 and 304 SS indicate that 304 SS is affected due to hydrogen diffusion into its passive film. The results of this work are shown in figures 4.1

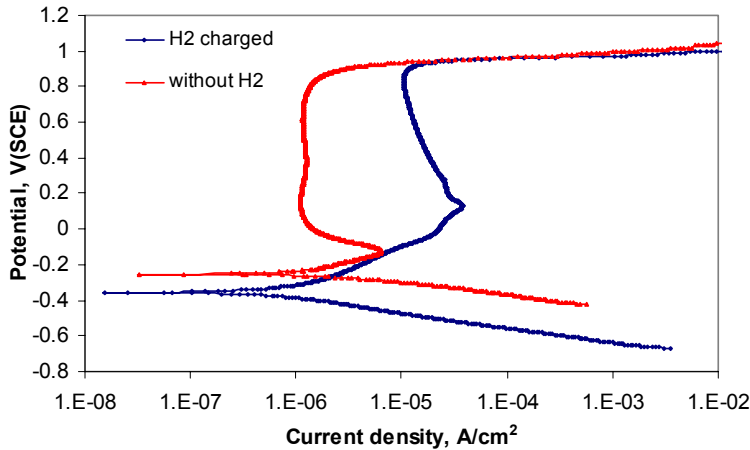


Figure 4.1 Effect of prior hydrogen charging on pitting potential of mill-annealed Alloy-22

and 4.2. Figure 4.1 shows the effect of prior hydrogen charging (in 0.5 N H<sub>2</sub>SO<sub>4</sub> + 250 ppm of As<sub>2</sub>O<sub>3</sub> at -20 mA/cm<sup>2</sup> for one hour) on the pitting potential of mill-annealed Alloy-22, in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.5 M NaCl solution at 25°C. Preliminary results indicate no significant change in the pitting potential due to hydrogen charging. The increase in anodic peak

current could be attributed to the hydrogen oxidation current. Figure 4.2 shows the effect of prior hydrogen charging (in 0.5 N H<sub>2</sub>SO<sub>4</sub> + 250 ppm of As<sub>2</sub>O<sub>3</sub> at -20 mA/cm<sup>2</sup> for one hour) on the pitting potential of 304 SS in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.5 M NaCl solution at 25°C. The pitting potential was

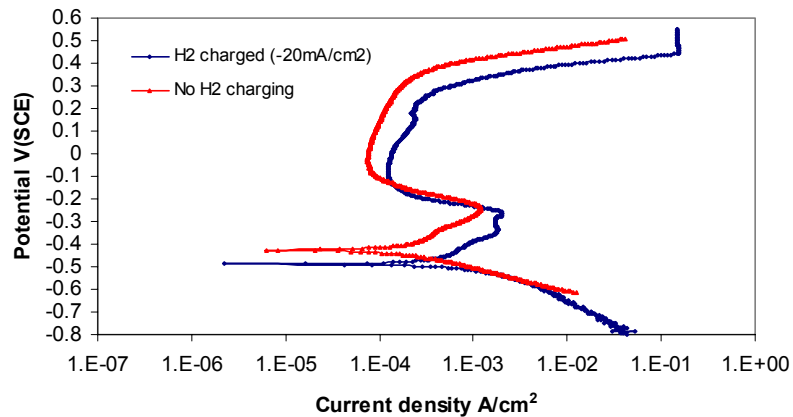


Figure 4.2 Effect of prior hydrogen charging on the pitting potential of 304 SS

observed to decrease with hydrogen charging. Although, the mill-annealed Alloy-22 did not show a significant change in the pitting potential with hydrogen charging in this preliminary work, the effect of microstructural changes on the hydrogen diffusion characteristics of Alloy-22 and the associated effects on localized corrosion have not been systematically investigated.

### 1.3.3 Objectives

The objectives of this subtask therefore are:

- To quantify the effect of hydrogen on the degradation of the corrosion resistance of the passive film of Alloy-22 in chloride containing environments.
- To understand the synergistic effect of hydrogen and chloride on the breakdown (if present) of passive film.

Technical Requirement:

Quantification of the effect of hydrogen on the degradation of the corrosion resistance of Alloy 22 in chloride-containing environments.

No previous work has been done / reported in support of this investigation on Alloy-22.

This work is subject to University and Community College System of Nevada (UCCSN) Quality Assurance (QA) Program requirements.

### **1.3.4 Approach**

The approach described here provides a degree of flexibility to allow leeway for improvements as the investigation continues. The work plan essentially consists of four major parts viz., 1. Material and heat treatment 2. Growing passive films of different thickness 3. Charging of Hydrogen in the passive film with Devanathan and Stachurski type and conventional 5-necked ASTM G5 cell 4. Characterization of passive film by SEM and TEM

#### *1.3.4.1 Materials and Heat Treatment:*

*Materials:* Alloy-22

*Heat Treatment:* 1. Solution Annealed and  
2. Aged at 600 – 850°C for 0.1 – 100 hours.

*Surface condition:* 1. Polished and passivated inside the cell  
2. Polished and thermally grown oxide film

(Different thickness and properties of passive film will help understand how hydrogen reduces the passive film)

*Electrochemical cell:* Devanathan and Stachurski type and conventional 5 necked ASTM G-5 type

#### *1.3.4.2 Hydrogen Charging*

Hydrogen will be charged electrolytically by applying different cathodic current densities in order to have different steady state concentration profiles in the specimen. When using a Devanathan type cell the hydrogen transport is assisted by both concentration and potential gradients. Hydrogen charging of the pre-passivated specimen using a conventional 5-neck cell will be different from that of a Devanathan type cell. Both methods will be studied.

*Environment:* Hydrogen Charging: 0.5 M H<sub>2</sub>SO<sub>4</sub> + 100 ppm As<sub>2</sub>O<sub>3</sub>  
Anodic side: Borate buffer or 0.25 M Na<sub>2</sub>SO<sub>4</sub> with varying amounts of chlorides from 100 ppm to 0.5 N

*Temperature:* 24-80°C

*Electrochemical Techniques:* Potentiostatic, Electrochemical Impedance Spectroscopy

and Mott- Schottky analysis.

Analytical Techniques: SEM, TEM, and XPS

#### *1.3.4.3 Transmission Electron Microscopy Studies*

Characterization of the passive film is very important to understand the hydrogen diffusion behavior in the film. Not many studies are available on the variation of metal/film interface structure after hydrogen charging. Transmission Electron Microscopy studies will be carried on the specimens with and without hydrogen charging to evaluate the variation in structure of the metal/film interface. Further, possible enhancement in pitting susceptibility due to hydrogen charging will be investigated by carrying out extensive TEM studies.

#### **1.3.5 Schedules**

The expected outcomes and project schedule of the proposed subtask are as follows:

Year 1: (Start Date June 01, 2004)

- Preparation of SIP for this subtask.
- Submission of SIP for technical and QA review for approval
- Initiation of development of IP's for the following activities:
  - o Gas Tungsten Arc Welding of Alloy-22 plates
  - o Heat treatment of Alloy-22
  - o Hydrogen Permeation studies
  - o Electrochemical impedance and Mott-Schottky Measurements
  - o User calibration of EDAX analyzer etc.

Year 2:

- Initiation of experimental work for the determination of the diffusivities of hydrogen in Alloy-22 at different microstructural conditions.
- Initiation of calculations of the activation energies through evaluation of diffusion coefficients at different temperatures.
- Development of IP's for the following activities:
  - o Gas Tungsten Arc Welding of Alloy-22 plates
  - o Heat treatment of Alloy-22
  - o Hydrogen Permeation studies
  - o Electrochemical impedance and Mott-Schottky Measurements
  - o User calibration of EDAX analyzer etc

Year 3:

- Continued experimental work for the determination of the diffusivities of hydrogen in Alloy-22 at different microstructural conditions.
- Continued work on the calculations of the activation energies through evaluation of diffusion coefficients at different temperatures.
- Experimental work for the determination of the effect of hydrogen on pitting susceptibility (solution annealed and aged conditions).
- Initiation of experimental work for the determination of the change in electronic properties of the passive film of Alloy-22 in the presence of hydrogen.

Year 4:

- Continued experimental work for the determination of the change in electronic properties of the passive film of Alloy-22 in the presence of hydrogen.

- Initiation of Transmission Electron Microscopy studies on the solution annealed specimens to investigate the interface between passive film/metal with and without hydrogen charging after polarization in pitting environments.

Year 5:

- Transmission Electron Microscopy and Electron Energy Loss Spectroscopy studies on the aged Alloy 22 specimens to investigate the interface between passive film/metal with and without hydrogen charging after polarization in pitting environments.

## **1.5 Interface Controls**

Dr. Shantanu Namjoshi of the University of Nevada, Reno, as the Task's Principal Investigator, will oversee the entire project and assure the project's integrity and scientific soundness as the work progresses. All the electrochemical and analysis work will be carried out in Electrochemistry and Corrosion Laboratory of the University of Nevada, Reno.

Administrative interfaces at UNR include Dr. Ted Batchman, Dean, College of Engineering, and Dr. Manoranjan Misra, Division Chair, Metallurgical and Materials Science Engineering. Dr. D.D. Macdonald of the Pennsylvania State University, will be closely involved with task planning and interpretation of results as a subcontractor (see Procurements and Subcontracts below). Planning, data, results, analysis, and conclusions will be shared and discussed with Dr. Raul Rebak, Dr. Frank Wong, and Dr. Tiangan Lian at Lawrence Livermore National Laboratories (LLNL), Gerald Gordon and V. Pasupathi of the Bechtel-SAIC team, and Robert Fish of Booz-Allen & Hamilton, the M&O contractor for DOE in Las Vegas.

## **1.6 Standards**

The following ASTM standards<sup>11</sup>, have been incorporated into existing IP's in the UCCSN IP-format., listed in section 1.7. The IP's planned to be used for this work are also listed in section 1.7.

Subtask 1:

- G5-94 (Reapproved 1999), Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements
- G100-89(1999) Standard Test Method for Conducting Cyclic Galvanostaircase Polarization
- E617 97(2003) Standard Specification for Laboratory Weights and Precision Mass Standards

Subtask 3:

- ASTM G5-94 (Reapproved 1999), Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements.
- G100-89(1999) Standard Test Method for Conducting Cyclic Galvanostaircase Polarization

- G61-86(1998) Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys (IPR018)

Subtask 4:

- Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements, ASTM G5-94 (Reapproved 1999) (IPR 018),

### **1.7 Implementing Procedures (IPs)**

The following existent IP's will be used in this task 1 and will be reviewed prior to use in accordance with e-mail dated 06/09/2004 from UCCSN QA:

Subtask 1:

- IPLV-003, 07/28/00, Analytical & Top-Loading Balance Use
- IPR-018 Electrochemical Corrosion Testing
- IPR-020 User Calibration of Gamry Potentiostats PC4/300mA/DC105 and PC4/750mA/DC105
- IPR-025 User Calibration and Use of the Cole-Parmer/Oakton pH/mV/°C Meter

Subtask 2:

- IPLV-003, 07/28/00, Analytical & Top-Loading Balance Use
- IPR-014 User Calibration of Gamry Potentiostat PC3/CMS100
- IPR-015 User Calibration of Gamry Potentiostat PC4/CMS105
- IPR-018 Electrochemical Corrosion Testing

Subtask 3:

- IPLV-003, 07/28/00, Analytical & Top-Loading Balance Use
- IPR-014 User Calibration of Gamry Potentiostat PC3/CMS100
- IPR-015 User Calibration of Gamry Potentiostat PC4/DC105
- IPR-018 Electrochemical Corrosion Testing
- IPR-020 User Calibration of Gamry Potentiostat PC4/300mA/DC105
- IPR-025 User calibration and use of Cole-Parmer / Oakton pH Meter

Subtask 4:

- IPLV-003, 07/28/00, Analytical & Top-Loading Balance Use
- IPR-014 User Calibration of Gamry Potentiostat PC3/CMS100
- IPR-015 User Calibration of Gamry Potentiostat PC4/CMS105
- IPR-018 Electrochemical Corrosion Testing

New IP's will be developed as indicated incorporating applicable ASTM standards in the UCCSN IP-format. This is applicable to all the new IP's. Implementing Procedures will be developed as the following activities, following QAP-2.0, and QAP-9.0 (where applicable):

- Heat Treatment of Alloy-22



- Potentiostatic Electrochemical Impedance Spectroscopy (EIS) Testing and Mott-Schottky Measurements
- Gas Tungsten Arc Welding of Alloy-22 plates
- Determination and Calibration of Ionic Strength of Electrolyte in the Heated Electrode Cell
- Conducting Heated Electrode Corrosion Tests
- Conducting and Calibration of TEM, EDAX and EELS studies
- Hydrogen Permeation Test procedure as per ASTM G 148-97

Use of the following standards is anticipated in the development of the above IP's.

- G59-97 Standard Practice for Conducting Potentiodynamic Polarization Resistance Measurements
- G102-89(1999) Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements
- G106-89(1999) Standard Practice for Verification of Algorithm and Equipment for Electrochemical Impedance Measurements
- G107-95 Standard Guide for Formats for Collection and Compilation of Corrosion Data for Metals for Computerized Database Input
- A167-99 Standard Specification for Stainless and Heat-Resisting Chromium-Nickel Steel Plate, Sheet, and Strip
- Standard Test Methods of Detecting Susceptibility to IGC in Wrought, Ni rich, Cr Bearing Alloys, G-28-97, Annual Book of ASTM Standards, vol. 3.02, ASTM, West Conshohocken, PA 19428-2959, USA.
- G31-72(1999) Standard Practice for Laboratory Immersion Corrosion Testing of Metals
- G48-99a Standard Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution
- G59-97 Standard Practice for Conducting Potentiodynamic Polarization Resistance Measurements
- G78-95 Standard Guide for Crevice Corrosion Testing of Iron-Base and Nickel-Base Stainless Alloys in Seawater and Other Chloride-Containing Aqueous Environments
- G102-89(1999) Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements
- G106-89(1999) Standard Practice for Verification of Algorithm and Equipment for Electrochemical Impedance Measurements
- G107-95 Standard Guide for Formats for Collection and Compilation of Corrosion Data for Metals for Computerized Database Input
- G108-94(1999) Standard Test Method for Electrochemical Reactivation (EPR) for Detecting Sensitization of AISI Type 304 and 304L Stainless Steels
- G129-95 Standard Practice for Slow Strain Rate Testing to Evaluate the Susceptibility of Metallic Materials to Environmentally Assisted Cracking

- A167-99 Standard Specification for Stainless and Heat-Resisting Chromium-Nickel Steel Plate, Sheet, and Strip Standard Practice for Hydrogen Uptake, Permeation, and Transport in Metals by an Electrochemical Technique, ASTM G 148-97
- G59-97 Standard Practice for Conducting Potentiodynamic Polarization Resistance Measurements
- G61-86(1998) Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys
- G107-95 Standard Guide for Formats for Collection and Compilation of Corrosion Data for Metals for Computerized Database Input
- G129-95 Standard Practice for Slow Strain Rate Testing to Evaluate the Susceptibility of Metallic Materials to Environmentally Assisted Cracking

Each staff member including the PI, visiting research professors, postdoctoral research associates, and graduate students will be trained in accordance with QAP 2.1, "Qualification, Indoctrination and Training of Personnel," and will have his/her own scientific notebook(s) (SN). Each SN will be the conventional bound lined book with numbered pages. Scientific notebooks will be kept in accordance with QAP 3.0, "Scientific Investigation Control." Dr. Digby Macdonald, a sub contractor for this task, will be included in required QA Program training as well as applicable IPs.

## 1.8 Samples

Samples for all subtasks will be controlled in accordance with QAP-8.0. The following lists specifics for each subtask.

Subtask 1: Alloy-22 plate stock of 0.75 inch thickness will be procured from reliable suppliers which may include Haynes International, Allegheny-Ludlum, and Inco. Rod stock may be procured if necessary. The heat numbers and batch numbers will be recorded for traceability. A single plate from a single heat will be used for the extensive anodic potentiostatic Electrochemical Impedance Spectroscopy (EIS) data collection as function of temperature, pH, and chloride concentration. The plates will be sampled and tested by a laboratory on the Qualified Suppliers List in accordance with ASTM standards in order to be qualified for use in the UCCSN/DOE Cooperative Agreement. Coupons of 4"x 0.75"x 0.75" size will be cut from the parent plates and will be uniquely identified, including a designation of "L" or "T" to indicate orientation with respect to the rolling direction, so that each coupon's location in the parent plate is traceable. Cylindrical specimens of 0.5" diameter and 10 mm long will be machined out of these coupons and uniquely identified to maintain traceability to orientation with respect to the rolling direction and location in the parent plate.

Subtask 2: In this subtask, the predominant work will be development of analytical expressions for electrochemical potential and current distribution during corrosion process and solving them for given boundary conditions. No experiments are planned in

this subtask. However, experimental data generated in the subtask 3 will be used for model validation.

Subtask 3: Alloy-22 plate(s) of 0.75 inch thick will be procured from a single heat from a reliable supplier. The heat number and batch number will be recorded for traceability. The plate will be sampled and tested by a laboratory on the Qualified Suppliers List in accordance with ASTM standards in order to be qualified for use in the UCCSN/DOE Cooperative Agreement. 12"x 12" X 0.75" size coupons will be cut from the large plate and will be identified as TASK ORD-FY04-014 C22 L or T followed by two-digit code to indicate its location in the parent plate. Disc shaped cylindrical specimens of 1 or 1.5" diameter and 0.75" thick will be machined out of these coupons and will be identified by alphabets such as a, b, c etc. The backside of each disc will be punched their ID such as T11a, L12a etc. A master drawing will be prepared to identify the specimen location from the parent plate for traceability.

Subtask 4: Alloy-22 plate(s) of 0.75 inch thick will be procured from a single heat from a reliable supplier. The heat number and batch number will be recorded for traceability. The plate will be sampled and tested by a laboratory on the Qualified Suppliers List in accordance with ASTM standards in order to be qualified for use in the UCCSN/DOE Cooperative Agreement. 4"x0.5"X0.75" size coupons will be cut from the large plate and will be identified as TASK ORD-FY04-014 C22 L or T followed by two-digit code to indicate its location in the parent plate. Small disc shaped cylindrical specimens of 0.5" diameter and 0.5" long will be machined out of these coupons and will be identified by alphabets such as a, b, c etc. The back side of each disc will be punched their ID such as T11a, L12a etc. A master drawing will be prepared to identify the specimen location from the parent plate for traceability. For hydrogen permeation studies 1.0 mm thick and 1" diameter Alloy-22 discs will be machined from the large plate stock and have unique ID number.

## **1.9 Equipment and Instrumentation**

- Gamry potentiostats:
  - PC4/750mA/DC105/EIS300, PCi4/750mA/DC105/EIS300
- Gamry electrochemical test system
- Thermometers/Thermocouples mercury, spirit, and Type J, K, and R thermocouples.
- Digital multimeter
- Calibrated electrical resistors
- pH meters: Cole-Parmer or Oakton
- Immersion heating baths with digital temperature controllers. (Calibration of heating bath controllers is not required; temperature in the test cells will be measured using calibrated thermocouples and thermocouple thermometers.)
- Weighing Scales / Balances
- Class A volumetric glassware: Volumetric flasks and pipettes

- Tube furnace with digital temperature controller. (Calibration of furnace controller is not required; temperature in the furnace tube will be measured using calibrated thermocouples and thermocouple thermometers.)
- Digital caliper
- Olympus PMG-3 optical microscope
- Hitachi Scanning Electron Microscope (SEM)
- JEOL 2100F Transmission Electron Microscope with EELS / EDAX Analyzer

All M&TE will be controlled and calibrated according to QAP-12.0, "Control of Measuring and Test Equipment." All these are in-house equipment and are dedicated for UCCSN/DOE Cooperative Agreement tasks; they are not available for public use. Password protection will be placed on all computers and PC-based potentiostats. All computers to be used have password protection capability. Physical access to calibrated instruments and test materials will be restricted by storage in locked cabinets, in locked offices, or locked laboratories where they are being used. Only personnel actually working on the tasks will have access to the keys and passwords. Potentiostats and pH meters are user calibrated by following applicable IP's. Thermometers, temperature controllers, multimeter, electrical resistors, digital caliper, and weighing scales will be calibrated by qualified suppliers. Class A volumetric glassware is NIST-traceable and does not require calibration.

### **1.10 Software and Models**

#### Subtask 1:

Experimental electrochemical data will be plotted and analyzed using one or more of the following: Microsoft Excel 2000 (9.0.6926 SP-3), SigmaPlot 2002 for Windows version 8.02a, or Gamry Instruments Echem Analyst version 1.21. SigmaPlot 8.02a will be used for graphical/display purposes only and is exempt according to QAP 3.2 paragraph 2.1.2. Microsoft Excel will be used primarily for graphical/display purposes; any user-written macros will be verified by hand calculation and documented in the Scientific Notebook as prescribed in QAP 3.2 paragraph 2.1.5. Gamry Echem Analyst will be qualified according to QAP 3.2 paragraph 2.1.5. Microsoft Office 2000 Professional suite will be used for general computing needs. Operating systems to be used are Microsoft Windows 98 and Microsoft Windows version 5.1 (XP Professional). Software for performing Kramers-Kronig Transforms, copyright M. Urquidi-Macdonald and D. D. Macdonald, may be used to verify validity of EIS data. Qualified software will be obtained from the Software Management Specialist in accordance with QAP-3.2, "Software Management." Unqualified software including macros and other routines in Excel or other commercially available qualified software suites will be qualified in accordance with QAP-3.2.

Software developed from the mathematical derivations of the Point Defect Model (PDM) for passive films on metals, developed by Dr. D.D. Macdonald, may be used for data analysis. Use and validation of the model will be controlled in accordance with QAP 3.3, "Models."

**Subtask 2:**

The software required for mathematical modeling includes: MATLAB, MATHMATICA, Visual Basic. Electrochemical data will be analyzed using EXCEL with macros as supplied by Gamry Instruments. Macros will be verified by hand calculation. Commercial software expected for use includes Microsoft Office suite, KaleidaGraph, MathCad, and others as necessary. Qualified software will be obtained from the Software Configuration Secretariat in accordance with QAP-3.2, "Software Management." Unqualified software will be qualified in accordance with that procedure.

**Subtask 3 & 4:**

Electrochemical data will be analyzed using Microsoft Excel with macros as supplied by Gamry Instruments. Macros will be verified by hand calculations. Commercial software expected for use includes Microsoft Office suite, KaleidaGraph, MathCad, and others as necessary. Qualified software will be obtained from the Software Configuration Secretariat in accordance with QAP-3.2, "Software Management." Unqualified software will be qualified in accordance with that procedure.

**1.11 Procurements and Subcontracts**

Quality-affecting calibration items and services will be purchased from qualified suppliers in accordance with QAP-7.0, "Control of Procurement and Receipt." Metal specimens may also be procured from a qualified supplier. Metal specimens not purchased from a qualified supplier will be qualified by a testing laboratory on the Qualified Suppliers List or by use of a qualified standard or calibrated measuring and test equipment.

***Subcontract to Dr. Digby D. Macdonald***

Consultant: Dr. Digby. D. Macdonald will provide technical expertise, assistance with experiment design protocols, data interpretation, and technical presentations or papers for Subtask 1. With the death of Professor Denny Jones in August 2003, Professor Macdonald is assisting with the task of supervising the technical work on the electrochemical and corrosion properties of Alloy C-22 in prototypical HLNW environments under QA protocols. In order to formalize this function, Professor Macdonald has been appointed Adjunct Professor by UNR. His principal function will be to supervise the research in Subtask 1 of this proposal. It is estimated that Professor Macdonald's supervisory duties will amount to 24 days over the next year (2 days per month) and will involve at least three trips to Reno and two visits to Pennsylvania State University to receive training in data analysis. Dr. Macdonald will continue providing these services over the course of the project. Dr. Macdonald will continue to serve these duties through FY 2008. The budget for the first year will be adjusted according to available funds.

Estimated Cost per year: Labor - \$38.4K

Travel \$ 3.6K

Total: \$42.0K/year

### **1.12 Hold Points**

No hold points applicable.

### **1.13 Quality Control – Accuracy, Precision, Error, and Uncertainty**

Subtask 1:

Applicable QAP's and IP's will be used to maintain data accuracy. Accuracy of measurements and data will be determined by comparison with known standards whenever possible.

A minimum of three points in the test matrix (Tables 1 – 3) will be tested in duplicate, and one point in triplicate, to determine precision. The conditions chosen for duplicate and triplicate testing will be determined during the course of experimentation based on equipment availability and time constraints. Comparisons within data sets and with similar data in the literature will demonstrate representativeness.

Uncertainty or scatter can be of the order of a factor of 2 in typical electrochemical data, such as passive corrosion current densities. This uncertainty is acceptable because these parameters will often change by several orders of magnitude as a function of time and metallurgical conditions. Uncertainties are presumably due to the stochastic nature of the metal surfaces and bulk solution properties. Potential sources of error include variation of flow condition of electrolyte, dissolved oxygen content, pH, temperature, surface condition of the working electrode from initial polishing and the effects of the test conditions, etc.; these factors will be controlled and maintained as closely as practical under laboratory conditions. Human error will be minimized by personal qualification requirements, indoctrination, and training. Instrumental error will be minimized by calibration of testing equipment and following the requirements of all applicable IP's.

Subtask 2-4:

Applicable QAPs will be used to maintain data accuracy. Accuracy of measurements and data will be determined by comparison with known standards whenever possible. Comparisons within data sets and with similar data in the literature will demonstrate representativeness. Experiments will be carried out using qualified procedures and standard conditions as described in subtask 3 and the data will be used for validating the model with known and well-defined boundary conditions. Uncertainty or scatter can be of the order of a factor of 2 in a typical data, such as passive corrosion current densities, crack growth rates, film rupture, and strains and repassivation rates. This uncertainty is acceptable because these parameters will often change by several orders of magnitude as a function of time and metallurgical conditions. Uncertainties are presumably due to the stochastic nature of the metal surfaces and bulk solution properties. Human error will be minimized by personal qualification requirements, indoctrination, and training. Instrumental error will be minimized by calibration of testing equipment and following the requirements of all implementing procedures.

### **1.14 Data Recording, Reduction, and Reporting**

Electronic data will be collected, reduced, and recorded according to QAP-3.1, "Control of Electronic Data." The data generated will be plotted/displayed using Microsoft Excel 2000 (9.0.6926 SP-3) and SigmaPlot version 8.02a. Data analysis will be performed using Microsoft Excel 2000 (9.0.6926 SP-3), Gamry Instruments Echem Analyst version 1.21, or the Point Defect Model software as appropriate, and reduced to graphical and/or numerical results as required. Significant graphical results will be printed and pasted into the appropriate SN's or attached to the SN's. Numerical results will be recorded in the appropriated SN's. Data will be submitted to the UCCSN Technical Data Archive (TDA) in accordance with QAP-3.6, "Submittal of Data to the Technical Data Management System" through the UCCSN data coordinator. Data that have not undergone technical review are non-qualified and will be labeled, "for corroborative use only," and traceability to their origin and nature will be maintained in documents in which the data are presented. Non-qualified data will be used for preliminary scoping purposes only and will not be used to reach any conclusions.

### **1.15 Reviews and Verifications**

Technical reviews of any reports and publications containing quality-affecting data will be conducted in accordance with UCCSN QA Program requirements. Scientific notebooks and associated data are to be reviewed in accordance with QAP-3.0, "Scientific Investigation Control." Technical reports and other data are to be reviewed in accordance with QAP-3.4, "Technical Reports." Publications, abstracts, presentations, or other public use of information produced as a result of this study will be approved by DOE as per guidelines.

### **1.16 Records and Submittals**

QA records generated as a result of the records sections of the implementing procedures and QA procedures and deliverables are controlled and transmitted to the Document Control Coordinator in accordance with QAP-17.0, "Quality Assurance Records." Records will be protected in accordance with QAP-17.0 para. 4.3.1. Electronic data will be periodically backed up to removable media, copies of which will be kept in a locked, fireproof file cabinet in a secured area (locked office). Scientific Notebooks and any other hard copy records will be periodically photocopied. The photocopies will be kept in a locked, fireproof file cabinet in a secure area (locked office). Technical reports and any other records that will be submitted to DOE will be written in accordance with QAP-3.4, "Technical Report Preparation". Data will be submitted to the TDA in accordance with QAP-3.6, "Submittal of Data to the Technical Data Management System" through the UCCSN data coordinator. Technical reports will be the primary deliverable. Non-qualified reports will be submitted quarterly and the final report will be submitted at the end of the task.

## 1.17 References

- <sup>1</sup> G. M. Gordon: Corrosion, 2002, vol. 58, pp. 811-825
- <sup>2</sup> Digby D. Macdonald: J. Electrochem. Soc., 1992, vol. 139, pp. 3434-3449
- <sup>3</sup> Digby D. Macdonald, Adan Sun, Namal Priyantha, and Palitha Jayaweera: J. Electroanal. Chem., In Press, 2004.
- <sup>4</sup> ASTM G5-94 (Reapproved 1999), Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements.
- <sup>5</sup> Final Report: Waste Package Materials Performance Peer Review Panel, February 28, 2002
- <sup>6</sup> J. Denk in Super Clean Steel, Ed. J. Nutting and R. Viswanathan, Institute of Materials, London, (1996) 133-155
- <sup>7</sup> F. F. Lyle Jr., Corrosion 39 (1983)121-131
- <sup>8</sup> L.J.Qiao and J.L.Luo, Corrosion 54 (1998) 281
- <sup>9</sup> Q. Yang and J.L.Luo, Electrochim. Acta 45 (2000) 3927
- <sup>10</sup> R.H.Song, Su Il Pyun and R.A. Oriani, Electrochim. Acta 36 (1991) 825
- <sup>11</sup> Annual Book of ASTM Standards, vol. 3.02, ASTM, West Conshohocken, PA 19428-2959, USA