# Office of
## Science and Technology and International
# Materials Performance Targeted Thrust
# FY 2004 Projects



## *December 2004*

***U.S. Department of Energy***
***Office of Civilian Radioactive Waste Management***
***Washington, DC***

# PREFACE

This booklet contains project descriptions of work underway by the Department of Energy (DOE), Office of Civilian Radioactive Waste Management (OCRWM), Office of Science and Technology and International's (OST&I) Materials Performance Targeted Thrust during Fiscal Year (FY) 2004. The Materials Performance Targeted Thrust is part of OST&I's Science and Technology Program which supports the OCRWM mission to manage and dispose of high-level radioactive waste and spent nuclear fuel in a manner that protects health, safety, and the environment; enhances national and energy security; and merits public confidence. In general, the projects described are planned to continue beyond FY 2004 subject to available funding of the Science and Technology Program.

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# Overview of Materials Performance Thrust

## Background

The Yucca Mountain site was recommended by the President to be a geological repository for commercial spent nuclear fuel and high-level radioactive waste. The multi-barrier approach was adopted for assessing and predicting system behavior, including both natural barriers and engineered barriers. A major component of the long-term strategy for safe disposal of nuclear waste is first to completely isolate the radionuclides in waste packages for long times and then to greatly retard the egress and transport of radionuclides from penetrated packages.

The goal of the Materials Performance Targeted Thrust program is to further enhance the understanding of the role of engineered barriers in waste isolation. In addition, the Thrust will explore technical enhancements and seek to offer improvements in materials costs and reliability.

## Materials Performance Targeted Thrust

The materials used for isolating waste in the proposed repository are an important component of the overall approach to the design of the repository system. Opportunities exist to enhance the understanding of material performance and to probe technical enhancements. These enhancements may include optimizing the performance of waste packages and drip shields for increased reliability and cost effectiveness.

Corrosion is a primary determinant of waste package performance at the proposed Yucca Mountain Repository and will control the delay time for radionuclide transport from the waste package. Intact waste packages fully contain and isolate radionuclides at the proposed repository. Corrosion is the most probable and most likely degradation process that will determine when packages will be penetrated and the shape, size, and distribution of those penetrations. The thrust program strives for increased scientific understanding, enhanced process models and advanced technologies for long-term corrosion performance.

Corrosion resistance is important to the long-term performance of waste packages. The waste packages are manufactured from highly corrosion resistant metals, and the surface of these metals is protected by the formation of a self-healing, passive layer. The metals for waste packages and drip shields have excellent corrosion resistance over a wide range of aqueous solution compositions and temperatures. Based upon measurements of corrosion rates of passive metals, the waste packages can remain intact with no penetrations due to corrosion for durations of 10,000's and even 100,000's years.

## Approach

Materials optimization is realized through a coordinated program of targeted, applied research. The program comprises directed technical goals and thrusts. A team of leading

scientists/engineers from major universities and national laboratories is working together to meet the program objectives. This group brings expertise and specialized facilities in important disciplines including corrosion science, materials science, electrochemistry, physical chemistry and geochemistry. The team is organized among collaborative technical thrusts focused on important topics:

- Long-term behavior of protective, passive films
- Composition and properties of moisture in contact with metal surfaces
- Rate of penetration and extent of corrosion damage over extremely long times.

Each technical thrust has a set of coordinated projects. As the program evolves, there will be additional technical thrusts and the collaborative effort will be expanded to include others from national laboratories, academia, and industry. The Materials Performance Targeted Thrust is coordinated with the Yucca Mountain Project through cooperative projects, technical exchanges and program reviews.


## Targeted Technical Thrusts

There are currently three, multi-investigator projects within the Materials Performance Thrust. Each of these is a coordinated set of collaborative efforts.

Corrosion of metal surfaces covered with particulate and deposits
The waste packages are supported in air, and they will never be fully immersed in water, rather the metal surfaces may be covered with dust, particulate and moisture from the surrounding rock and humidity. This technical thrust examines corrosion in thin moisture films and layers of particulate and deposits.

Evolution of corrosion damage by localized corrosion
Localized corrosion processes and particularly crevice corrosion are high priorities. This technical thrust examines the rate of penetration and extent of corrosion damage by localized corrosion over extremely long times.

Evolution of environment on metal surfaces
The corrosion performance of a metal is determined by the inherent corrosion resistance of the metal and the corrosivity of the environment. The amount, distribution and chemical composition of the moisture on waste packages are important.

In addition to the multi-investigator projects, there are bridging projects that coordinate process modeling activities in the Materials Performance Thrust to those in the Natural Barriers Thrust and the Source Term Thrust. The Materials Performance Thrust has been an "incubator" for work that transitioned to full development projects in the Advanced Materials program, e.g. advanced welding techniques and high performance amorphous metal coatings.
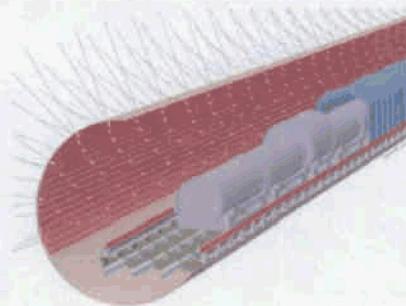
### *Materials Performance Thrust Program Team*

Leading scientists and engineers from universities form a multi-university Corrosion Cooperative (CorrCoOp) that works closely with scientists and engineers at several national laboratories. The CorrCoOp is based at Case Western Reserve University and other participants include Arizona State, Ohio State, Pennsylvania State, University of California-Berkeley, University of Minnesota, University of Toronto, University of Western Ontario and University of Virginia. National laboratories participants include Argonne (ANL) Lawrence Livermore (LLNL), Oak Ridge (ORNL), Pacific Northwest (PNNL), and Lawrence Berkeley (LBNL). The Atomic Energy of Canada Limited (AECL) also participates.

The Director of the Materials Performance Targeted Thrust is Dr. Joe H. Payer at Case. He is supported by an executive committee, a technology/research committee comprised of all program principal investigators, an external review panel and several international affiliates.

# Organization of Progress Report

Three, multi-investigator projects within the Materials Performance Thrust are described in the following sections. Each section presents an overview of the multi-investigator project and a description of the individual efforts that comprise the project. Brief biosketches of the Principle Investigators that are leading the work in the Materials Performance Thrust are presented in an Appendix.

Three major sections follow:
- Corrosion of metal surfaces covered with particulate and deposits
- Evolution of corrosion damage by localized corrosion
- Evolution of environment on metal surfaces

Within each section, the objectives and approach of the multi-investigator project is presented, the individual projects in the technical thrust are highlighted, and the objective and approach of the individual projects are presented.

A team of leading scientists and engineers from major universities and national laboratories is working together to meet the program objectives. This group brings expertise and specialized facilities in important disciplines including corrosion science, materials science, electrochemistry, physical chemistry and geochemistry. A sampling of the specialized capabilities and facilities is shown below.

# Specialized Capabilities and Facilities

A sampling of the specialized capabilities and facilities utilized within the Materials Performance Thrust of the OST&I Science and Technology Program are shown below.
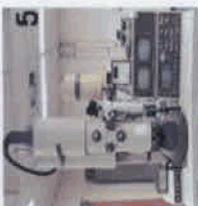


1. Kelvin Probe and Scanning Kelvin Probe
2. Laser-directed powder deposition for graded Ni-Cr-Mo compositions
3. Experimental apparatus for thin-layer electrochemical studies of stability of corrosion sites
4. X-ray Photo-Electron Spectrometry
5. 200KV Transmission Electron Microscope
6. Salt Particle Deposition System
7. Scanning Electrochemical Microscope
8. Thermogravimetric Analysis System at LLNL
9. Electrochemical Quartz Crystal Microbalance
10. Microelectrode Array
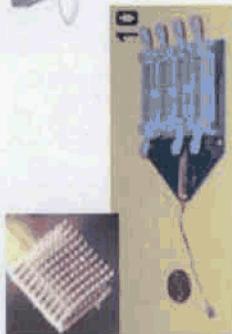
# Corrosion of metal surfaces covered with particulate and deposits

The objective is to determine the corrosion behavior of corrosion resistant metals that are covered by thin layers of moisture and moist particulate and deposits. Advanced analytical and computational methods for corrosion processes in thin films, particulates, and deposits are developed. Inputs are generated for advanced, next-generation models and alternate conceptual models based on less conservative assumptions. Enhanced scientific understanding to the chemical, electrochemical, and corrosion processes is provided.

> **Thrust Objective:** *Develop technical basis and demonstrate reduction in passive corrosion rate with time. Currently in TSPA, no reduction of passive corrosion rate with time is included and a constant rate is used. There is a potential to extend waste package life by 100 to 1000 times compared that with a time-constant rate.*

Highly corrosion resistant materials are selected for the waste packages and drip shields for the proposed Yucca Mountain Repository, i.e. Alloy 22, a nickel-chromium-molybdenum alloy and titanium, respectively. Both Alloy 22 and titanium have high corrosion resistance in oxidizing environments that are of interest for the proposed repository. These alloys depend upon the formation and the tenacity of a passive film, i.e. a thin oxide on the surface, for their corrosion resistance. Measured corrosion rates for passive metals decrease with time to on the order of 0.1 to 0.01 micrometer per year. At these rates, it takes 10,000 to 100,000 years to penetrate 1 millimeter of metal, and the Alloy 22 outer layer of the waste packages is on the order of 20 millimeters thick.

> **Thrust Objective:** *Identify corrosion processes for metal covered with particulate and deposits. Currently, the corrosion treatment is based on fully immersed solutions and not corrosion in moist layers of dust/particulate. This treatment is conservative in many cases.*

In the proposed repository, metal surfaces will be dry (no corrosion) or exposed to thin layers of moisture and moist particulates or deposits. The waste packages are placed on support pallets and sit in air at atmospheric pressure. There is no feasible scenario that will lead to waste packages being fully immersed in water. There is a limited amount of water moving through the rock, and there is a limited amount of salts and minerals available to deposit on the packages. The ambient waters in the mountain are dilute; however, those ambient waters can be modified and become concentrated by the thermal-hydrological-chemical processes. The sources of water that can contact metal surfaces in the proposed repository are deliquescence, condensation and drips or seepage. Deliquescence is determined by the amount and composition of soluble salts in the particulate layers, the relative humidity, and temperature. Drips and seepage of water from the drift walls onto the metal surfaces is possible after the thermal barrier period, i.e., when the drift wall has cooled to below the boiling point of water. Metals will be exposed to thin layers of moisture and moist particles in deposits of dust and particulate.

The approach is to meet the objectives through a coordinated set of projects. A team of leading scientists/engineers from major universities (The Corrosion Cooperative [Corrosion CoOp]) and national laboratories are working together within the OCRWM/OST&I Materials Performance Targeted Thrust. This group brings specialized expertise, methods and facilities in corrosion science, materials science, electrochemistry, and geochemistry. Individual projects in this technical thrust are highlighted below.

**Technical Thrust: Corrosion of metal surfaces covered with particulate and deposits**

Kinetics of the Cathodic Reduction of Oxygen on Passive Metals
David W. Shoesmith and Jamie Noel; University of Western Ontario

Oxygen Electro-reduction on Passive Metals in Particulate and Deposited Layers
Dominic Gervasio; Arizona State University

Corrosion Cells beneath Thin Films, Particulate and Deposited Layers
Joe H. Payer; Case Western Reserve University

Kelvin Probe Measurements of Corrosion under Thin Deliquescence Brine Layers
Gerald S. Frankel and Rudy G. Buchheit; The Ohio State University

Mechanism of Mixed-Ion Effects on Corrosion in Thin Films
Roger C. Newman; University of Toronto

Effect of Environmental Variables on the Structure and Composition of Passive Films
Thomas M. Devine; University of California, Berkeley

# Corrosion in Thin Layers of Particulate
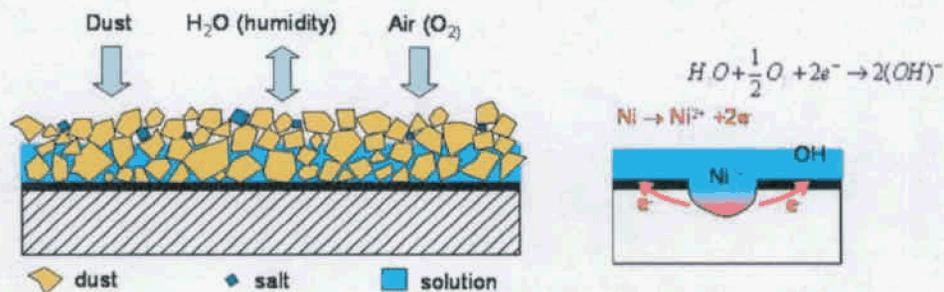


Dust    H₂O (humidity)    Air (O₂)

$$H_2O + \frac{1}{2}O_2 + 2e^- \rightarrow 2(OH)^-$$

$$Ni \rightarrow Ni^{2+} + 2e^-$$

- dust    ◆ salt    ▦ solution

- Dust deposited
- Degree of wetness
- Soluble salts
- Gas composition and property, T, RH
- Particulate layer properties, such as conductivity, temperature, pH, degree of wetness etc.
- Localized environment on the surface
- Anode: $Ni \rightarrow Ni^{2+} + 2e^-$
- Cathode: $H_2O + 1/2O_2 + 2e^- \rightarrow 2OH^-$

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## Kinetics of the Cathodic Reduction of Oxygen on Passive Metals

David W. Shoesmith, University of Western Ontario

**PROJECT OBJECTIVES AND APPROACH:** The primary goal of this project is the elucidation of the mechanism and kinetics of the cathodic reduction of oxygen on Ni-Cr-Mo(W) alloys. The results are important to the development of models to predict the rate and extent of accumulation of corrosion damage within crevices and under thin aqueous films and wet particulate deposits formed on the surface of the alloys.

Experiments will be conducted at rotating ring-disk electrodes to allow corrections for transport effects to be made. The ring electrode will allow the determination of the extent of reduction; i.e., whether it proceeds via only two electrons to hydrogen peroxide or whether reduction involves four electrons to produce water. Since the composition of the alloy surface is expected to have a very significant effect on reduction kinetics, techniques such as X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (TOFSIMS) will be employed to correlate kinetics with surface condition.

## Oxygen Electro-reduction on Passive Metals in Particulate and Deposited Layers

Dominic Gervasio, Arizona State University

**PROJECT OBJECTIVES AND APPROACH:** The objective is to determine the corrosion behavior of corrosion resistant metals that are covered by thin layers of moisture and moist particulate and deposits. This work is intended to develop advanced analytical and computational methods for corrosion processes in thin films, particulate and deposits to produce advanced, next generation conceptual models with significantly reduced uncertainty and provide integrated scientific understanding to the chemical, electrochemical and corrosion processes

The approach is to experimentally study the oxygen ($O_2$) electro-reduction or other cathodic redox reactions in thin layers of moisture and layers of moist particulate and deposits on metal surfaces. $O_2$ reduction is of particular interest (although other redox reactions may also contribute) as the cathodic current at the metal surface that can sustain pitting, crevice corrosion, stress corrosion cracking and galvanic action. Fresh and aged Ni alloy surfaces in brine and with sub-monolayer and thicker coverage of particles are to be studied. Results are important inputs to the determination of the onset and extent of cathodic stifling of corrosion processes. A series of well-planned experiments will be conducted to investigate oxygen reduction on fresh and aged Ni alloy surface as a function of saturated and unsaturated particulate, chemical composition of moisture and particulate, temperature and relative humidity. These experiments provide input to modeling of corrosion of the Ni alloy, and the results provide a basis for model validation.

Task 1: Design and construction of experimental setup with rotating ring-disk electrode (RRDE) and stationary planar electrodes for measurement of $O_2$ reduction, oxide growth and possibly other redox reactions on passive metal as a function of potential and current.
Task 2: Measure $O_2$ reduction on freshly abraded and aged surfaces in brine.
Task 3: Characterize effects of exposure with time, temperature and polarization using voltammetry and/or infrared surface spectroscopy.
Task 4: Characterize the effect of particulate layers on the alloy surface and $O_2$ electro-reduction.

Task 5: Characterize $O_2$ reduction and possibly other redox reactions on the alloy surface with thick particulate coverage by electrochemical measurement including impedance spectroscopy.

Task 6: Freshly abrade a line along the diameter of a disk of passive surface and study two cases: first, $O_2$ reduction on the scored disk in brine by the RRDE method; and second, the scored disk covered in brine saturated with air, inspecting and comparing both cases for induced defects.

## Corrosion Cells beneath Thin Films, Particulate and Deposited Layers

Joe H. Payer; Case Western Reserve University

**PROJECT OBJECTIVES AND APPROACH:** The objective of this project is to examine the behavior of macro and micro corrosion cells in experiments that create conditions for passive metals covered by thin layers of moisture, particulate and deposits. The operation of corrosion cells beneath thin films, particulate, and deposited layers can vary significantly from the behavior observed in fully immersed conditions. Corrosion of active metals, e.g., iron and zinc, in thin layers of moisture that pertain to atmospheric corrosion has been studied extensively; however, the behavior of passive metals in thin layers of moisture may be further elucidated. The results will provide input to the modeling efforts to describe the behavior. The focus is on the post-initiation stages of the corrosion cells to gain insight on the propagation and potential stifling processes that will affect corrosion damage evolution over time.

A series of experiments will be conducted to investigate the geometric effects, saturated and unsaturated particulate, chemical composition of moisture and particulate, temperature, and relative humidity. The experiments are closely coupled to modeling of the current flow and potential gradients. The current flow patterns and distribution in thin layers of moisture and layers of moist particulate and deposits on metal surfaces will be studied experimentally. Of particular interest is the flow of current representative of corrosion scenarios at the metal surface: pitting, crevice corrosion, stress corrosion cracking, and galvanic action. The range of layer thicknesses is from a mono-layer coverage of particulate to 1-cm and greater. Moisture layers on clean surfaces and for sub-monolayer coverage of particles are studied in a companion project. Results are important inputs to the determination of the onset and extent of cathodic stifling of corrosion processes.

## Kelvin Probe Measurements of Corrosion under Thin Deliquescence Brine Layers

Gerald S. Frankel and Rudy G. Buchheit; The Ohio State University

**PROJECT OBJECTIVES AND APPROACH:** The objective is to make electrochemical measurements on corrosion resistant alloys under layers representative of dust, particulate and adsorbed moisture (from monolayers to millimeters in thickness) and characterize the relationship between the physical characteristics of the layers and the electrochemical behavior of the alloys. Specially-designed artificial particulate brine layers will be created. These thin layers will have specific physical characteristics and will be dosed with known amounts of soluble constituents. Physical characteristics include particulate packing fraction, particulate size distribution, and layer thickness, among others. A range of techniques will be used to characterize the thin layers and to determine the corrosion behavior of alloys covered by these layers. A focus of the work

will be the use of Scanning Kelvin Probe measurements and potentiodynamic scanning using non-contact Kelvin Probe measurement of potential.

The two general pursuits of this work are to examine the time evolution of environments in thin particulate layers and to determine the effects of the thin layer properties on corrosion behavior. Variables include layer thickness, chemistry, solids fraction, and solids type. Local cell action on heterogeneous electrode arrays will be characterized.

*Simulation of Thin Brine Layers:* Development of an effective method to simulate the thin brine layers is important, and a range of techniques will be examined to fabricate the particulate layer, including sol gel processing, partial sintering of fine particulate, and physical vapor deposition of porous oxide layers. Initially, the sol gel method is evaluated for generation of controlled thin silica xerogel layers into which electrolytes might be dispersed and retained in a controlled manner. A controlled temperature and humidity chamber will be constructed for forming and stabilizing thin electrolyte layers on electrode arrays.

*Multi-Electrode Arrays:* Wires of corrosion resistant alloys with diameters ranging from tenths to a few millimeters will be imbedded with periodic spacing into epoxy. This structure results in a regular planar array of circular electrodes for environmental exposure and electrochemical testing. In thin layer electrolytes, the Scanning Kelvin Probe technique will be used to simultaneously measure the potentials of the array elements. A configuration that simulates a localized corrosion cell is an array of multiple Alloy 22 wires with a central electrode of a more-susceptible material such as type 316 stainless steel.

*Electrochemical Measurements:* A major challenge in making electrochemical measurements in thin electrolyte layers is the incorporation of a viable reference electrode with the ability to provide spatial resolution of the potential. In this task, a Kelvin Probe and Scanning Kelvin Probe techniques will be utilized to make electrochemical measurements in the thin layers. The Kelvin Probe provides a non-contact measurement of potential. The first step is to measure the cathodic kinetics on passive metals in a thin film electrolyte.

## Mechanism of Mixed-Ion Effects on Corrosion in Thin Films

Roger C. Newman; University of Toronto

**PROJECT OBJECTIVES AND APPROACH:** The objective is to determine whether non-chloride anionic inhibitors, especially nitrate, are as effective in thin layers and deposits as they are in bulk solutions, and to understand any associated depletion mechanisms. The approach is to use micro-electrode studies in thin layers and deposits, using electrochemistry to monitor growth of corrosion sites and the properties of the thin electrolyte layer.

Alloy 22 was developed to have excellent resistance to hot saline environments, combining the passivating ability of Cr III and the blocking or inhibiting role of Mo IV. This project will deal with the consequences of localized corrosion initiation, which has been shown to be feasible under severe conditions of temperature, chloride concentration, and crevice geometry. Usually, atmospheric or thin-film corrosion of stainless steels (and by extension nickel-base alloys) is much slower than corrosion under full immersion. This probably reflects a process of repetitive initiation and repassivation of pits, which cannot grow beyond a certain size without exhausting the local supply of cathodic current.

In an environment containing nitrate and other non-chloride anions, new phenomena can arise. In general, lack of electrolyte reduces the stability of pits. Processes to be examined include the electroactivity of nitrate and other anions, the effect of inherently slower growth rate of corrosion sites in a thin liquid film on the inhibition, and the role of formation of membranous layers over corrosion sites. In prior work, the PI used an artificial pit or pencil electrode technique to study the inhibition mechanism of nitrate on pitting of austenitic stainless steel and concluded that strong inhibition was associated with a redox or electroreduction reaction of nitrate within an anodic $FeCl_2$ salt film. An additional inhibiting effect was observed for nitrate prior to salt precipitation that which resembled the effect of alloyed nitrogen. It was summarized that electrochemical kinetics of pitting including a range of inhibition effects, e.g., sulphate affects pit development in various ways, not all of them beneficial.

The objectives here include:
- To measure and understand the effect of liquid layer thickness on localized corrosion kinetics in the presence and absence of nitrate
- To determine and understand the conditions, if any, in which a thin electrolyte layer containing inhibiting anions is more aggressive, in terms of localized corrosion, than a bulk solution of the same aqueous composition
- To determine the effect of the total quantity of corrodent on the distance to which a single corrosion site can propagate, and to understand such behavior in terms of chloride mass balance
- To measure and understand the effects of minor constituents of the environment, such as fluoride.

Defined quantities of electrolyte will be retained on Ni-Cr-Mo alloy surfaces, including Alloy 22 but also less resistant alloys. The electrolytes will contain chloride and nitrate as anions, in a few different relative concentrations. Potential, current and potential noise, and pit propagation rate will be measured at different liquid layer thickness, and impedance measurements between pairs of microelectrodes will be used to monitor the layer thickness. Microscopy and application of Faraday's second law will reveal the extent to which current is lost (does not flow through the external measuring circuit) for the smaller layer thicknesses.

Foil samples will be used in some experiments, so that perforation can be monitored and related to the electrochemical signals. Systematic measurements of corrosion potential, current-potential curves, 2-electrode potential and current noise, and pit propagation stability (using very low applied anodic currents) will reveal the relationship between liquid layer thickness and lateral extent, its chemistry, and corrosion stability.

## *Effect of Environmental Variables on the Structure and Composition of Passive Films*

Thomas M. Devine; University of California, Berkeley

**PROJECT OBJECTIVES AND APPROACH:** The objective is to characterize the surface films formed on Ni-Cr-M0 alloys and less corrosion resistant metals by two experimental approaches. First, the early stages of film formation will be directly observed through the use of environmental transmission electron microscopy (TEM) and environmental x-ray photoelectron (XPS) microscopy. Collectively, these conventional *ex situ* techniques will provide atomic-resolution, *in situ* information on the nucleation and early growth of surface films on the passive

alloys in moist environments. The second experimental approach employed to probe the structure and composition of surface films that form on the alloys will constitute the bulk of the research.

This work will also investigate the effects of aqueous solution chemistry, applied potential, temperature, and wet/dry cycling on the structure and composition of surface films that form. Solution chemistries will span a range of compositions of single and multi-species brines. The films will be examined as a function of the applied potential, which will be varied from the reducing values to values within the transpassive region. Tests will be conducted at temperatures over a range from 25° C to approximately 120° C. Wet/dry cycling effects are to be examined.

The films that form on the passive metals will be characterized by two *in situ* techniques: surface enhanced Raman spectroscopy (SERS) and electrochemical impedance spectroscopy (EIS), and three *ex situ* techniques: SERS, atomic resolution transmission electron microscopy (TEM), and X-ray Photoelectron Spectroscopy (XPS). SERS will provide the vibrational spectra of the surface films. Comparison of the *in situ* and *ex situ* SER spectra will indicate if and how the films have changed as a result of removal of the samples from the aqueous solutions. It is expected that the passive films on the Ni-Cr-Mo alloys will consist of one to three layers and depend on solution pH and applied potential. The inner layer might be chromium rich, and the two outer layers might be enriched in iron, nickel, and molybdenum. The SERS and TEM will confirm the structures and compositions of the films. Mott-Schottky (M-S) plots will be generated from the impedance spectra and the M-S plots will identify the semiconductor-like properties of the individual layers of the film as a function of potential. The films' electronic properties, which are extracted from the M-S plots, will identify the specific layer(s) of the film that are responsible for corrosion resistance at different potentials.

The surface films that form on Ni-Cr-Mo alloys immersed in aqueous solutions might depend on the initial condition of the sample's surface. Tests will be performed on samples of passive metals with three different initial surface conditions:

      1) bare surface,

      2) surface with an air-formed oxide, or

      3) surface coated with a thermal oxide.

The thermal oxide will be formed by heat treating and cooling samples in a manner that simulates the heat treatments to create surface compressive stresses for mitigation of stress corrosion cracking. To help interpret the data (SERS, EIS, TEM, and XPS) obtained from films on the Ni-Cr-Mo alloys, similar tests will be conducted on films formed on pure elements: nickel, chromium, molybdenum, and iron.

# Evolution of Corrosion Damage by Localized Corrosion

Localized corrosion processes and particularly crevice corrosion are high priorities. This technical thrust examines the rate of penetration and extent of corrosion damage by localized corrosion over extremely long times. Advanced analytical and computational methods for the time evolution of crevice corrosion damage are developed. Examine requirements for initiation of localized corrosion, and address propagation and arrest phenomena that lead to a reduction in the rate of crevice corrosion.

> **Thrust Objective:** *Develop and analyze a logic-tree approach for the damage to waste packages by localized corrosion. Currently in TSPA, a go/no-go initiation criterion is used with a set of complex, empirical rules. The logic-tree approach provides a clear and transparent treatment to account for contributing factors.*

> **Thrust Objective:** *Develop technical basis and demonstrate processes that slow penetration rates by localized corrosion. Currently, once damage (crevice corrosion) is started there is no slowing or stopping of penetration rate. In many cases, amount of damage would be greatly reduced.*

> **Thrust Objective:** *Demonstrate factors that limit the initiation of localized corrosion. Current treatment presumes crevices and supporting processes are always available. It is likely that localized corrosion will not occur under many conditions.*

Corrosion is a primary determinant of waste package performance and will control the delay time for the onset of radionuclide transport from the waste package. In addition, corrosion will determine when packages are penetrated and the shape, size, and distribution of those penetrations.

The evolution of crevice corrosion damage is determined by the initiation, propagation, stifling, and arrest stages of localized corrosion. Crevice corrosion is affected by the crevice geometry and properties of the crevice former. For waste packages, metal surfaces can be covered with dust. Particulate, scale and deposits can form from dust, minerals from waters, and corrosion products. An important issue is how effective particulate layers and deposits are as crevice formers compared to metal/metal crevices and polymer/metal crevices used in laboratory tests. Chemical, electrochemical and metallurgical factors control the formation and evolution of the crevice chemistry. For crevice corrosion to persist, the critical crevice chemistry must be formed and maintained. These and other crucial issues are addressed by the projects in this technical thrust area.

The approach is to meet the objectives through a coordinated set of projects. A team of leading scientists/engineers from major universities (Corrosion CoOp) and national laboratories are working together within the OCRWM/OST&I Materials Performance Thrust. This group brings specialized expertise, methods and facilities in corrosion science, materials science, electrochemistry and geochemistry. Individual projects in this technical thrust are highlighted below.

**Technical Thrust: Evolution of corrosion damage by localized corrosion**

Crevice Corrosion Electrochemistry
    John R. Scully; University of Virginia

Modeling of Critical Chemistry for Crevice Corrosion
    Robert G. Kelly; University of Virginia

Experimental Determination of the Evolution of Crevice Corrosion Damage
    David W. Shoesmith and Jamie Noel; University of Western Ontario

Coupled Crevice Tests for Initiation, Propagation and Arrest of Crevice Corrosion
    Brian Ikeda; Atomic Energy of Canada Limited

Localized Corrosion Stability in the Presence of Non-Chloride Anions
    Roger C. Newman; University of Toronto

Metallurgical Effects on Localized Corrosion of Ni-Cr-Mo Alloys
    Gerald S. Frankel and Rudolph G. Buchheit; The Ohio State University

Combinatorial Chemistry Approaches for Alloy Composition and Corrosion Behavior
    Rudolph G. Buchheit and Gerald S. Frankel; The Ohio State University

Prediction of the Time Evolution of Localized Corrosion Damage
    Digby D. Macdonald; Pennsylvania State University

Data Mining of Experimental Localized Corrosion Data
    Mirna Urquidi-Macdonald; Penn State University



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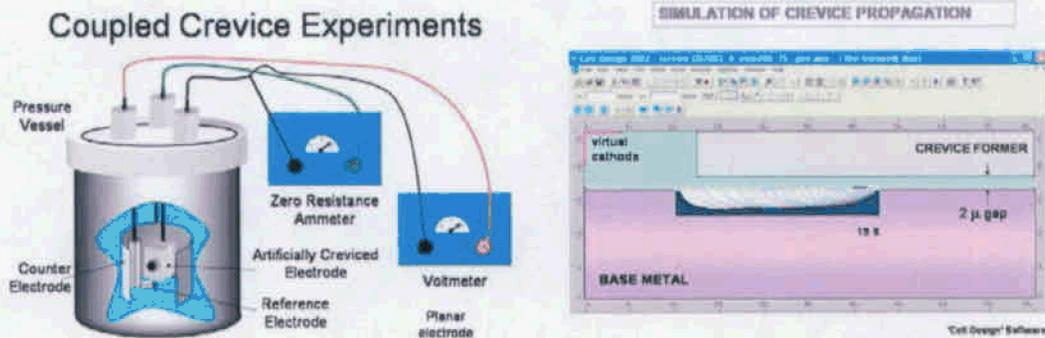
# *Crevice Corrosion Electrochemistry*

John R. Scully; University of Virginia

**PROJECT OBJECTIVES AND APPROACH:** The objective is to understand the impact of alloy crevice corrosion electrochemistry on maintaining critical crevice solution chemistries which in turn effects propagation, repassivation/stifling phenomena. Elucidation of the effects controlling these phenomena is important to the understanding of how or whether crevice corrosion damage evolves for corrosion resistant alloys exposed to aggressive corrosion conditions. The specific objective is to characterize Ni-Cr-Mo alloy corrosion electrochemistry focusing on active dissolution properties, as a function of well-controlled conditions in crevices and artificial crevice solutions typical of acid-chloride crevice corrosion.

A variety of alloy compositions will be studied with an infinite cathode area using a potentiostat and remote counter electrodes. These studies are aimed at elucidating effects of alloying additions on crevice corrosion rates and to define critical crevice chemistries. Electrode arrays coupled to crevice anodes are used to examine the anodic electrochemistry associated with alloy dissolution in crevice solutions when mediated by finite cathode area (such as in a thin film). These studies will help elucidate how the crevice dissolution properties and resultant crevice chemistries associated with anodic crevices are affected by cathode limitations.

The long-term objective is to determine whether anode properties and environmental conditions favor stabilization of a crevice as well as whether those conditions promote crevice corrosion stifling and repassivation. Stifling and repassivation are affected by corrosion product formation, inadequate maintenance of critical crevice chemistries for a given set of conditions and other causes. This work will be conducted in collaboration with other projects in the Corrosion CoOp particularly those that are modeling crevice corrosion chemistry evolution and stabilization. Resulting propagation rate data will also serve as input to studies of damage evolution.

A series of experiments will be conducted to investigate the electrochemical corrosion properties of model and commercial Ni-Cr-Mo alloys in novel artificial crevice geometries as well as in the form of conventional three electrode setups in artificial crevice environments. The experiments are closely coupled to and serve as inputs for modeling of crevice chemistry. The results indicate conditions under which crevice stabilization, repassivation due to non-maintenance of crevice solution chemistries and stifling can occur.

The overall approach includes the following tasks:

Task 1: Establish generic $X^2/G$ crevice scaling laws for particular material composition, environmental and solution conditions representative of a stable crevice assuming no chemistry change. The scaling laws calculations will be done based on the literature and on polarization behavior measurement conducted in task 3.

Task 2: Select alloys with range of Ni-Cr-Mo-W contents (less than – up to alloy 22)

Task 3: Isolate anode from cathode (infinite of finite cathode simulated via potentiotstat versus finite cathode simulated with a galvanostat or galvanic couple). Acquire E-I data independent of Ohmic voltages, etc. Establish intrinsic material behavior independent of extrinsic (ohmic, mass transport, geometric) effects (input to modelers)

Task 4-5: Conduct crevice stabilization tests in model rescaled crevices (artificial pit, rescaled pit, instrumented crevice with addressable sites, and sensors) using "lesser" alloys to

enhance reproducibility and to minimize need for extreme environments and temperatures. Accept input on bulk and simulated thin film environments from other CorrCoOp projects.

Integrate isolated anode material behavior with crevice details – (study crevice stabilization, propagation, repassivation, stifling) with focus on spatial location of crevice attack, propagation rate and damage accumulation as a function of geometric, physical and environmental variables.

Task 6: Develop insight on crevice corrosion arrest and/or stifling mechanisms (e.g., effect of cathode limitations on spatial distribution of anodes, effects of precipitation on stifling)

Task 7: Integrate isolated anode material behavior with crevice details – (study crevice stabilization, propagation, repassivation, stifling) with incorporation of proximate cathode and anode of various size and position.

Task 8: Compare experiment and models (both crevice chemistry and damage evolution) validate models for stabilization

Task 9: Integrate isolated anode material behavior with crevice details – (study crevice stabilization, propagation, repassivation, stifling) with incorporation of non-conventional effects of non-inert (reactive) crevices, selectively permeable crevices, etc.


## *Modeling of Critical Chemistry for Crevice Corrosion*
Robert G. Kelly; University of Virginia (UVA)

**PROJECT OBJECTIVES AND APPROACH:** The primary objective of this project is to establish an advanced scientific basis for the calculation of the stability of crevice corrosion propagation for Ni-Cr-Mo alloys as a function of temperature, alloy composition, relative humidity, external solution layer composition, and cathodic kinetics on the outside surface.

Crevice corrosion represents one of the primary modes of corrosion that may affect waste package performance. In addition to crevices that are part of the design (e.g., at the waste package/support contact), additional crevices may form under deposits and scales. In order for crevice corrosion to represent a substantial challenge to waste package performance, the corrosion must initiate and must stabilize at a significant rate. Stabilization requires the maintenance of a highly acidic, highly concentrated solution composition within the crevice. The balance between the anodic kinetics within the crevice, the cathodic kinetics outside the crevice, and the transport conditions between them determines the stability of the crevice.

For a stable crevice, a surface solution exists on the area outside the crevice, and the rate of crevice corrosion can be controlled by:

1) Total cathodic current that the external surface can supply to the crevice,

2) Rate of anodic dissolution within the crevice, or

3) Potential drop between the dissolution position in the crevice and the external surface.

For stifled crevices, the rate of crevice corrosion will be controlled by the rate of the anodic and cathodic reactions within the isolated crevice.

The interactions amongst these factors are complex and therefore difficult to control and understand based solely on experiments. In addition, the effects of the primary variables of interest (temperature, RH, external environment, alloy composition) add significantly to the dimensionality of the problem. Computational studies can aid in narrowing the domain space over which experimental studies should be concentrated. Such process models can also be abstracted for use by life prediction codes.

While a substantial amount of crevice corrosion modeling has been done, the crevice corrosion models have limitations with regards to the several conditions of interest:

a) Difficulty handling the non-linear electrochemical boundary conditions characteristic of actual corroding interfaces,

b) Difficulties with inclusion of new physiochemical data without extensive reprogramming,

c) Inability to consider open circuit conditions (i.e., most models must assume that the mouth of the crevice be held at a constant potential), and

d) Limited coupling to conditions outside the crevice, and none explicitly couple the crevice to a gaseous atmosphere.

In addition, under some of the conditions of interest, precipitation will occur both within the crevice and on the surface outside of the crevice, and will have important effects on transport. Developing a computational code that can overcome these limitations will serve as a basis for predictions of crevice stability and serve as an input to life prediction models.

A series of computational experiments will be conducted to investigate under what conditions and at what rate crevice corrosion can propagate in corrosion resistant alloys exposed to aggressive corrosion conditions. Two cases will be considered: an isolated crevice (i.e., no external cathode), and a crevice with thin layer of solution outside the crevice on which cathodic reactions can be supported. The effects of geometry (length, gap), metallurgical condition, temperature, and relative humidity will be investigated. Results are important inputs to the determination of the extent of potential damage caused by crevice corrosion.

The overall approach includes the following tasks:

Task 1: Adapt the existing UVA computational code for crevice chemistry for Ni-Cr-Mo alloys under aggressive corrosion conditions. This adaptation will include the inclusion of relevant species, thermodynamic and physiochemical properties of all species at elevated temperature, and precipitation.

Task 2: Modify the code to introduce appropriate electrochemical kinetics as a function of crevice chemistry and external cathodic kinetics based on experimental results from other tasks.

Task 3: Calculate stability of crevice corrosion attack for the two types of cases considering the external variables of temperature, relative humidity, and external solution layer chemistry (coupled to other task outputs).

There will be extensive interactions with the other modeling tasks in the Materials Performance Targeted Thrust. Primary links will be made to the tasks involved with modeling of the environment on the waste package, as well as to the damage evolution tasks. Input will be taken from the tasks involved with the anodic kinetics within the localized site and the cathodic kinetics

on the exposed surface outside of the crevice. The outcome of the task will be a tool for calculating conditions within the crevice.

## Experimental Determination of the Evolution of Crevice Corrosion Damage

David W. Shoesmith and Jamie Noel; University of Western Ontario

**PROJECT OBJECTIVES AND APPROACH:** The objective of this project is the measurement of damage functions that can be used either to develop models for waste package damage accumulation due to crevice corrosion or to validate alternative models developed for the same purpose. The key deliverables will be direct measurements of the time-dependence of the depth and distribution of corroded sites within a well-defined crevice area for corrosion resistant metals exposed to aggressive corrosion conditions.

In many corrosion applications, the exposure conditions are not constant but rather the environmental conditions evolve with time. For example, within the proposed repository after a heat-up period on closure, the conditions evolve from hotter and greater potential for aggressive conditions to eventually cooler and more benign conditions. A primary goal for damage evolution models is to demonstrate the severity of damage accumulation that develops over the long-term. Consequently, a major focus of this project will be the experimental identification of those alloy features that determine the propagation, stifling/repassivation, and reinitiating processes of crevice corrosion.

A range of electrochemical and surface analytical techniques will be used to accelerate and/or monitor the progress of crevice corrosion. In particular, a galvanic coupling technique that simulates crevice corrosion in the absence of any applied electrochemical driving force will be used. Measurements of the accumulation of crevice propagation damage as a function of time will be made for a number of Ni-Cr-Mo alloys (Alloy C22, Alloy C276, Alloy G30) in sodium chloride solutions at elevated temperature. The majority of experiments will be performed at temperatures in the range 70° C to 120° C, although a small number of experiments at higher temperatures will also be included. The total extent of damage will be determined by measuring crevice currents. The morphology of distribution will be measured using profilometry and confocal laser microscopy. A primary goal is to determine the depth and distribution of damage with alloy composition.

Secondary ion mass spectrometry (SIMS) and other surface analytical techniques will be used to determine changes in surface composition on metallographic cross sections cut through crevice corroded specimens to determine whether significant changes in alloy surface composition influence the rate and direction of crevice corrosion (into, or across, the creviced surface). These measurements will be correlated with measurements of critical crevice chemistries measured by other researchers working within the Corrosion CoOp.

Critical stifling/repassivation parameters such as temperature and chloride concentration will be determined by monitoring the currents and potentials measured in galvanic coupling experiments. The evolution of these parameters as temperature or environment is changed will indicate whether the tendency in crevice behavior is towards stifling/repassivation or continued propagation. Correlations between physical parameters (depth of penetration, area of creviced surface corroded) and corrosion parameters (current, charge, potential) will be explicitly specified

since these correlations will be the key relationships for incorporation into, or comparison to the predictions of crevice corrosion models.

The galvanic coupling technique is used to investigate a number of key parameters which are important in determining crevice propagation rates:

1) Anode to cathode area is easily changed and always known,

2) Since the electrodes are contained within a pressure vessel, corrosion can be studied at temperatures up to ~ 200°C, and

3) Since the anode and cathode are physically separated the technique can be used to study the influence of either the anodic or cathodic reaction on the overall crevice corrosion process.

The arrangement can also be used in experiments in which the crevice is stimulated (or retarded) by electrochemical control, thereby enhancing either the anodic or cathodic reactions.

## *Coupled Crevice Tests for Initiation, Propagation and Arrest of Crevice Corrosion*

Brian Ikeda; Atomic Energy of Canada Limited

**PROJECT OBJECTIVES AND APPROACH:** Crevice corrosion, and hydrogen absorption leading to embrittlement within acidified crevices, are possible failure modes for corrosion resistant passive metals. An understanding of crevice corrosion is important to provide a basis for predicting the performance of such metals. Oxygen reduction at an external cathodic surface is a necessary driving force to maintain crevice propagation and the characteristics of the cathodic process may limit the damage caused by crevice corrosion. The purpose of this project is to describe the role of the cathodic reaction on crevice corrosion under nearly natural corroding conditions. The project consists of two tasks: A) the measurement of crevice propagation and repassivation of an active crevice, and B) the determination of conditions that may lead to crevice initiation. Alloys with a range of corrosion resistance will be examined to highlight the influence of environmental factors on crevice corrosion and develop an understanding of the processes driving crevice corrosion. One alloy that is more susceptible to crevice corrosion than the high Ni-Cr-Mo alloys will be chosen and its behaviour compared to an alloy more resistant to crevice corrosion, e.g., Alloy 22. The data obtained from this project will be used to help define parameters required for advanced process modeling, and to provide data for verifying model predictions against measurable quantities.

*Measurement of Crevice Propagation and Repassivation*

Experiments will be performed to demonstrate the occurrence, spontaneous cessation, or continuous propagation of crevice corrosion as a function of the size and surface conditions of a coupled cathodic surface. Using instrumented crevice assemblies, diagnostic values of current and potential will be obtained to support more quantitative determinations of crevice susceptibilities. The crevice design will be optimized to promote crevice initiation. Alloy 22 and a less corrosion resistant, nickel-based material (such as Inconel 625) will be chosen to develop the experimental methodology.

The galvanic coupling technique is suitable for monitoring the corrosion current and potential under nearly natural crevice corrosion conditions. The experimental conditions simulate the large cathode-small anode conditions normally encountered for crevice corrosion situations. The coupled cathodic reaction is an important variable that could influence the three stages of crevice corrosion. The size (effective area) and efficiency of this cathode could limit the crevice corrosion rate, could induce the corrosion reaction to stop, or could prevent the initiation of a

damaging crevice reaction. The effect of the cathodic reaction on crevice corrosion can be examined by varying the cathodic area, or the anodic area, or both areas. The effect of silicate precipitation will also be examined to determine if a silicate layer simply blocks the cathodic area or changes the cathodic kinetics.

The initial reference solution will be 0.5 mol·L$^{-1}$ NaCl (near seawater chloride concentration) to avoid synergistic interactions between common groundwater species. The effect of varying the chloride concentration and the effect of groundwater constituents on the crevice propagation rate or repassivation time will be examined. The effect of the cathodic surface area will be studied at critical concentration points to determine if the groundwater species are more effectively influencing the anodic or cathodic reaction. The temperature will be varied, both for the duration of an experiment and transiently throughout an experiment. The effect of constant temperature on the coupled current can provide mechanistic information on the corrosion reaction. The effect of temperature transients on the coupled current can be also be used to determine the steady-state temperature dependence, but a sudden drop to zero current concomitant with a positive shift in coupled potential is characteristic of a repassivation of the crevice. Such an experiment will be used to determine the critical temperature for repassivation as a function of solution composition for critical cathode dimensions.

### Initiation of Crevice Corrosion

The coupled current tends to pass through zero as the crevice reaction initiates, indicating that the crevice is initially more cathodic than the counter electrode. This shift in current is often accompanied by an increase in electrochemical noise, suggesting the occurrence of individual initiation events within the crevice. These signals provide a convenient and direct measure of the susceptibility to crevice initiation, although sustained propagation may or may not follow. A sustained current following these initial indicators suggests the formation of a stable crevice propagation reaction.

A fixed anode-to-cathode surface area ratio will be used to perform crevice initiation experiments as a function of solution composition and temperature. The initiation time, and the time to stable crevice corrosion can be used to predict the probability of crevice initiation.

The results of the experimental work will contribute to the characterization of the crevice process as it relates to the development of advanced process models for the evolution of damage by crevice corrosion. A focus of the experiments is the role of the cathodic reaction on crevice corrosion under nearly natural corroding conditions. The measured values will be used to compare with advanced process models being developed to predict long-term localized corrosion damage functions. These results complement other experimental and computational tasks and the technical thrust for Evolution of Corrosion Damage by Crevice Corrosion.

## Localized Corrosion Stability in the Presence of Non-Chloride Anions

Roger C. Newman; University of Toronto

**PROJECT OBJECTIVES AND APPROACH:** Localized corrosion stability and propagation rates in chloride containing waters can be affected by non-chloride anions, and nitrate and sulfate are of particular interest. This project will examine the corrosion inhibition mechanisms with specific focus on the nitrate-chloride interactions. The proposed methodology is based on the artificial pit or pencil electrode technique. Newman and Ajjawi used the artificial pit or pencil electrode technique to study the inhibition mechanism of nitrate on pitting of austenitic stainless

steel. They concluded that strong inhibition was associated with a redox or electroreduction reaction of nitrate within an anodic $FeCl_2$ salt film, thus explaining the anodic passivation of pits observed in conventional electrochemical pitting tests in chloride/nitrate solutions. Newman and Shahrabi showed that there was some additional inhibiting effect of nitrate prior to salt precipitation, and that this resembled the effect of alloyed nitrogen. The electrochemical kinetics of pitting includes a range of such inhibition effects. Sulfate affects pit development in various ways, not all of them beneficial; it can actually lower the critical pitting temperature.

*Objectives:*

- Validate a mechanistic approach for inhibition of localized corrosion, previously used for stainless steel, for Ni-Cr-Mo alloy systems
- Examine the inhibition criteria for nitrate in particular, and consider slow stable propagation processes
- Investigate the effects of surface deposits that may facilitate propagation of corrosion and challenge the inhibition mechanism.

*Project Tasks:*

Task 1: Determine the differences, if any, between the response of simple Ni-base alloys and stainless steels to the presence of non-chloride anions - specifically nitrate. Determine the nitrate/chloride ratio required for successful inhibition as a function of the characteristic length associated with the corrosion site. Examine, test and update the 1986 Newman/Ajjawi suggestions as to the mechanism of the nitrate effect with these possible differences in mind.

Outputs: localized corrosion stability map as a function of equivalent diffusion length and nitrate concentration; qualitative theory covering both stainless steel and Ni base alloys.

Task 2: Using sensitive electrochemical measurements, determine whether the apparent arrest of corrosion sites in the presence of nitrate is really arrest or slow continuing propagation. Identify the black corrosion products produced as a result of such arrest, in stainless steels and Ni-base systems.

Outputs: definition of passivation in mixed-salt systems; definite upper limit on propagation rate for a range of conditions.

Task 3: For a range of model alloys that range from susceptible to nearly immune to localized corrosion (in particular conditions), measure and interpret any changes in propagation rate in the presence of nitrate; address whether these alloys 'repassivate' at different nitrate levels or at the same level but with different residual rates. Generate a rational modeling scheme for further study.

Outputs: valid extrapolation scheme from susceptible alloys to highly corrosion resistant alloys.

Task 4: Determine whether the presence of surface deposits with anion-selective properties can alter the assessment of propagation stability, specifically with respect to the effect of nitrate but also more generally.

Outputs: Consideration of alternative propagation criteria.

Several Ni-Cr-Mo alloys will be manufactured and drawn into thin wire (ideally 0.25 mm diameter). The experimental method is to establish stable propagation at constant potential, then inject nitrate into the bulk solution and follow the inhibition. If propagation remains stable, scan the potential in the positive direction and observe (or not) anodic passivation of the corrosion site. Using wider artificial pit electrodes, repassivation by nitrate, with (and, if possible, without) prior formation of an anodic chloride salt film will be followed for long periods under potentiostatic control. Conduct experiments on plate material as well as artificial pit cavities. The alloys studied will form a matrix systematically depleted in Mo and/or Cr compared with Alloy 22. Membranous or other ion-selective deposits will be formed on plate samples of the alloys used in Tasks 1 and 3. Candidates include simple metal hydroxides, mixed hydroxides, and minerals.

Propagation stability of localized corrosion will be determined at temperatures below the normal critical pitting temperature (CPT) and potentials below the normal pitting potential, as appropriate, with and without the co-presence of nitrate.

## *Metallurgical Effects on Localized Corrosion of Ni-Cr-Mo Alloys*

Gerald S. Frankel and Rudolph G. Buchheit; The Ohio State University

**PROJECT OBJECTIVES AND APPROACH:** This project will probe the metallurgical effects on the localized corrosion behavior of Ni-Cr-Mo alloys. The focus will be upon examination of alloy composition on localized corrosion behavior. The goal is to establish relationships for the trends in behavior from lower, more corrosion prone alloys to the higher, more corrosion resistant Ni-Cr-Mo alloys. The relationships will provide a basis or comparison and extrapolation. Also of interest is the effect of the concentration of major alloying elements. A considerable amount of data exists on "lower" alloys with less alloying element and more data can be easily generated. In contrast, experiments with the "higher" alloys with more alloying elements are difficult owing to their superior corrosion resistance.

The higher Ni-Cr-Mo alloys are so resistant to corrosion that it is difficult to generate localized corrosion damage in experiments. Extremely aggressive conditions (solution pH and concentration, temperature, and potential) are required. In contrast, a considerable amount of localized corrosion data exists on "lower" alloys and more data can be easily generated for these alloys. If fundamental understanding and behavior of the lower alloys is to be utilized to predict the behavior of the highly corrosion resistant alloys, then it is important to understand the relevance of such an extrapolation.

Task 1: Behavior of Prepared Alloys. Measurements will be performed on a range of specially prepared alloys containing a controlled variation of specific alloying elements, such as Cr, Mo, and W. The range of variation will span compositions from 3xx stainless steels to beyond the higher Ni-Cr-Mo alloys. The alloys will be prepared by electric arc melting of pure elemental stock material. These buttons will be homogenized prior to testing. They will be tested under conditions aggressive enough to generate localized corrosion in all of the samples. Measurements of breakdown and repassivation potentials will be performed as well as critical pitting and crevice temperatures. The variation in the measured properties with composition will be used to formulate a meaningful basis to develop extrapolations in other data. Artificial neural networks will be used as a tool to assess these relationships.

Task 2: Thin Film Pitting Studies. As part of the study of compositional effects, experiments will also be performed on thin metal films deposited onto inert substrates. Frankel and colleagues have developed a technique to study the growth of 2-D pits in thin film metal samples. Pits in thin film samples (on the order of hundreds of nm in thickness) quickly penetrate to the substrate and then grow in two dimensions with a fixed depth. The rate of pit growth is determined from the velocity of the 2-D pit wall as revealed by optically magnified images of the growing pit, and the pit polarization curve can be resolved by measuring the growth rate at various applied potentials. Unlike pits in bulk samples, which quickly become rather large, the pit depth is frozen in by the film thickness. Pits in thin films are analogs of very small pits in bulk samples, and by studying the behavior of pits in thin films with varying thickness; it is possible to determine the pit kinetics of

the very early stages of pit growth in bulk samples. The dissolution kinetics of very small pits is related to the susceptibility to localized corrosion initiation.

In this work, thin films will be deposited by a physical vapor deposition technique. Films with a range of composition will be produced by using alloy targets and by co-sputtering techniques. Sputter deposition targets will be fabricated from Alloy 22 and the range of comparison lesser alloys decided upon by the team. Controlled composition films will also be deposited to explore the effects of Cr, Mo, and W concentration. Environmental variables will include the temperature and chloride/oxyanion ratio. Crevice corrosion can also be studied with this technique by using a transparent crevice former such as a glass slide. The rate of dissolution within the crevice will be studied as a function of the position from the crevice mouth.

The results of these studies on thin metal films will be provided as input to the crevice corrosion models by providing the dissolution kinetics as a function of solution composition, pit depth and crevice position.

# *Combinatorial Chemistry Approaches for Alloy Composition and Corrosion Behavior*

Rudolph G. Buchheit and Gerald S. Frankel; The Ohio State University

**PROJECT OBJECTIVES AND APPROACH:** The objective of this task is to develop and apply combinatorial chemistry-type approaches to characterize the effect of Ni-Cr-Mo-W(Nb) alloy chemistry on the corrosion behavior in high temperature, multi-ionic species brines. In addition to the highly corrosion resistant Ni-Cr-Mo alloys, less corrosion resistant alloys are examined for comparison. The general approach is based on the use of a potentiostat capable of simultaneously measuring up to 100 independent channels of current on a segmented working electrode operated in an otherwise conventional three electrode configuration. Alloy composition will be varied systematically across specially prepared arrays comprised of millimeter to sub-millimeter diameter electrodes to develop relationships between alloy composition and electrochemical behavior in selected environments characteristic of crevices and thin electrolyte layers.

It is envisioned that this project will be conducted in two phases. The first phase will involve a broad survey of electrochemical behavior as a function of alloying element content. Cr, Mo, W(Nb) and possibly Fe will be varied in a way that represent the compositional variations in C grade Ni-base alloys. In some cases, it may be of interest to produce alloys that are leaner or richer in one or more alloying elements. The results of this study will compliment electrochemical characterization of commercial corrosion resistant alloys (CRAs) by filling gaps between these alloy composition windows. It will be possible to conduct interrupted exposure experiments to develop passive films on electrode elements to support passive film characterization tasks. Composition-electrochemical response data sets may be of utility for interpolative empirical modeling tasks.

The second phase will involve exploring in greater detail composition-environment combinations that help illuminate fundamental mechanisms of corrosion resistance and susceptibility that are suggested by survey results or by new understanding generated by other tasks in the project. Experiments targeted at resolving the behavior of certain alloying elements (e.g., Mo) as a function of environment chemistry will also be possible. It is also envisioned that this approach will be useful for experimental validation of certain types of model predictions.

Initial work involves a broad survey of electrochemical behavior as a function of alloying element content. Cr, Mo, W(Nb) and possibly Fe will be varied in a way that represent the compositional variations in commercial Cr-Ni-Mo and other Ni-base alloys. Initial work will focus on determining the suitability of Laser Engineered Net Shaping (LENS™) for array fabrication. This method uses a high powered focused laser, typically Nd:YAG, to melt metal and deposit or alloy powders. The process is intended for near net shape processing, fabrication of compositionally graded materials and rapid prototyping. Direct deposition of an electrode array of millimeter to sub-millimeter alloy "dots" with a range of compositions appears feasible. Deposit purity and inclusion-type defects that might affect electrochemical response are potentially an issue. LENS deposition equipment is available at OSU. The multi-array electrochemical methods will be extended to the higher temperatures and environmental ranges of interest in this program.

## *Prediction of the Time Evolution of Localized Corrosion Damage*
Digby D. Macdonald; Pennsylvania State University

**PROJECT OBJECTIVES AND APPROACH:** This project will continue previous studies on developing damage function analysis (DFA) as a means of predicting the evolution of localized corrosion damage. DFA is unique in damage prediction, in that it emphasizes determinism as the fundamental philosophy in predicting the nucleation, growth, and repassivation (death) of localized corrosion events. Here, the important feature of determinism is that solutions are constrained to being physically meaningful by natural laws, i.e. mechanistically based. The project will be carried out in four tightly coupled tasks.

Task 1: Development of Models for Predicting Prompt and Delayed Repassivation Kinetics. Currently available experimental data indicate that both the prompt repassivation of meta-stable pits and the delayed repassivation of stable pits arise from the same fundamental cause; failure of the system to maintain separation between the local anode and the local cathode, such that the required aggressive conditions cannot develop in the pit enclave. In the case of prompt repassivation, the great majority of the passivity breakdown events never achieve initially a sufficient separation of the local anode and the local cathode to be self-sustaining and the event dies to mark a meta-stable event. It is believed that a principal reason is the difficulty of the coupling current to penetrate through the oxide "cap" that exists over the pit nucleus, on the one hand, and the tendency of the pit enclave to "wash out" in the absence of a cap, on the other. In any event, prompt repassivation is a mass transfer/charge transfer issue and the development of a model will focus on these phenomena. The reasons for delayed repassivation are discussed at some length above. Briefly, all of the mechanisms for delayed repassivation, except "death by misadventure", are amenable to deterministic modeling through the "coupled environment" concept, which states that the internal and external environments are strongly coupled by charge conservation. Thus, a model for estimating the delayed repassivation constant will be sought within the framework of the coupled environment concept together with Avrami's theorem for the overlap of the hemispheres of influence (HOIs).

Task 2: Development of Survival Probability Model. Once the theory for prompt repassivation has been developed in Task 1, it will be used to estimate the survival probability as the ratio of the number of pit nuclei that transition to stable pits divided by the total number of passivity breakdown events. The survival probability will be calculated as function of

[Cl⁻], pH, potential, and temperature, these being the independent variables of principal interest.

Task 3: Inhibition of Passivity Breakdown by Oxyanions. This task will concentrate on further developing the competitive adsorption concept within the Point Defect Model for accounting for the inhibition of passivity breakdown by oxyanions, such as nitrate. Work to date on this theory predicts that the critical voltage for passivity breakdown of a metal in mixed $Cl^- + XO_x^{y-}$ electrolyte systems decreases linearly with $\log([Cl-]/[XO_x^{y-}])$, in agreement with experiments, at least for stainless steels. The impact of $[XO_x^{y-}]$ on the critically important induction time has not yet been established theoretically, but it is expected that increasing $[XO_x^{y-}]$ will lengthen the induction time for passivity breakdown.

Task 4: Generalization of DFA to Time Varying Environmental Conditions. The final task will involve generalizing DFA to time-varying environmental conditions, as are expected to occur as the proposed repository evolves along the corrosion evolutionary path. The approach will be to modify the fundamental condition for passivity breakdown. This depends upon the flux of cation vacancies across the barrier layer from the film/solution interface to the metal/film interface, the rate of cation vacancy annihilation at the metal/film interface, the critical, areal concentration of condensed cation vacancies at the same location, and the time of dissolution of the oxide cap over the breakdown site until rupture. The modified treatment recognizes that fluxes will be time-dependent under proposed repository evolutionary conditions. Definition of these time-dependencies and the subsequent derivation of the breakdown voltage and induction time, followed by insertion into DFA, are the principal goals of this task.

The basic structure of DFA is well-developed and is currently being used to predict the evolution of localized corrosion damage in a variety of systems, including high-level nuclear waste repositories. Accordingly, the project seeks to modify the current theory to render it more applicable to predicting the accumulation of localized corrosion damage under conditions that are directly applicable to the corrosion damage evolution by localized corrosion.

## *Data Mining of Experimental Localized Corrosion Data*

Mirna Urquidi-Macdonald; Penn State University

**PROJECT OBJECTIVES AND APPROACH:** This project involves the mining of existing experimental databases on metal-alloys. Data mining of existing experimental databases on metal-alloys will be aimed at establishing the conditions under which certain parameter sets (i.e., pH, temperature, time of exposure, electrolyte composition, metal composition, metallographic characteristics, etc) greatly impact the alloy's localized resistance characteristics. The data mining results allow parameters under specific experimental conditions to be categorized and prioritized. It will also add to understanding, along with the information gained through theoretical models, the synergetic effects of those variables on the electrochemical potentials and corrosion rates (e.g., pitting, crack, and crevice growth rates).

Corrosion data analysis can be difficult. Most of the parameters that play a role in the alloy's potential response are difficult to directly measure or quantify. Because the experimental work domain includes parameters hard to quantify and evaluate, producing data and fitting polynomials to that data in order to extrapolate alloy behaviors over extended ranges of time may not be

suitable. This project will use data mining techniques, or soft computing techniques such as cluster analysis, neural networks, wavelet and fuzzy representation, on the available data and aim to establish relationships, clustering, and categorizations of the parameters involved. Data mining is an assortment of tools available to quantify, to the best of our knowledge, the response that a given alloy sample will have under a given imposed environment and the effect that the environmental changes have on the alloy sample. These tools require controlled experimentation in chemically well-defined environments.

Task 1: Database creation. This task will include visiting laboratories that are producing the data and witnessing the methodologies used and the problems overcome during the data production. The data will be formatted and formed into different tables containing different types of data. The data will be transformed into different types of representations (such as FFT, Wavelets, etc.). This step will be time consuming, but is very important because the degree of learning from a database strongly depends on the way the data is represented and the type of analysis applied.

Task 2: Database mining. The overall data analysis approach will include the following steps:

- Data reprocessing, that will include data filtering (for bias information), data transformation (to accentuate certain data features) and data normalization (to give all variables the same order of importance)

- Filtering based on knowledge, (i.e., based on experimental tests)

- Representing the data in different ways to look for different types of clusters. Correlation Plot, hierarchical unsupervised neural networks growing trees, and Newick trees are to be used

- Cluster hierarchy and cluster analysis using Self Organizing Maps (SOM) and SOM trees

- Statistical analysis using t-test, z-test, analysis of variance (ANOVA), and survival analysis using Cox and Fisher's exact models

- Data mining techniques to compare two lists of variables and find terms differentially represented between them by means of p-values and other statistical techniques.

Task 3: Feedback and Interaction. The results will be shared and discussed, with all the data and model providers, and the feedback will be incorporated into the theoretical models. Experimental results from other CorrCoOp projects will be used to test the data mining predictions.

# Evolution of Environment on Metal Surfaces

The corrosion performance of a metal is determined by the inherent corrosion resistance of the metal and the corrosivity of the environment. The amount, distribution and chemical composition of the moisture on waste packages are important. The objective is to determine the properties of thin layers of moisture, moist particulates and deposits that will affect the corrosion performance of metals. Advanced analytical and computational methods for the evolution of the environment on metal surfaces are developed. Scientific understanding is enhanced for moisture formation, chemistry and evolution with time and for the properties of thin layers of particulates and deposits on metal surfaces.

> **Thrust Objective:** *Develop and demonstrate evolution of environment (moisture) on waste package surface. Current model addresses dust/moisture and corrosion, but in a limited way based on limited understanding. This work is designed to enhance that understanding.*

Key issues for corrosion behavior and long-term performance are determination of the presence of moisture on metal surfaces, the corrosive properties of the moisture and the corrosion resistance of materials in these environments. Thin layers of electrolyte, particulates and deposits are the conditions of interest for the analysis of corrosion of waste packages. A special feature of the proposed Yucca Mountain Repository is the extremely long time frame of interest. Thus, the time evolution of the environment in contact with waste package surfaces and the time evolution of corrosion damage that may result are of primary interest in the determination of expected performance.

In the proposed repository, moisture can form on the metal surfaces by deliquescence and condensation processes as the waste packages cool from high temperatures after the heat-up period. Another source of moisture on the metal surfaces is from drips or seepage from the rock formation onto waste packages after the thermal barrier period. A thermal barrier prevents drips and seepage into the drifts as long as the drift wall is hotter than the boiling point of water.

It is well accepted that dry metals, without the presence of an aqueous phase, do not corrode at an appreciable rate in the proposed repository environment. Furthermore, full immersion in waters will not occur under any realistic scenario. Corrosion in thin layers of electrolyte, particulate and deposits are the conditions of interest. These thin layers of moisture are a sufficient aqueous environment to support electrochemical dissolution. Anodes, cathodes and the electrochemical corrosion cell can operate in a thin moisture layer.

The approach is to meet the objective through a coordinated set of projects. A team of leading scientists/engineers from major universities (Corrosion CoOp) and national laboratories are working together within the OCRWM/OST&I Corrosion Targeted Thrust. This group brings specialized expertise, methods and facilities in corrosion science, materials science, electrochemistry and geochemistry. Individual projects in this technical thrust are highlighted below.

**Technical Thrust: Evolution of environment on metal surfaces**

Evolution of Solution Layer Chemistry in the Presence of Particulate
    Robert G. Kelly; University of Virginia

Modeling and Measurement of Current Distribution in Particulate and Deposited Layers
    Uziel Landau and Joe H. Payer; Case Western Reserve University

Microelectronic and MEMS Devices for Combinatorial Methods for Corrosion Evaluations
    C.C. Liu and Joe H. Payer; Case Western Reserve University

Optical Probes and Sensors for Concentration Distributions in Thin Films on Reactive Surfaces
    William H. Smyrl; University of Minnesota

(Multi-Investigator Project led by ORNL)

High-Temperature, Multi-Species Solution Properties and Behavior
    Don Palmer; Oak Ridge National Laboratory with Lawrence N. Anovitz, Pascale
    Bénézeth, David R. Cole, Miroslaw S. Gruszkiewicz, Lee R. Riciputi, David J.
    Wesolowski, ORNL; George Engelhardt, OLI Systems, Inc.; Digby D. Macdonald,
    Pennsylvania State University

# Corrosion in Thin Layers of Particulate
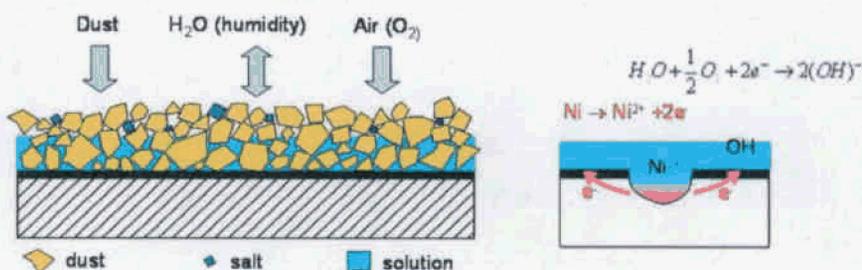


- Dust deposited
- Degree of wetness
- Soluble salts
- Gas composition and property, T, RH
- Particulate layer properties, such as conductivity, temperature, pH, degree of wetness etc.
- Localized environment on the surface
- Anode: $Ni \rightarrow Ni^{2+} + 2e^-$
- Cathode: $H_2O + 1/2 O_2 + 2e^- \rightarrow 2OH^-$

## Evolution of Solution Layer Chemistry in the Presence of Particulate

Robert G. Kelly; University of Virginia

**PROJECT OBJECTIVES AND APPROACH:** A combination of experimental and computational work is focused on the controlling variables and enhancing the basis for the prediction of localized corrosion of metals in thin layers of particulate. The chemistry, electrochemistry, and transport properties of the thin electrolyte on the surface are determinants of the corrosion behavior. Understanding the atmospheric electrochemistry requires a determination of the extent to which cathodic and anodic sites under thin films and covered by deposits communicate with one another.

There has been some study of localized corrosion in thin electrolytes. The environmental conditions of atmospheric corrosion are similar to crevice corrosion in the sense that there are geometric restrictions to the mass transport along the surface as well as homogeneous chemical reactions taking place that can alter the electrochemical kinetics. The main differences are that there is the delivery of additional cathodic reactants (oxygen) occurring across the entire surface, and atmospheric systems are by their nature under open circuit conditions, i.e., the surface is not externally polarized.

Task 1: Design and construction of experimental setups for:

- establishing dependence of thin solution chemistry on gaseous environment, and

- current and potential distributions.

There is an opportunity to enhance models of the environment, and this requires direct measurements of accessible parameters and their dependencies. A multi-pronged analytical approach will be used that involves the quartz crystal microbalance, capillary electrophoresis, and microfabricated conductivity sensors. Of particular interest are the effects of particulates and deposits on the water layer thickness and properties. A recent project at UVA resulted in the development of microfabricated solution conductivity sensors, and these will be used to determine the conductivity of the electrolyte layers as a function of the experimental variables.

Task 2: Measurement of steady state solution layer chemistry as a function of gas environment above surface, temperature, relative humidity, and dust composition. The composition of the electrolyte present at the surface controls the electrochemical kinetics at the metal surface. The most important aspect of the composition is the types and concentrations of ionic species. Understanding the dependence of this composition on the important variables will provide important boundary condition information for both measuring and modeling of corrosion processes. Capillary electrophoresis will be used for the analysis of ionic species. A microbalance will be used to measure the amount of absorbed water. Planar conductivity sensors fabricated using methods developed for microelectronics manufacture will be used to measure the solution layers formed in the presence and absence of particulate.

Task 3: Modeling of steady state solution layer chemistry as a function of gas environment above surface, temperature, relative humidity, and dust composition. One of the issues in life prediction for corrosion damage is the need to develop models that link different processes. These processes occur over different length and time scales, making

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computational linkages difficult. There is an opportunity to develop improved means of linking the chemical environment to the conditions on the metal surface. The work of Graedel on developing a multi-regime model of atmospheric corrosion chemistry (*GILDES*) will serve as a framework for this project. The *GILDES* (*G*as-*I*nterface-*L*iquid-*D*eposition-*E*lectrodic-*S*olid) model describes the six regions and their interactions with mathematical formulations based on a combination of fundamental principles and parameterization of data. The GILDES framework is adapted to the relevant conditions of localized corrosion of passive metals with realistic electrochemical kinetics. The model is used to determine the steady-state solution layer chemistry as a function of gas environment above surface, temperature, relative humidity, and dust composition. The experimental data in Task 2 will be used to validate the model. Once validated, the model will be exercised to expand the domain of variable space over which plausible extremes of environment can be determined.

Task 4:  Simulation of current and potential distributions in the presence of an active corrosion site (crevice, pit, stress-corrosion crack) as a function of thin layer thickness and current demand of active site. The mass transport conditions for atmospheric conditions are similar to those for crevice corrosion. Thus, the extension of models of crevice chemistry and electrochemistry represents an efficient approach to modeling effort. The UVA team recently adapted their crevice corrosion model, CREVICER, to atmospheric corrosion conditions. The code can handle polarization curves that reflect the pitting-limited passivity exhibited by most corrosion-resistant alloys in bulk environments, as well local-chemistry-dependent active behavior known to occur within localized corrosion sites. The code will be extended to consider the restricted mass transport conditions in a thin film or wet deposit that is coupled to an active corrosion site. It will also be linked to the corrosion chemistry model described in Task 3. This modeling will provide an enhanced basis to determine both the maximum rate of localized corrosion and the conditions that must be maintained in order for propagation of the localized corrosion to become a structural integrity issue.


# *Modeling and Measurement of Current Distribution in Particulate and Deposited Layers*

Uziel Landau and Joe H. Payer; Case Western Reserve University

**PROJECT OBJECTIVES AND APPROACH:** The objective is to model and measure the current flow patterns and distribution in thin layers of moisture and layers of moist particulates and deposits on metal surfaces. Of particular interest is the flow of current representative of corrosion scenarios at the metal surface: pitting, crevice corrosion, stress corrosion cracking, and galvanic action. Layer thicknesses range from monolayer coverage to thicker particulate layers. Results provide important inputs to the determination of the extent of cathodic stifling of corrosion processes.

The model will examine geometric effects, saturated and unsaturated particulate layers, chemical composition of moisture and particulates, temperature, and relative humidity. A series of experiments will complement the modeling effort. The model and experiments are closely coupled to determine current flow and potential distribution. The experiments provide a basis for model validation.

Task 1: Design model framework for parameters of interest and for interfacing with the experimental study. Models for corrosion in thin and thick layers of particulates on metal substrates of varying compositions and passivation states will be developed. The behavior of passive metals and localized corrosion are considered. Analytical models will elucidate the relationships between the critical parameters in representative model geometries. Numerical simulations will model more detailed geometries with realistically complex chemical systems. This task will prepare the framework for the analysis and outline the investigated parameters and the general approach. The investigated parameters include:

a. Substrate related parameters -

- *Materials*: Passive alloys constitute the main focus. Experimental studies will establish the essential parameters for the analytical and the numerical modeling. The latter include bulk metal conductivity, and surface and film resistivity for lateral and transverse current passage. Polarization curves will provide the kinetic parameters.

- *Geometry*: Features (e.g., pits, crevices, patches) with non-planar configuration will give rise to higher electrical fields (proportional to the radius of curvature) and affect mass transport. Those may lead to pH variations. Concentration variations will also give rise to concentration cells with corresponding potentials. Numerical models capable of modeling moving boundaries will simulate the transient surface behavior, i.e., will simulate the pit formation and the feature curvature variations.

- *Passive films*: Continuous and broken passive films on the metal surfacetop of the substrate, of different thickness, composition, and resistivity will be considered.

b. Electrolyte related parameters -

- *Liquid layer*: Different liquid layers covering the substrate will be considered. Thicknesses ranging from sub-monolayer to a few millimeters will be analyzed. Different ionic compositions and concentrations, pH, ionic strength, and conductivity will be considered. Continuous layers as well as broken films, lenses, and droplets of various sizes will be considered.

- *Chemical composition*: The effect of different ions including silicates, carbonates, sulfates and chlorides as well as a number of cations (alkali, alkaline earth and metals) will be studied. The pH effects and differential aeration are expected to be among the major factors driving corrosion processes and will be analyzed.

- *Particulates*: It is expected that the substrate will become fully or partially covered by particulate matter. Particles of different size, shape, and wettability will be considered. These will affect mainly the conductivity of the medium, however, they may also modify the chemical composition of the reactants. Depending on their water absorption and retention capability and their wetting (hydrophobicity/hydrophilicity and surface tension), the particulates are likely to affect the moisture content and distribution.

Numerical modeling methods will be applied to analyze electrochemical systems. Cell-Design is a software that can be applied to either the macroscopic scale where the phenomena are driven by the electric field (and the electrode reactions) or to the microscale where mass transport and diffusion effects are dominant.

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Task 2:  Models for idealized configurations and baseline properties. Simplified geometries that are amenable to analytical solutions or to relatively simple numerical solutions are considered here. Initially, the project will model a linear configuration to analyze the effect of the distance between an anodic site and a cathodic region. The one-dimensional simplified model discussed above will be extended to more complex model systems for which the fields and current distribution are still analytically tractable. Additional, more complex extensions (that most likely will have to be modeled numerically) include time dependent conductivity and transport numbers.

Task 3:  Model for macro-cell conditions. Corrosion phenomena on the macro scale (e.g., ~1 cm) will be analyzed using classical modeling methods with the special proviso that concentration variations extend much farther than in conventional simulations. Of particular importance to this scale is the modeling of thicker electrolyte layers. Particulate material (rock, corrosion products, deposited minerals, etc), degrees of porosity, wetting, and macroscopic conductivity will be considered. On this scale the project will apply numerical models to explore the effects of different configurations including different passivating film properties and defects, electrolyte film thickness and particulate layer thickness. While on the micro-scale model (see below) the project will consider mostly small pits and narrow crevices, we will analyze on the macro-scale larger patches of anodic regions.

Task 4:  Model for micro-cell conditions. This project will first develop a one-dimensional model that will be applicable to very thin layers. The work will address the surface diffusion of the species (that is expected to be different than the bulk diffusion), and attempt to solve the transport equations (Nernst-Planck- considering both diffusion and migration) for multiple species, starting with binary and well-supported systems. The objective is to account both for an impermeable film with localized defects, and for a resistive film with limited electronic conductance. A major extension will be to introduce the consideration of a partially passive (resistive) film along the surface. Three types of film will be considered: impermeable, homogenous film with constant or variable (with position and time) permeability, and a film with distributed holes.

## *Microelectronic and MEMS Devices for Combinatorial Methods for Corrosion Evaluations*

C.C. Liu and Joe H. Payer; Case Western Reserve University

**PROJECT OBJECTIVES AND APPROACH:** The objective of this task is to develop and apply combinatorial chemistry-type approaches to characterize the effect of multi-species environments on the corrosion behavior of Ni-Cr-Mo alloys. The focus is on the high temperature, chloride containing brines. In addition to the highly corrosion resistant Ni-Cr-Mo alloys, less corrosion resistant alloys are examined for comparison. The general approach is based on the use of a potentiostat capable of simultaneously measuring up to 100 independent channels of current on an array of electrochemical cells in a three electrode configuration. In these tests, a compositional range of environments are examined for a given alloy using a statistically designed matrix to favor determination of single and coupled environmental effects. The benefits of this approach are high efficiency of data generation and the generation of a statistically significant database for environmental effects on corrosion behavior.

A further aspect of this project is the development and application of sensors to measure important environmental parameters. These include temperature, pH, oxidizing potential, and chemical species. Data from these sensors will supplement the information from electrochemical tests. The sensors will be used individually and in multi-sensor arrays.

Task 1: Combinatorial Electrochemical Test System. An initial task will involve development of fixtures, test cells and environmental chambers for controlled high temperature and solution composition conditions. Another initial task is to apply conventional electrochemical methods for the measurement of resistance to localized corrosion to the combinatorial electrochemical system. This early work will focus on the measurement of localized corrosion behavior of more corrosion prone alloys, e.g., austenitic stainless steel, than the Ni-Cr-Mo alloys. Susceptibility will be measured as a function of temperature and chloride concentration in order to compare the results to those from conventional electrochemical tests.

Task 2: Sensors for Environmental Parameters: Individual sensors for pH, oxidizing potential and oxygen concentration will be developed and demonstrated for use with the combinatorial test cells. Emphasis is upon sensors made using microelectronic fabrication methods and amenable to incorporation using multi-sensor arrays.

## Optical Probes and Sensors for Concentration Distributions in Thin Films on Reactive Surfaces

William H. Smyrl; University of Minnesota

**PROJECT OBJECTIVES AND APPROACH:** The objective of this work is to reveal the reaction distributions on heterogeneous, reactive metal surfaces. Previous work in our laboratory has revealed the current/potential distributions on galvanically coupled surfaces, including those under thin films of electrolytes. More recently, we have used fluorescent dyes to explore the chemistry and distribution of reaction products on and near reactive inclusions. As part of that research, we have demonstrated that optical fiber spectroscopy and functional near field optical scanning microscopy (f-NSOM)) can be used to obtain enhanced chemical characterization with high resolution. We will emphasize fluorescent probe techniques for mapping and chemical characterization in the laboratory and in the field.

Fluorescence techniques are powerful tools to measure physico-chemical conditions (pH, gas concentration) and analyte species *In Situ*. We have adapted some of these methods to monitor localized corrosion on aluminum alloys with a sub-micrometric spatial resolution. Our goal in the present study is to design fluorescent multi-probe sensors capable of monitoring oxygen partial pressure, pH, temperature, and specific metal ions at and near reactive (corroding) surface.

The present report describes the progress made in developing a poly (dimethylsiloxane) (PDMS) membrane doped with the oxygen sensitive fluorescent dye dichlorotris (1,10phenanthroline) ruthenium (II) hydrate, abbreviated as *Ru (phen)*. There are numerous descriptions in the literature of fluorescent-based oxygen sensing devices. These devices work well only in a laboratory-controlled environment. Very few of them have seen a commercial application and none have been designed for corrosion monitoring. Our efforts have been concentrated in developing a highly fluorescent sol-gel doped PDMS film with the largest possible dynamic range and good mechanical properties. The dynamic range is the value $[I(N_2) - I(O_2)]/ I(N_2)$, where $I(N_2)$ and $I(O_2)$ are the fluorescence intensities measured in 100% $N_2$ and 100% $O_2$ respectively. The highest dynamic range was observed in the Sol-Gel only configuration. A loss of dynamic range was observed when the sol-gel is embedded in the PDMS film. This led to the development of two doping procedures for PDMS that had some success.

## High-Temperature, Multi-Species Solution Properties and Behavior

Don Palmer; Oak Ridge National Laboratory (ORNL) with Lawrence N. Anovitz, Pascale Bénézeth, David R. Cole, Miroslaw S. Gruszkiewicz, Lee R. Riciputi, David J. Wesolowski, ORNL; George Engelhardt, OLI Systems, Inc. (OLI); Digby D. Macdonald, Pennsylvania State University

**PROJECT OBJECTIVES AND APPROACH:** The objective of this multi-investigator project is to develop an enhanced scientific understanding of the behavior of high-temperature, multi-species solutions with reference to the evolution of the environment on metal surfaces and its affect on localized corrosion processes. The approach is to take advantage of unique and independent experimental techniques developed at ORNL to quantify the solid/liquid/vapor interactions as a function of temperature, solution composition, prevailing humidity and time. These results will also be used in a chemical modeling subtask being conducted by OLI to enhance the understanding of the corrosion evolutionary path of a system.

The experimental component at ORNL will concentrate on the solution chemistry through an integrated approach that will involve a number of unique facilities at ORNL. The composition of liquid films in contact with air, and/or dust particulates, and/or alloy coupons, as well as those that develop during crevice corrosion, will be measured directly over a range of conditions. In separate experiments the thermodynamics of the partitioning of acids, mainly $HCl$ and $HNO_3$, between the liquid and vapor phases will be determined for a series of solution compositions. Other techniques will be applied to monitor the transport of material through the solution-oxide film-metal interface. The results of these experiments will be used by OLI under a subcontract to model the evolution of localized corrosion. The ORNL project team will also interface closely with other principal investigators who are involved in various aspects of corrosion and transport modeling.

Scoping Tasks: Three tasks are undertaken in scoping tasks for this project.

Task 1: Development of liquid films containing multi-ionic species electrolytes (Ca- MgK-Na - Cl-NO3-SO4) on inert surfaces. The "Isopiestic Apparatus" is simply a large silver-lined autoclave operating from 100 to 250 ($\pm$ 0.3)° C and housing a flat copper block on which 20 platinum cups reside. The cups can be weighed on an internal balance to determine the concentration of the solutions within the cups.

Task 2: Determination of the evolution of brine chemistry in equilibrium with a vapor phase. The first experiment of this nature will be carried out in the "Volatility Apparatus". A solution containing calcium, magnesium, sodium, potassium, chloride, and nitrate will be confined in a sealed, pressure-balanced platinum liner within an autoclave and equilibrated with the co-existing vapor phase initially at 140° C.

Task 3: Determination of solution pH of highly saline brines. The hydrogen-electrode concentration cell (HECC) will be used to measure the *in situ* pH of highly saline brines over the temperature range 60 to 200° C.

Experimental Tasks (ORNL)

Task 1: Experiments with isopiestic vessel with tuff particulate and alloy coupons present.

Task 2: Experiments with the volatility apparatus with tuff particulate and alloy coupons present.

Task 3: Experiments with the HECC containing tuff particulates and alloys.

Task 4: Experiments with plug flow reactors containing Alloy C-22 with direct continuous measurement of pH, corrosion potential, and concentrations of metals released.

Task 5: Measurements in small autoclaves of concentrated solutions with tuff particulates and alloy coupons present.

Task 6: Secondary Ion Mass Spectaumeter (SIMS) and other measurements of liquid/oxide/bulk metal interfacial processes.

## Modeling Tasks (OLI)

Task 1: Qualifying OLI Software for the ORNL Task. The pre-existing OLI software for predicting speciation, vapor-liquid equilibria, activity coefficients and solubility in multi-component solutions will be subjected to independent review.

Task 2: Preliminary Estimation of Physical Values that will be Measured Experimentally at ORNL. The existing OLI code will be used for preliminary estimation of the phase equilibria and the solution pH of highly saline brines containing the cations $Na^+$, $Mg^{2+}$, $Ca^{2+}$ and $K^+$, and the anions $Cl^-$, $SO_4^{2-}$, $F^-$ and $NO_3^-$ including the effect of influx of metal ions and $CO_2$ over a wide range of concentrations and temperatures.

Task 3: Define the Corrosion Evolutionary Path (CEP) for conditions where the environment changes over time. This involves the generalization of the Point Defect Model (PDM) for the case when external conditions change, since the current version of the PDM describes pit nucleation only for the case when the external conditions do not depend on time. Develop an advanced general corrosion model that will permit calculation of the corrosion potential, corrosion rate, and integrated corrosion damage (metal loss) at the service life of the system.

Advanced computational and analytical methods enhance the analysis of corrosion performance, through determination of the amount, distribution and chemical composition of the moisture on waste packages.

# APPENDIX-Biosketches of Principal Investigators

**Joe H. Payer, Ph.D.** – Dr. Payer is a professor in the Materials Science and Engineering Department at Case Western Reserve University. He is an internationally recognized expert in corrosion science and engineering. Dr. Payer has expertise in materials performance and reliability, corrosion, and electrochemistry. His research interests are corrosion, electrochemistry, adhesion, hydrogen effects on materials, integrity/reliability, life prediction, life cycle costs, surface treatments, protective coatings, failure analysis, materials selection, cathodic protection, and sensors and monitoring devices. Dr. Payer's honors include the Wittke Award for Distinguished Undergraduate Teaching, the ASTM Sam Tour Award for Distinguished Contribution to Research, Development and Evaluation of Corrosion Testing Methods, and the Edward C. Greco Award. Dr. Payer was also recognized in 2004 as a Distinguished Alumnus of The Ohio State University.

**David W. Shoesmith, Ph.D.** – Dr. Shoesmith is a professor of Nuclear Fuel Disposal Chemistry at the University of Western Ontario. He is also the NSERC/Ontario Power Generation Industrial Chair. Dr. Shoesmith's research interests include electrochemistry and corrosion science, environmental systems modeling, thin films and materials reactivity, and nuclear waste storage and disposal. Dr. Shoesmith has been honored with the Lash Miller Award for Research, the AECL Discovery Award, the Canadian Chemical Society Outstanding Chemist Award, and the Cohen Award. Dr. Shoesmith has refereed 114 journals and conference proceedings. He has 17 reviews and book chapters to his credit and has written over 100 scientific and technical reports.

**Don Gervasio, Ph.D.** – Dr. Gervasio is an associate research professor at Arizona State University. His background as an inorganic chemist emphasizes the synthesis and characterization of biomimetic macrocyclic coordination compounds and binuclear compounds. The majority of his professional experience has involved electrochemical research and development of fuel cells with some experience in catalysis, sensors, and corrosion. His work with fuel cells has involved system and component developments. Dr Gervasio has authored numerous peer-reviewed publications and has 5 U.S. patents.

**Rudolph G. Buchheit, Ph.D.** – Dr Buchheit is a professor in the Department of Materials Science and Engineering at The Ohio State University. His primary research interests are metallurgical factors in localized corrosion and environment assisted cracking phenomena focusing on Al alloys, environmentally acceptable and novel corrosion inhibition, novel methods for corrosion sensing, deterministic factors in pit initiation, and the use of empirical modeling methods for corrosion prediction. Dr. Buchheit has been the recipient of the NACE H.H. Uhlig Educator Award, the Morris Cohen Award, the Lumley Research Award, and the DOE Outstanding Accomplishment Award. Dr. Buchheit has 5 patents and has co-authored over 50 technical publications.

**Gerald S. Frankel, Ph.D.** – Dr. Frankel is a professor in the Materials Science and Engineering Department and director of the Fontana Corrosion Center at The Ohio State University. Dr. Frankel's current research interests are in localized corrosion focusing on pitting, intergranular, exfoliation corrosion, corrosion inhibition of Al alloys, AFM and Scanning Kelvin Probe Force Microscopy welding of SS with Cr-free consumables, NDE of corrosion, and hydrogen embrittlement of oxide dispersion strengthened Ni-based superalloy. He has received the H.H. Uhlig Young Educator Award, the Alexander von Humboldt Foundation Research Award, and numerous awards from The Ohio State University. Dr. Frankel has over 140 publications to his credit.

**Roger C. Newman, Ph.D.** – Dr. Newman is a professor at the University of Toronto. He also serves as the NSERC Senior Industrial Research Chair in Nuclear Engineering. His current research interests include stress corrosion cracking of metals, alloying effects in electrochemical dissolution and passivation, thin surface films and nanoscale electrochemical processes, corrosion engineering, aspects of polymers, composites, sensors, and molecular modification of oxides. Dr. Newman's awards and honors include the U.R. Evans Award, the W.R. Whitney Award and the Helmuth Fischer Medal of DECHEMA. Dr. Newman has authored some 120 journal publications.

**Thomas M. Devine, Ph.D.** – Dr. Devine is a professor in the Department of Materials Science and Engineering at the University of California, Berkeley. His current research interests include the use of surface enhanced Raman spectroscopy to investigate in-situ the surface films formed on stainless steels and nickel-base alloys, development of a thin film sensor for detecting initiation of stress corrosion cracking, and mechanism of corrosion of magnetic hard disks covered with 1-5mm thick coatings of diamond-like carbon. Dr. Devine has been given the Exxon Education Foundation Award, the Jacob Wallenberg Research Award, the Alfred H. Geisler Memorial Award, the Marcus A. Grossman Young Author Award, and the Joseph Vilella Award. Dr. Devine has authored over 80 technical publications, has16 U.S. patents, and has authored many book chapters.

**Robert G. Kelly, Ph.D.** – Dr. Kelly works as a professor and co-director of the Center for Electrochemical Science and Engineering at the University of Virginia. He has recently become director of the Rodman Scholars program at the School of Engineering and Applied Science. His present work includes studies of the electrochemical and chemical conditions inside localized corrosion sites in various alloy systems, corrosion in aging aircraft, development of embeddable corrosion microinstruments, as well as the use of microfabrication methods to probe the fundamentals of localized corrosion. He has co-authored over 70 papers and one book. Dr. Kelly is a recipient of the A.B. Campbell Award, the H.H. Ulhig Award, and has won three teaching awards while at UVA

**Uziel Landau, Ph.D.** – Dr. Landau is a professor of Chemical Engineering at Case Western Reserve University. Dr. Landau's research interests include engineering and modeling of electrochemical systems, electrodeposition and electrodissolution, electrosynthesis of materials and alloys, batteries and fuel cells, and electrochemical separations. He is the developer of the first CAD program for simulating electrochemical cells. He established a company that further develops the software for this program in 1986. In 2000 while on sabbatical leave at Applied Materials in Santa-Clara, CA, Dr. Landau developed the prototype cell for their machine for copper metallization of semiconductor wafers. Dr. Landau has co-authored numerous technical publications.

**Donald A. Palmer, Ph.D.** – Dr. Palmer is a Senior Research Scientist at Oak Ridge National Laboratory. He is the co-editor of the Journal of Solution Chemistry. Dr. Palmer has been chairman of the Physical Chemistry Aqueous Solutions Working Group, member of the International Adviser Board of Sixth/Seventh International Symposia on Hydrothermal Reactions, and member of the NEA OECD update review group. Dr. Palmer has been given the Paul Cohen Memorial Award at the International Water Conference and the Technical Achievement Award at Oak Ridge National Laboratory. He has published over 200 articles in peer reviewed journals.

**David J. Wesolowski, Ph.D.** – Dr. Wesolowski is a Distinguished R&D Staff Scientist in the Chemical Sciences Division at Oak Ridge National Laboratory. He is an internationally-recognized expert in hydrothermal geochemistry and fluid-solid interactions, emphasizing experimental studies of aqueous acid-base and metal complexation reactions, mineral solubilities and surface adsorption properties, and the molecular-level structure and dynamics of fluid-solid interfaces. Dr. Wesolowski's honors include the Eugene P. Wigner Fellowship and numerous technical achievement awards at ORNL. He served as the Secretary of the Geochemical Society for six years and has been an Associate Editor of the Society's flagship journal *Geochimica et Cosmochimica Acta* for the last 12 years. He has authored over 100 scientific articles, book chapters and technical reports.

**Miroslaw Gruszkiewicz, Ph. D.** – Dr. Gruszkiewicz joined the High Temperature Aqueous Chemistry and Geochemistry Group at Oak Ridge National Laboratory in 1995. His work includes experimental research in the areas of chemistry and thermodynamics that are relevant to various issues of basic science, energy efficiency, and waste disposal. He has published over 20 papers in peer-reviewed journals and has given a number of conference talks on thermal, volumetric, transport, and surface and properties of electrolytes and non-electrolytes. He currently serves as the chairman of the Calorimetry Conference (Calcon).

**Chung Chiun Liu, Ph.D.** – Dr. Liu is a professor in the Chemical Engineering Department at Case Western Reserve University. He is the Wallace R. Persons Professor of Sensor Technology and Control as well as the director of the Electronics Design Center at Case. Dr. Liu has worked on a wide range of sensor and other microsystem research ventures. He has won honors at Case Western Reserve University and National Cheng-Kung University, Taiwan. Dr. Liu has 110 referred publications to his credit and 9 U.S. patents.

**William H. Smyrl, Ph.D.** – Dr. Smyrl is a professor in the Department of Chemical Engineering and Materials Science at the University of Minnesota. His research specialties are structure and stabilization of thin anodic oxide films, photoelectrochemistry of thin oxide films, atmospheric corrosion of thin film electronic and magnetic materials, modeling of heterogeneous reaction distributions in corrosion and electrochemical systems, visualization of reaction distributions on heterogeneous surfaces in catalytic and corrosion systems, intercalation materials, impedance analysis of intercalation processes, impedance analysis of corrosion processes, and corrosion science. Dr. Smyrl has received the H.H. Uhlig Award of the Electrochemical Society. He has edited 4 books and has over 190 publications to his credit.

**John R. Scully, Ph.D.** – Dr. Scully is a professor and co-director of the Center for Electrochemical Science and Engineering at the University of Virginia. He studies structure-property relationships governing time-dependent degradation of materials ranging from ferrous, nickel, aluminum, and titanium-base alloys, as well as amorphous metals and coated metals. His area of research involves electrochemical corrosion processes that cause various modes of corrosion including crevice corrosion. Dr. Scully has received the H.H. Uhlig Award, the A.B. Campbell Award, the T.P. Hoar Award, and the W. Blum Award among others. He has refereed many book chapters and journal articles. He is the author of numerous journal articles and has co-edited several books.

**Brian M. Ikeda, Ph.D.** – Dr. Ikeda is a research scientist at Atomic Energy of Canada Limited, Whiteshell Laboratories. His current projects include crevice corrosion of dissimilar passive metals, stress corrosion cracking of copper, corrosion of historical artifacts, crevice corrosion of titanium, hydrogen assisted cracking of titanium, hydrogen absorption by titanium, underdeposit corrosion of incoloy 800, crevice corrosion of nickel based alloys, effect of radiation on corrosion processes, delayed hydrogen cracking of zirconium fuel sheaths, stress corrosion cracking of zirconium fuel sheaths, and oxidation of zirconium in warm air. Dr. Ikeda has authored numerous technical reports. He is a member of the Electrochemical Society, ASM, and NACE.

**Digby D. Macdonald, Ph.D.** – Dr. Macdonald is the director of the Center for Electrochemical Science and Technology and a professor of materials science and engineering at Penn State University. Two of Dr. Macdonald's principal research areas are defining the mechanisms of the growth and breakdown of passive films on reactive metal surfaces in contact with aqueous environments, and the prediction of corrosion damage. Dr. Macdonald's honors include the U.R. Evans Award, the Wilson Teaching Award, the Wilson Research Award, the H.H. Uhlig Award, the Carl Wagner Memorial Award, the Willis Rodney Whitney Award, and the W.B. Lewis award. Dr. Macdonald is credited with 9 U.S. patents and over 600 publications.

**Mirna Urquidi-Macdonald, Ph.D.** – Dr. Urquidi-Macdonald is a tenured professor of Engineering Science and Mechanics at Penn State University. Her research interests include deterministic and soft computing modeling of materials systems including aging process, corrosion process, and batteries, lithium/water fuel cells, corrosion detection of underground pipelines, electrochemical potential of nuclear reactors, radiation fields, life prediction of primary and secondary batteries, and the use of neural network pattern recognition in the analysis of materials data. Dr. Urquidi-Macdonald's honors include the ALCOA Foundation Research Award, and the Stanford Research Institute Professional Excellence Award. She has published a total of 180 papers and 2 books.