

# **Research Opportunities in Corrosion Science for Long-Term Prediction of Materials Performance**

*A Report of the DOE Workshop on  
“Corrosion Issues of Relevance to the Yucca Mountain Waste Repository”*

sponsored by

United States Department of Energy

Division of Basic Energy Sciences

and

Division of Office of Civilian Radioactive Waste Management

Report prepared by: Workshop Co-Chairpersons

Joe H. Payer, Case Western Reserve University

John R. Scully, University of Virginia

Contributors and participants: John Beavers, CC Technologies; Jeff Braithwaite, Sandia National Laboratories; Rudy Buchheit, Ohio State University; Clive Clayton, State University of New York; Thomas M. Devine, Jr., University of California; Steve Dexter, University of Delaware; Joe Farmer, Lawrence Livermore National Lab.; Jerry Frankel, Ohio State University; Greg Gdowski, Lawrence Livermore National Lab.; Andrew Gewirth, University of Illinois; Woods Halley, University of Minnesota; Hugh Isaacs, Brookhaven National Laboratory; Russ Jones, Pacific Northwest National Lab.; Larry Kaufman, Massachusetts Inst. of Tech.; Rob Kelly, University of Virginia, Digby Macdonald, Pennsylvania State University; Nancy Missert, Sandia National Laboratories; Roger Newman, UMIST; Chris Orme, Lawrence Livermore National Lab.; Joe H. Payer, Case Western Reserve; Peter Scott, Framatome ANP; John R. Scully, University of Virginia; David Shoosmith, University of Western Ontario; David J. Wesolowski, Oak Ridge National Laboratory; Frank Wong, Lawrence Livermore National Lab.

Workshop held on July 29-30, 2003 in Bethesda, MD.

December, 2004

## TABLE OF CONTENTS

<b>COVER SHEET</b> .....	<b>1</b>
<b>TABLE OF CONTENTS</b> .....	<b>2</b>
<b>LEGAL NOTICE AND DISCLAIMER</b> .....	<b>3</b>
<b>EXECUTIVE SUMMARY</b> .....	<b>4</b>
<b>INTRODUCTION</b> .....	<b>7</b>
Benefit and Impact of Advances in Corrosion Science and Technology .....	7
<b>CORROSION PERSPECTIVES AT YUCCA MOUNTAIN</b> .....	<b>10</b>
Introduction.....	10
Natural System at Yucca Mountain .....	10
Repository Conditions Relevant to Waste Package Performance .....	11
Corrosion Performance of Highly Corrosion Resistant Materials .....	12
Time Evolution of Environment .....	14
Other Considerations .....	15
<b>SELECTED RESEARCH OPPORTUNITIES</b> .....	<b>28</b>
Life Prediction and Evolution of Corrosion Damage .....	28
Evolution of Corrosive Environments .....	29
Localized Corrosion.....	30
Passivity .....	31
Stress Corrosion Cracking .....	32
Materials Stability and Aging.....	33
Fabrication and Advanced Materials .....	33
Methods and Tools.....	34
<b>TOPIC AREA GOALS AND OPPORTUNITIES</b> .....	<b>35</b>
Predictive Modeling of Life and Materials Performance .....	36
Evolution of Corrosive Environments .....	45
Localized Corrosion.....	52
Passivity .....	64
Stress Corrosion Cracking .....	75
Effects on Aging and Phase Stability.....	81
Methods and Tools.....	85
<b>ACKNOWLEDGEMENTS</b> .....	<b>93</b>
<b>APPENDIX</b> .....	<b>93</b>
Appendix A-Corrosion Workshop Participants .....	94

## **LEGAL NOTICE AND DISCLAIMER**

This DOE Corrosion Workshop was a scientific workshop that is not intended to provide or serve as a work plan or directive to the U.S. Government or any of its agencies. This report represents the opinions and views of the workshop participants that met on 29 and 30 July, 2003 in Bethesda, MD, USA. The views and opinions expressed in the scientific report and the report to be published in an archival scientific journal will not necessarily state or reflect views, opinions or policy of the U.S. Government or any of its agencies. The fact that any particular issue or opportunity is not mentioned in this report does not necessarily imply that it is not important. As such, the report does not intend to be all-inclusive.

The Yucca Mountain Project believes that it has a sufficiently strong safety case to proceed with a License Application to the USNRC. However, advances in a number of areas may be feasible which, if realized, could help the Project either through better understanding of the long-term performance of the waste packages, or through better performance, or perhaps through cost savings that do not compromise performance.

## EXECUTIVE SUMMARY

The report summarizes the findings of a U.S. Department of Energy workshop on “Corrosion Issues of Relevance to the Yucca Mountain Waste Repository”. The workshop held on July 29-30, 2003 in Bethesda, MD and was co-sponsored by the Office of Basic Energy Sciences and Office of Civilian Radioactive Waste Management. The workshop focus was corrosion science relevant to long-term prediction of materials performance in hostile environments and with special focus on relevance to the permanent disposal of nuclear waste at the Yucca Mountain Repository. The culmination of the workshop is this report that identifies both generic and Yucca-Mountain-Project-specific research opportunities in basic and applied topic areas. The research opportunities would be realized well after the U.S. Nuclear Regulatory Commission’s initial construction-authorization licensing process. At the workshop, twenty-three invited scientists deliberated on basic and applied science opportunities in corrosion science relevant to long-term prediction of damage accumulation by corrosive processes that affect materials performance.

### **Benefit and Impact of Advances in Corrosion Science and Technology**

In 1999 the U.S. Congress mandated the determination of corrosion costs, and a breakthrough 2-year study, “Corrosion Costs and Preventive Strategies in the United States”, was issued in 2002. The study determined that the total annual estimated direct cost of corrosion in the U.S. is a staggering \$276 billion—approximately 3.1 percent of the nation’s Gross Domestic Product (GDP). The total costs (direct and indirect effects) to society can be twice that or greater.

The nation’s infrastructure is essential to the quality of life, industrial productivity, international competitiveness, and security. Corrosion is a primary cause of the degradation and a principal threat to the nation’s infrastructure. The infrastructure replacement cost is a major driver on the economic impact of corrosion and can still be greater if corrosion preventive strategies are not properly employed. The opportunities for savings by improved corrosion control are significant in every industrial and government sector.

### **Opportunities in Corrosion Science for Long-Term Prediction of Materials Performance**

Scientific advances for life prediction and performance assessment can result in an increase in reliability and safety, reduction in costs, and conservation of materials and energy. The prediction of long-term performance for corrosion is the most important and challenging matter for corrosion science and engineering. The determination of current status and future performance as a function of materials, design and service conditions are important to guide rationale, reliable and cost effective decisions by policy-makers, managers and engineers.

The long-term corrosion performance of waste packages at Yucca Mountain Repository provides a crucial application and a special challenge due to the exceptionally long times (10,000 years and beyond) required. Several categories of research opportunities were identified in this workshop:

- Opportunities to advance corrosion science as applied to highly corrosion resistant alloys, e.g. Ni-Cr-Mo-W alloys and titanium alloys. This is accomplished through the development of new theories tailored to these alloys and through the extension of corrosion theories developed for Fe-based materials.
- Opportunities to extend corrosion science for thin film of electrolytes formed by deliquescence and condensation processes. For waste package performance, these conditions pertain for episodic dripping and electrolytes formed by combination of ionic species, water and dusty-particulate layers. This entails extensions and novel advances to the treatments of corrosion behavior in bulk electrolytes and under fully immersed conditions.

- Opportunities for models for localized corrosion that include propagation, arrest and stifling of corrosion phenomena. Corrosion science for corrosion initiation processes is rich and substantial; however, the treatments of propagation, stifling and arrest phenomena are quite limited. On the other hand, corrosion processes that initiate can become kinetically limited under many realistic conditions, and this retardation should be factored into models and analysis. There is major impact on determination of damage evolution, life prediction, and performance acceptance when full immunity to corrosion is difficult to confirm or is uncertain.
- Opportunities to advance predictive capability via enhanced computational capability and advanced modeling and prediction protocols. There was a consensus of the potential for large gains and opportunities in this area. Recognition was also given opportunities for advances to verification of long term predictions of material performance via accelerated testing. A path to progress was identified through the use of more susceptibility analogs and extensions to extremely corrosion resistant alloys.
- Opportunities for advances in computational and experimental methods. The former is represented by application of advanced thermodynamics and computational materials science to metallurgical aging issues and the corresponding corrosion behavior. For the latter, there is a plethora of new techniques with unprecedented ability to interrogate materials with high resolution, improved data acquisition, and higher analytical efficiency and throughput.
- Opportunities to adapt and apply state of the art developments in other fields to corrosion science. A specific opportunity was the advancement and application of combinatorial methods after those in the pharmaceutical industry. Another was for advanced sensors and diagnostic methods after those in the medical community.

The opportunities identified at the Corrosion Workshop provide a special opportunity for advances in the state of corrosion science to benefit not only analysis of nuclear waste disposal systems but a wide-range of applications. Advances in the analysis of performance and life prediction will contribute to advanced solutions for our nation's aging infrastructure, advanced equipment and systems for energy production, transportation and a range of other industrial sectors.

## **Organization and Outputs of the DOE Corrosion Workshop**

This Corrosion Workshop developed from the leadership of the Office of Basic Energy Sciences (BES) and Office of Civilian Radioactive Waste Management (OCRWM). There was recognition of major opportunities for synergy and collaboration between scientists and engineers working on (a) advances in corrosion science and (b) the analysis of a crucial application of nuclear waste disposal. The workshop technical topic areas were divided into fundamental scientific topics in corrosion regarding forms of corrosion relevant to nuclear waste containers. It also included cross-cutting issues relevant to each form of corrosion. The former were

- Localized Corrosion
- Passivity
- Stress Corrosion Cracking

The later were

- Life Prediction and Evolution of Corrosion Damage
- Evolution of Environments on Metal Surface
- Material Stability and Aging
- Advanced Materials and Fabrication
- Methods and Tools

For each topic area, workshop participants discussed its relevance to corrosion science and to the Yucca Mountain Repository. Current status of understanding and relevant background information was presented and discussed in work groups and plenary sessions. The outputs were research opportunities for critical, unresolved scientific and/or technological issues.

Corrosion perspectives at Yucca Mountain were presented as background on important issues in corrosion science in the context of long-term prediction of materials performance. The long-term strategy for safe disposal of nuclear waste at the Yucca Mountain Repository is to completely isolate the radionuclides for long times (1000's of years and longer). Long-lived waste packages are essential to safe performance. The prediction of materials performance is important and common to a broad range of industries and systems; however, the extraordinarily long time period of interest for Yucca Mountain presents a special challenge.

Corrosion is clearly the primary determinant of waste package performance and will control the delay time for radionuclide transport from the waste package. Crucial scientific issues remain for a better understanding of corrosion processes and the time evolution of corrosion damage. The application of corrosion science to performance assessment and life prediction is an evolving discipline. The opportunities for advancements in corrosion science for life prediction and performance assessment are important and have great potential benefit. Yucca Mountain provides an application where the public benefits of increased confidence in performance are clear. Progress and advancements in life prediction at Yucca Mountain would also have major impact and extend to condition assessment and life extension for plants and systems for energy production and transportation as well as other industries.

For each of the workshop topic areas, an overarching goal is presented along with selected research opportunities identified from the DOE Corrosion Workshop. Comments and findings from the workshop are presented in separate sections for each topic area. A list of participants and information on the organization and logistics of the workshop are presented in appendices.

## INTRODUCTION

This report summarizes the findings of a U.S. Department of Energy workshop on “Corrosion Issues of Relevance to the Yucca Mountain Waste Repository”. The workshop was Co-Sponsored by the Office of Basic Energy Sciences and Office of Civilian Radioactive Waste Management. The workshop was held on July 28-30, 2003 in Bethesda, MD. This workshop identified opportunities in corrosion science including the improved prediction of long-term corrosion behavior. It had particular relevance to the post-USNRC license approval state for the permanent disposal of nuclear waste at the Yucca Mountain Repository and generic research opportunities for both basic and applied corrosion research.

The culmination of the workshop is this report that identifies research opportunities in basic and applied topic areas. The research opportunities would be realized well after the US Nuclear Regulatory Commission’s initial construction-authorization licensing process. This research, if conducted, may (a) improve the technical basis of Yucca Mountain Repository safety case, and/or (b) improve the cost or schedule aspects of the design for the underground waste packages that are an important part of the overall repository engineering design. Twenty-three scientists accepted invitations to participate in the workshop.

The Yucca Mountain Project believes that it has a sufficiently strong safety case to proceed with a License Application to the USNRC. However, advances in a number of areas may be feasible which, if realized, could help the Project either through better understanding of the long-term behavior of the waste packages, through better performance, or perhaps through cost savings that do not compromise performance.

### **Benefit and Impact of Advances in Corrosion Science and Technology**

#### **Cost of Corrosion to the United States**

Three landmark studies have documented the remarkable costs of corrosion to the United States. In 1949, a study was led by H.H. Uhlig [H.H. Uhlig, “The Cost of Corrosion to the United States,” *Chemical Engineering News*, Vol. 27, p 2764, 1949; or *Corrosion*, Vol. 6, p 29, 1950.] The annual cost of corrosion was estimated by summing the materials and protection method costs related to corrosion control. Corrosion costs were estimated to be \$5.5 billion or 2.1 percent of the 1949 Gross National Product (GNP). In 1978, in response to a Congressional Directive, the National Bureau of Standards [now the National Institute of Standards and Technology] and Battelle determined the cost of metallic corrosion in the United States. The Battelle-NBS study was the first to combine the expertise of corrosion and economics experts to determine the economic impact of corrosion on the U.S. economy [J.H. Payer, W.K. Boyd, D.G. Lippold, and W.H. Fisher, “NBS-Battelle Cost of Corrosion Study (\$70 Billion!),” Part 1-7, *Materials Performance*, May-November 1980]. The results of the Battelle-NBS study for the base year of 1975 were:

- The total U.S. cost of metallic corrosion per year was estimated to be \$70 billion, which comprised 4.2 percent of the GNP in 1975, and
- 15 percent or \$10 billion was estimated to be avoidable by the use of the most economically effective, presently available corrosion technology.

A number of studies for other nations have been carried out, and similar large corrosion costs were determined.

In 1999, the U.S. Congress mandated the determination of corrosion costs, and a breakthrough 2-year study on the direct costs associated with metallic corrosion was issued in 2002. The study entitled ‘Corrosion Costs and Preventive Strategies in the United States [www.nace.org/nace/content/publicaffairs/cocorrindex.asp]. Results of the study show that the total annual estimated direct cost of corrosion in the U.S. is a staggering \$276 billion—approximately 3.1 percent of the nation’s Gross Domestic Product (GDP). It reveals that, although corrosion management has improved over the past several decades, the U.S. must find more and better ways to encourage,

support, and implement optimal corrosion control practices. An important feature of this latter report is that *preventive strategies* were developed for savings and reduction of corrosion costs.

### **Protection and Life Extension for the Nation's Infrastructure**

The nation's infrastructure is essential to the quality of life, industrial productivity, international competitiveness, and security. Our society depends upon a functional, reliable, and safe infrastructure system, including food, water and energy needs, transportation for work, education and recreation, the production and delivery of goods and services, communications, and the treatment and long term disposal of wastes. Each component of the nation's infrastructure, such as highways, airports, water supply, waste treatment, energy supply, and power generation, represents a complex system and large investments.

Corrosion is damage that results from the interaction of structures and materials with its environment. In some cases, corrosion damage is tolerable and perhaps only leads to somewhat higher maintenance costs and minimal losses; however, corrosion can result in catastrophic failures with loss of life and disruption of essential services. In fact, corrosion is a primary cause of the degradation and a principal threat to the nation's infrastructure. As documented above, the direct costs of corrosion represent 3.2 percent of the U.S. GDP. The total costs (direct and indirect effects) to society can be twice that or greater. The infrastructure replacement cost is a major driver on the economic impact of corrosion and can still be greater if corrosion preventive strategies are not properly employed. The opportunities for savings by improved corrosion control are significant in every industrial and government sector.

### **Opportunities in Corrosion Science for Long-Term Prediction of Materials Performance**

Scientific advances for life prediction and performance assessment can result in an increase in reliability and safety, reduction in costs, and conservation of materials and energy. The prediction of long-term performance for corrosion is the most important and challenging matter for corrosion science and engineering. The determination of current status and future performance as a function of materials, design and service conditions are vital to guide rationale, reliable and cost effective decisions by policy-makers, managers and engineers.

Opportunities for scientific advances in corrosion are clearly linked to progress in materials science and electrochemistry. However, corrosion is truly multi-disciplinary and advances can stem from progress in the sciences of physical chemistry, electrolytes, surface science, geochemical science, microbiology and others. Because of complex and coupled processes during the long-term degradation of materials, the formation of multi-investigator teams to collaborate on important aspects of these complex systems can create synergies that overcome barriers that stifle scientific advances and enhance the opportunity for major advances.

Nuclear energy provides several crucial and important opportunities for major impact of advanced corrosion science and technology. Useful perspectives are available from the "Basic Research Needs to Assure a Secure Energy Future", a report from the Basic Energy Sciences Advisory Committee (BESAC), February 2003.

"It is clear from the analysis presented in this (BESAC) report that there are a number of opportunities. Essentially all of these are interdisciplinary in character."

"The magnitude of the energy challenge should not be underestimated. With major scientific discoveries and development of the underlying knowledge base, we must enable vast technological changes in the largest industry in the world (energy), and we must do it quickly."

"Nuclear energy provides somewhat more than 20 percent of electricity in the U.S., 35 percent in the European Union, 24 percent in all OCED countries, and about 16 percent worldwide. The importance of this power source may increase due to concerns of greenhouse gas emissions from fossil-fired plants."

"Public acceptance of nuclear power as an important energy source depends upon developing acceptable solutions to the back end of the nuclear fuel cycle. Scientifically based and carefully engineered solutions are more likely to gain public acceptance."

The importance of understanding corrosion processes as they affect nuclear waste packages at the Yucca Mountain Repository is noted in the BESCA report. A host of other groups have also identified the analysis of long-

term performance of waste packages as crucial: NRC, ACNW, NWTRB, DOE Peer Panels and International Peer Panels.

The long-term corrosion performance of waste packages at Yucca Mountain Repository provides a crucial application and a special challenge due to the exceptionally long times (10,000 years and beyond) required. Therefore, analysis for Yucca Mountain provides a special opportunity for advances in the state of science to benefit not only nuclear waste disposal, but advance performance and life prediction for a wide-range of applications. Advances will benefit solutions for our nation's aging infrastructure, advanced equipment and systems for energy production, transportation and a range of other industrial sectors.

### **Origin and Basis for DOE Corrosion Workshop**

This Corrosion Workshop developed from the leadership of the Office of Basic Energy Sciences (BES) and Office of Civilian Radioactive Waste Management (OCRWM). There was recognition of major opportunities for synergy and collaboration between scientists and engineers working on (a) advances in corrosion science and (b) the analysis of a crucial application of nuclear waste disposal. In order to identify basic and applied research opportunities in corrosion that are relevant to the Yucca Mountain repository, a group of active researchers was gathered from BES, OCRWM and other institutions.

The workshop technical topic areas were divided into fundamental scientific topics in corrosion regarding forms of corrosion relevant to nuclear waste containers. It also included cross-cutting issues relevant to each form of corrosion. The former were

- Localized Corrosion
- Passivity
- Stress Corrosion Cracking

The later were

- Life Prediction and Evolution of Corrosion Damage
- Evolution of Environments on Metal Surface
- Material Stability and Aging
- Advanced Materials and Fabrication
- Methods and Tools

For each topic area, workshop participants discussed its relevance to corrosion science and to the Yucca Mountain Repository. Current status of understanding and relevant background information was presented and discussed in work groups and plenary sessions. The outputs were research opportunities for critical, unresolved scientific and/or technological issues.

# CORROSION PERSPECTIVES AT YUCCA MOUNTAIN

Joe H. Payer  
Case Western Reserve University

## Introduction

*Opportunities for advances in corrosion science for life prediction and performance assessment provide the greatest potential benefit*

The long-term strategy for safe disposal of nuclear waste at the Yucca Mountain Repository is first to completely isolate the radionuclides in the waste packages for long times (1000's of years and longer) and secondly, to greatly retard the egress and transport of radionuclides from penetrated packages. Therefore, long-lived waste packages are essential to safe performance. Further, a high-quality analysis to predict waste package performance and the strength of the technical basis to support that analysis will contribute greatly to a high level of confidence for the repository.

The Yucca Mountain Repository presents a common materials performance application that is encountered in energy, transportation and other industries. The widely accepted approach to dealing with materials performance is to identify the performance requirements, to determine the operating conditions that materials will be exposed to and to select materials of construction that perform well in those conditions. The special feature of Yucca Mountain is the extremely long time frame of interest. There is interest in performance behavior for periods of 10,000 years and longer. 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.

Corrosion is clearly the primary determinant of waste package performance and will control the delay time for radionuclide transport from the waste package. 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 general issues in corrosion science, materials science and electrochemistry are well defined, and the knowledge base is substantial for understanding corrosion processes. However, crucial scientific issues remain for a better understanding of corrosion processes and the time evolution of corrosion damage.

The application of corrosion science to performance assessment and life prediction is an evolving discipline. Advancements in corrosion science for life prediction and performance assessment provide the greatest opportunities and have the greatest potential benefit. Yucca Mountain provides an application where the public benefits of increased confidence in performance are clear. Progress and advancements in life prediction at Yucca Mountain would also have major impact and extend to condition assessment and life extension for plants and systems for energy production and transportation as well as other industries.

## Natural System at Yucca Mountain

*It is important to recognize that conditions at the repository evolve with time, and conditions are quite different after periods of 500 years, 5,000 years and 50,000 years. A consequence of this is that various processes rise and fall in importance with time.*

The combination of natural conditions at the mountain and the engineered features of the repository determine the corrosion issues at Yucca Mountain. The natural conditions include the amount of water moving through the mountain to the water table below the repository and the mineralogical, chemical and mechanical properties of the rock. The engineered features include the design, materials of construction and operation of the repository. For example, the time-temperature response for the waste packages and surrounding rock will depend upon the thermal load from spent fuel within packages and the spacing between packages and between adjacent storage tunnels (drifts).

It is important to recognize that conditions at the repository evolve with time, and conditions are quite different after say 500 years, 5,000 years and 50,000 years. A consequence of this is that various processes rise and fall in importance with time. Radiation fluxes at the waste package surface are highest initially and decrease to small levels over several hundred years. Heat flux from the waste packages decreases even more slowly over time, and results in a temperature increase over 10-20 years when the repository is closed, and this heat-up period is followed by a long, slow cooling back to ambient temperature over several 1000's of years.

The natural system at Yucca Mountain is multiple layers of geologic formations as shown in Figure 1. The repository is in an unsaturated zone about 300 meters below the ground surface and about 300 meters above the water table. In the unsaturated zone, the pores in the rock matrix and fractures in the rock are only partially filled with water. Water moves downward through the unsaturated zone to the water table (saturated rock). An important aspect is that the repository is at near atmospheric pressure at all times, and there are no processes by which pressure can build-up to higher levels.

The water flow through the mountain is a critical issue. The climatology and the amount of infiltration will determine how much water enters the unsaturated zone above the repository. At the repository level, water can move through the rock between disposal drifts and/or interact with the drifts and waste packages. Water then continues its movement through unsaturated rock beneath the repository and into the saturated zone at the water table.

Thermal-hydrological-chemical effects determine the environment, i.e. the chemical composition and properties of moisture and gases in contact with metal surfaces. Both the environment and the materials of construction determine the corrosion behavior. The dimensional scale of interest will vary over many orders of magnitude depending upon the process being considered. Mountain scale processes are macro-scale (10's to 100's meters). Drift and waste package processes are meso-scale (cm's to meters). Particles and droplets are micro-scale ( $\mu\text{m}$ -mm). Passive films, moisture layers and sorption processes can be described at the molecular level or nano-scale (nm- $\mu\text{m}$ ).

## **Repository Conditions Relevant to Waste Package Performance**

*The overall repository time frame can be divided into relevant time periods for analysis. The critical issues for long term performance are determination of the presence of moisture on metal surfaces, the realistic corrosive properties of the moisture and the corrosion resistance of waste package materials exposed to these realistic environments.*

In the repository, the waste packages are placed on support pallets and sit in air at atmospheric pressure. The relative humidity, depending upon the time/temperature, can range from very low values up to full saturation at 100%. There is no feasible scenario that will lead to waste packages being fully immersed in water; rather metal surfaces will be exposed to thin layers of moisture and moist particulate or deposits. 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.

Waste packages are exposed to one long, slow cycle. There are no start-up/shut-down cycles. There are no moving parts, and the static exposure does not subject waste packages to cyclic mechanical loads. When the waste packages are emplaced in the repository, and the repository is closed after some 50 years, there is a heat-up and then a very long, slow cool-down. Waste package surfaces heat to a maximum temperature in the range of 120 to 180 C depending upon the particular package. The heat-up period covers 10-20 years after repository closure. This is followed by cooling to ambient temperatures over several hundreds to thousands of years. Compared to industrial equipment, e.g. heat exchangers and steam generators, the heat fluxes and thermal gradients for waste packages are modest.

One of the major challenges for analysis of the Yucca Mountain Repository is the extremely long time frame of interest. The prediction of behavior of materials over thousands of years and 10,000's years is unprecedented for engineering applications. While information can be gathered from the behavior of natural analogues and from metal archaeological artifacts that have remained stable for thousands of years, there are opportunities to extend current practices for materials performance and life prediction.

The overall repository time frame can be divided into relevant time periods for analysis. Five relevant time periods for a medium temperature waste package are shown in Figure 2. The first period, "I-Preclosure", spans the time of waste package emplacement for 50 years. During this period, the repository is ventilated and temperatures remain low. At 50 years, the repository is closed, and the temperature starts to rise. The second period, "II-Heat-up", extends over 10 to 15 years, i.e. from years 50 to 65. During this period, a thermal barrier results from the drift wall heating to above the boiling point of water, and no drips or seepage onto waste packages will occur. The third period, "III-Thermal Barrier", is from years 65 to 750. At 750 years, the drift wall has cooled to the boiling point, and drips or seepage is possible. The fourth period, "IV-Cool down post-thermal barrier", starts when the drift wall cools to boiling and extends until the waste package surface cools to a temperature below a critical corrosion temperature for corrosion in realistic repository environments. For the case shown here, the critical corrosion temperature was 90 C, and Period IV extends from years 750 to 1375. "Period V-Packages below the critical corrosion temperature" is all time from year 1375 and beyond.

This analytical framework defines critical issues for analysis of long-term materials performance:

- When will moisture be present on waste package surfaces?
- What are the realistic corrosive characteristics of the moisture?
- What is the corrosion resistance of waste package materials for these conditions?
- What is a realistic critical temperature below which no significant corrosion will occur?

The critical issues for long term performance are determination of the presence of moisture on metal surfaces, the realistic corrosive properties of the moisture and the corrosion resistance of waste package materials in these realistic environments.

In the 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. Deliquescence/condensation is of concern during Period III and IV, and drips/seepage is of concern in Period IV. After the waste packages have cooled to the critical corrosion temperature (Period V) corrosion is not likely.

## **Corrosion Performance of Highly Corrosion Resistant Materials**

*Understanding the durability of passive films under realistic conditions for the repository is crucial.*

*Localized corrosion processes (pitting, crevice corrosion, stress corrosion cracking) are the most likely degradation modes to be considered in the repository environments.*

*Determination of damage evolution by localized corrosion over a long service period would be enhanced by improved understanding of localized corrosion processes to include initiation, propagation, stifling and arrest processes*

Highly corrosion resistant materials are selected for the waste packages and drip shields for the repository: Alloy 22, a nickel-chromium-molybdenum alloy and titanium, respectively. Both Alloy 22 and titanium have high corrosion resistant in oxidizing environments that are of interest for the Yucca Mountain Repository. In any corrosion application, the corrosion behavior is determined by the combination of the corrosion resistance of the material and the corrosively of the environment. There are environments that will attack any material. Since no

material is immune to all environmental conditions, the challenge is to specify a material with proper corrosion resistance in realistic environments.

Alloy 22 belongs to a family of corrosion resistance alloys that have nickel-chrome-molybdenum as the primary alloying constituents. 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 are on the order of 0.1 to 0.01 microns per year. At these rates, it takes 10,000 to 100,000 years to penetrate 1 millimeter of metal. So for passive metals that remain passive, extremely long lives are not unrealistic. The challenge is to determine the boundaries of passive behavior and to compare these boundaries to the realistic environments that pertain to the repository.

Localized corrosion processes (pitting, crevice corrosion, stress corrosion cracking) are the most likely degradation modes to be considered in the repository environments and with materials that are being selected. So basing materials selection and design on high localized corrosion resistance is both prudent and a well-accepted corrosion engineering practice.

A montage of figures for localized corrosion is shown in Figure 3. There is a rich literature on the chemical, electrochemical, metallurgical processes that pertain for localized corrosion. The figure in the upper left shows the corrosion behavior of a series of alloys in an oxidizing-acid environment in laboratory tests. In this environment, Alloy 825 did not fare well and exhibited severe localized corrosion. In the same environment, Alloy 22 and titanium showed no corrosion. The schematic polarization curves at the bottom of the figure provide a well-accepted method for determination of susceptibility to localized corrosion under laboratory conditions. Comparison of the corrosion potential and the repassivation potential provides a criterion for initiation of crevice corrosion. The rationale is that if the passive film is disturbed at a potential above the repassivation potential, then the crevice can remain active for extended periods of time and significant corrosion damage could occur. The figures in the upper right show conditions within a crevice before and after initiation of crevice corrosion.

Figure 4 describes the “susceptible zone” for localized corrosion related to the corrosion resistance of the metal and the corrosivity of the environment. For localized corrosion to occur, the conditions must be in the region of overlap. For realistic conditions, if there is no overlap between the corrosive environments and the susceptible material, localized corrosion will not occur. If the fields overlap, then it is only those environments that overlap with the corrosion resistance of the material that could cause localized corrosion. Where an overlap (susceptible zone) exists there are additional requirements for crevice corrosion to occur. Water of the aggressive composition has to form and persist on the waste package surface, and these conditions must to persist over a long enough time to cause damage. Thus, a crucial issue is the time evolution of the corrosive environment on metal surfaces under realistic conditions for the repository.

Figure 5 shows many of the processes that pertain to localized corrosion. These processes pertain to the initiation, propagation, stifling, and arrest stages of localized corrosion. The process 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 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.

Important questions for determination of damage evolution with time are do conditions exist to support localized corrosion, will the corrosion initiate, will it persist, and what damage might result? A localized corrosion fault tree approach identifies key factors to determine the evolution of corrosion damage over long exposure periods:

- Does a “susceptible zone” exist where corrosive waters that can initiate localized corrosion exist on the waste package surface?
- Is the corrosion potential under natural conditions more positive than the repassivation potential?
- Is there a sufficient crevice former on the waste packager surface to support crevice corrosion?
- If the above criteria are met, then localized corrosion can initiate.

- What is the initial corrosion penetration rate within the crevice, and how does the rate change with time?  
For localized corrosion, a power law dependence often pertains and the penetration rate decreases with time.

For determination of waste package performance, the above would be applied over the five relevant time periods in the repository.

## **Time Evolution of Environment**

*A crucial issue is the time evolution of the corrosive environment on metal surfaces under realistic conditions for the repository.*

*Thin layers of electrolyte, particulate and deposits are the conditions of interest.*

*A methodology is available to determine the restricted time period when a waste package is susceptible to localized corrosion and information on the solution chemistry during that period.*

The time evolution of the movement of water into the tunnels and the composition of the waters on waste package surfaces are primary concerns. The flux of water in the repository is described similarly to annual rainfall and at the repository level is approximately 5 mm per year. When the temperature of the tunnel walls are above boiling, a thermal barrier exists that vaporizes water and no drips or seepage into the tunnels will occur. Strong capillary forces in the rock also hinder dripping and cause significant amounts of water to remain in the rock and divert around the tunnels. Nevertheless, some dripping and seepage into the tunnels can occur. Water that seeps into the drifts and drips onto waste package surfaces will create an aqueous environment along with any condensation or deliquescence on waste package surfaces. Dilute waters dripping onto hot surfaces can evolve to more concentrated solutions through evaporation.

It is well accepted that dry metals, without the presence of an aqueous phase, do not corrode at an appreciable rate in the 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 temperature and relative humidity over time are determined by thermal-hydrological analysis, and the temperature-relative humidity of a medium temperature waste package was shown above. Based on these data and the critical corrosion temperature, the five relevant time periods were described. Other aqueous solution properties of interest include the acidity/alkalinity (pH), oxidizing potential (Eh) and chemical composition of waters. The pH and Eh are determining factors for stability of passive films and localized corrosion processes. The mountain “breathes” and the tunnels are at atmospheric pressure. The waste packages sit upon supports in air which results in an oxidizing environment.

The ambient waters at Yucca Mountain are non-corrosive and benign. The ambient waters are near-neutral with low amounts (parts per million) of dissolved solids and mixed salts. There are a number of anions, cations, salts and minerals available. Chemical divide methodology is used to determine the aqueous solution types resulting from the concentration of dilute waters. The types of waters are shown in Figure 6. A controlling factor is the relative ratio of calcium and carbonate ions in the water. On concentration by evaporation, calcium carbonate precipitates and the predominant ion determines the water type branch that is followed at the divide. This methodology can be used to analyze concentration processes such as evaporation of dilute solutions. The corrosion behavior of waste package and drip shield materials can be determined in the various types of solutions, and the results feed into performance and life prediction.

Figure 7 is a montage to show several aqueous solution chemistry principles that pertain to the determination of repository environments. The figure in the upper left is a plot of relative humidity and temperature and indicates conditions (to left and above the line) that are inaccessible because the repository is at atmospheric pressure. For any condition in the inaccessible region, water would vaporize, and there can be no aqueous solution. The figure in the upper right shows the deliquescence curves for a number of salts. These identify the minimum relative humidity necessary to form an aqueous solution of the salt as a function of temperature. For conditions below the curve, a dry salt would be present. The behavior of a salt mixture is shown in lower left. The mixture forms an aqueous solution at relative humidity lower than either of the pure salts. The figure in the lower right combines this information and shows the behavior of sodium nitrate and sodium chloride mixtures as a function of temperature and relative humidity. At 100 C, the mixed salts are dry for relative humidity below 45 percent. Between 45 percent and 70 percent relative humidity, an aqueous solution with nitrate:chloride ratio greater than 0.5 will be present. Above 70 percent relative humidity, a solution with nitrate:chloride ratio less than 0.5 will be present.

The temperature-relative humidity behavior for a waste package and the solution chemistry behavior are combined in Figure 8 for the time evolution of the environments on the waste package surface. The times and conditions that pertain for Period IV are determined. From the T-RH behavior, the waste package at year 750 is at 101 C, and the relative humidity is 65 percent. That point is shown on the solution chemistry plot. By matching the chemistry constraints to the behavior of the waste package, and the trajectory of possible waters throughout Period IV are determined. For this waste package, the period starts at year 750. As it cools, it follows the chemistry trajectory until it cools to 90 C at year 1375. The nitrate:chloride ratio of 0.5 is shown because at 100 C, a ratio greater than 0.5 was found to inhibit localized corrosion. This methodology gives insight into the times when waste packages are susceptible to localized corrosion and information on the solution chemistry during that period. The analysis also identifies time periods when localized corrosion will not occur under realistic repository conditions.

## Other Considerations

Other considerations for corrosion performance at Yucca Mountain include

- Stress corrosion cracking
- Long term stability of alloys
- Design and fabrication processes

Montages for each of the topics are presented.

Figure 9 is for stress corrosion cracking. Important factors include residual stresses and specific cracking environments. Alloy stability and aging effects can affect stress corrosion cracking behavior. The microstructural and chemical heterogeneities associated with welds can be a factor. A challenge is the measurement of cracking rates at the very low rates of interest. Advances in both models and experimental methods for SCC can be beneficial.

Figure 10 is for long term stability of alloys. The long time periods of interest for Yucca Mountain require consideration of solid-state processes at lower temperatures than pertain for most engineering applications. Extension of the combined experimental and computational approaches being utilized to analyze aging processes for Yucca Mountain conditions can lead to significant benefits to life prediction for other applications as well as for the repository.

Figure 11 shows design and fabrication considerations for waste packages and the tunnels (drifts) for the repository. For corrosion, important factors are materials of construction, metallurgical structure and residual stresses. Fabrication processes, particularly welds, are of interest.

**For more information**

This section was based upon a presentation the writer made at the Corrosion Workshop and recent updates from a presentation on “Corrosion Resistance of Alloy 22 at the May 18-19, 2004 Spring Board meeting of the United States Nuclear Waste Technical Review Board. Other presentations on corrosion and environments were also made and are available from the NWTRB website <http://www.nwtrb.gov>.

Figure 1-The Yucca Mountain Repository is ~300 meters below surface and ~300 meters above water table. Water transport at Yucca Mountain depends upon external climate, infiltration, movement in unsaturated rock above repository, interaction with drifts and waste packages at repository level, and movement in unsaturated rock below repository to water table.

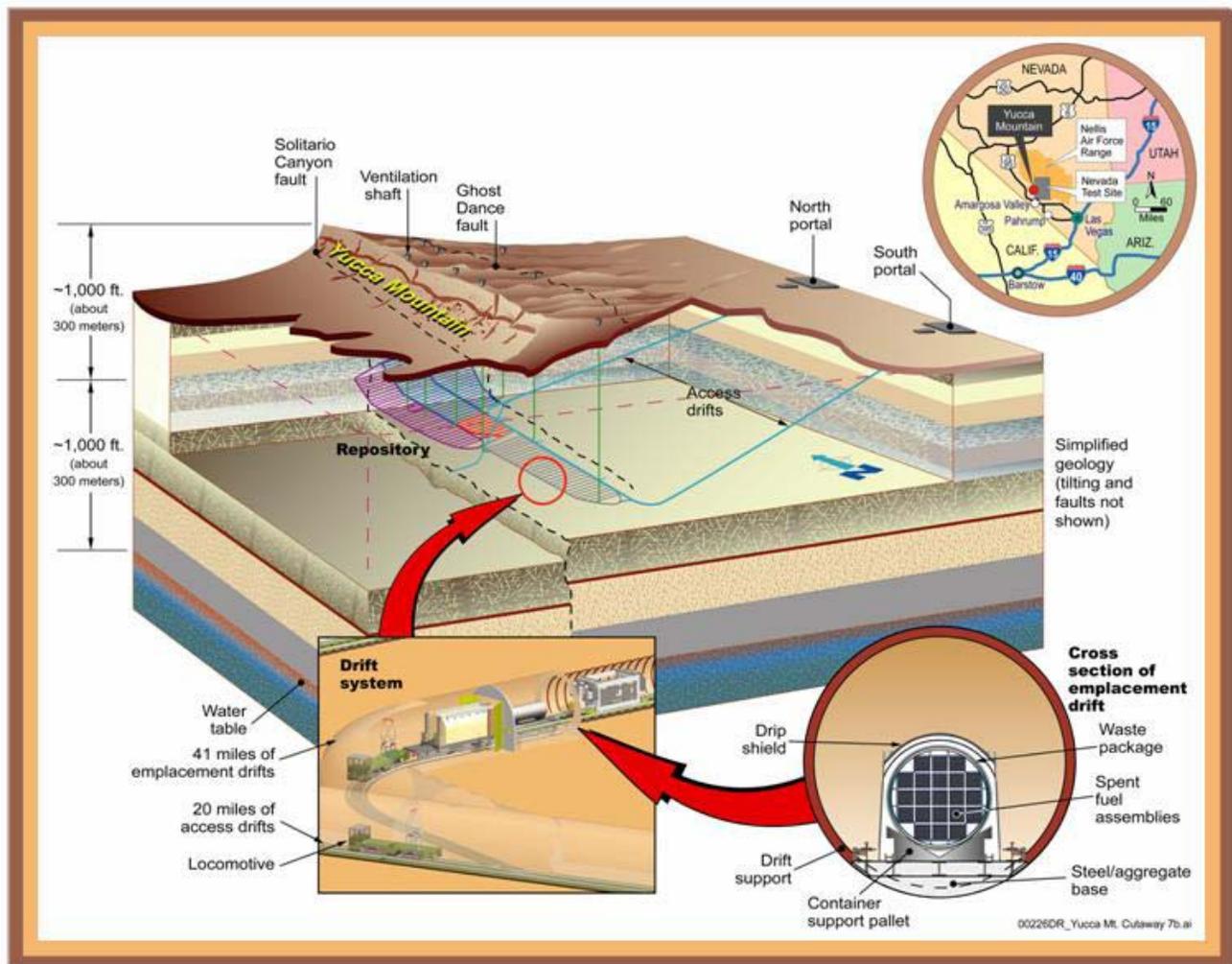
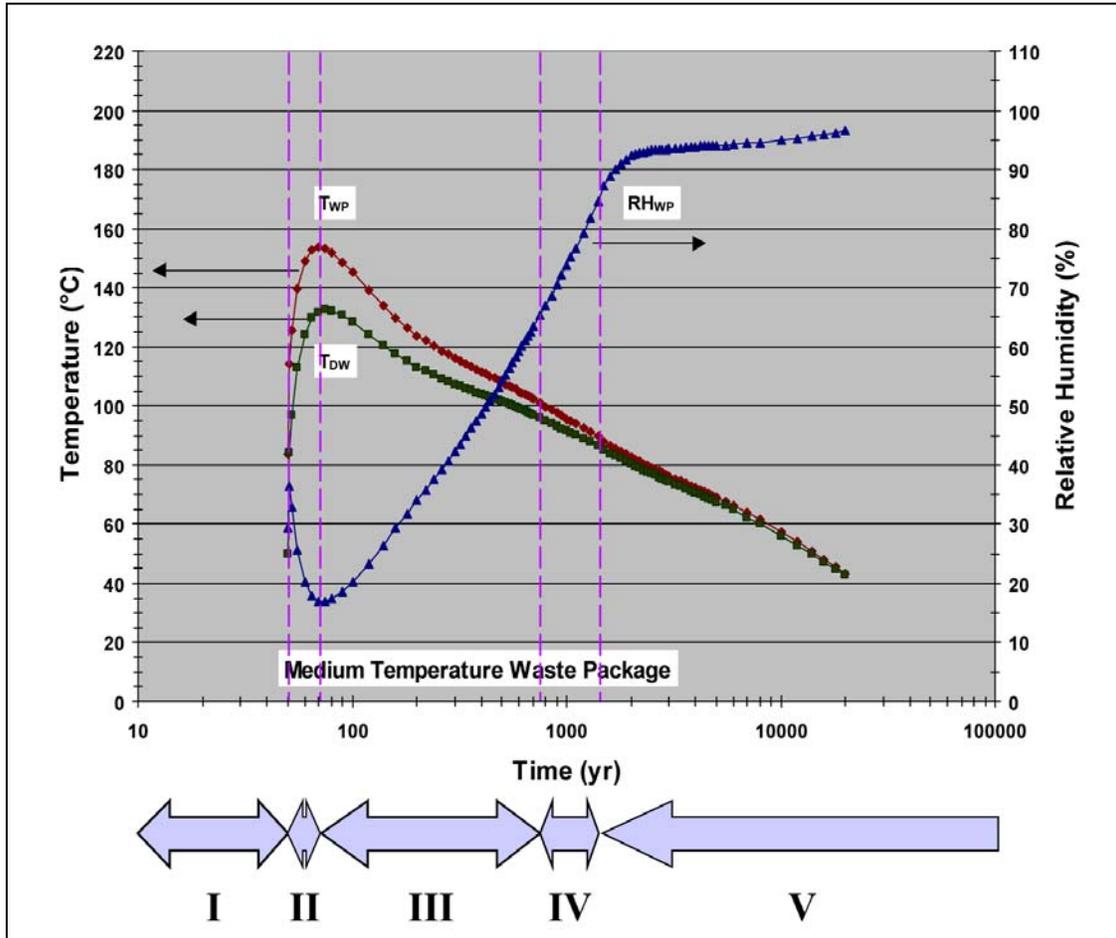


Figure 2-Relevant time periods for corrosion based upon the temperature-relative humidity behavior of a waste package.

## Relevant Time Periods Regards Corrosion

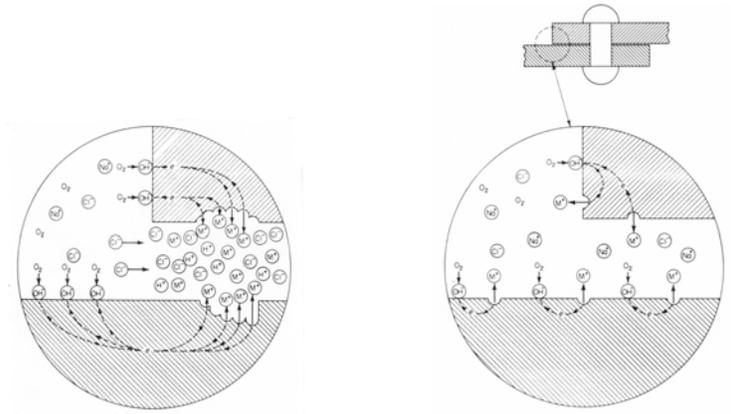
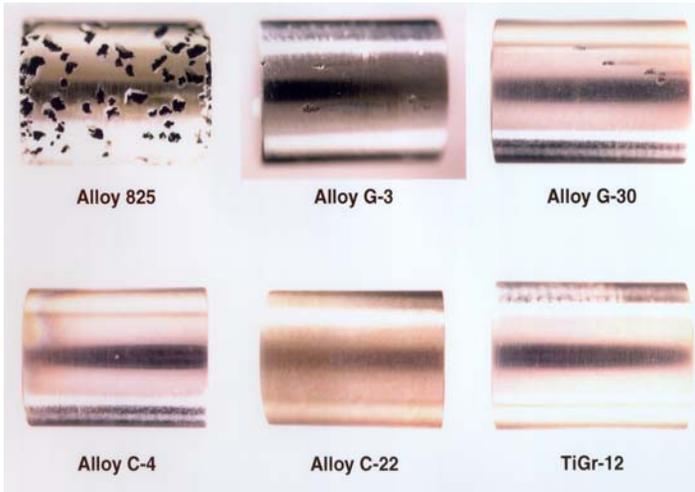


- For Conditions Below Temp-Relative Humidity behavior as shown
- Waste Package at 101°C when Drift Wall cooled to 96°C
- Critical Corrosion Temp 90°C

**I-Preclosure:** —————→ Start to Year 50  
**II-Heat up:** —————→ Year 50 to ~65  
**III-Thermal barrier:** —————→ Year ~65 to 750  
**IV-Cool down post-thermal barrier** —————→ Year 750 to 1375  
**V-Packages below critical corrosion temperature** —————→ Year 1375 and beyond

Figure 3-Montage of localized behavior and processes.

# Localized Corrosion Processes



After Fontana *Corrosion Engineering*

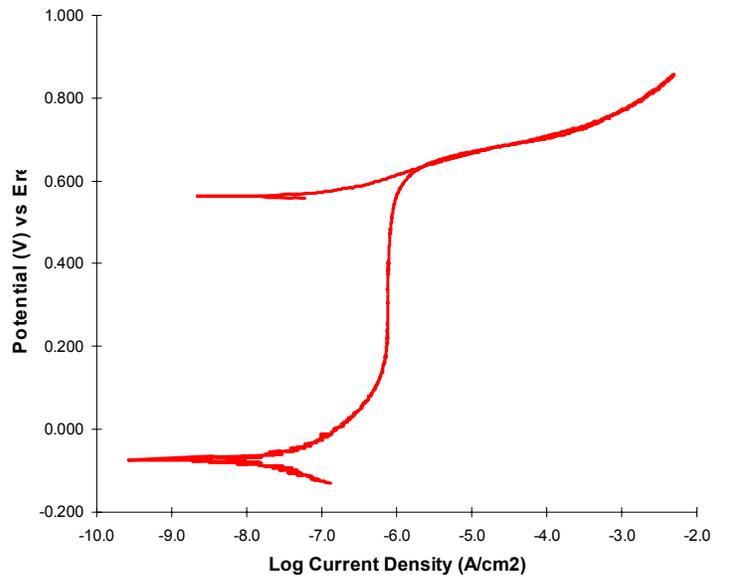
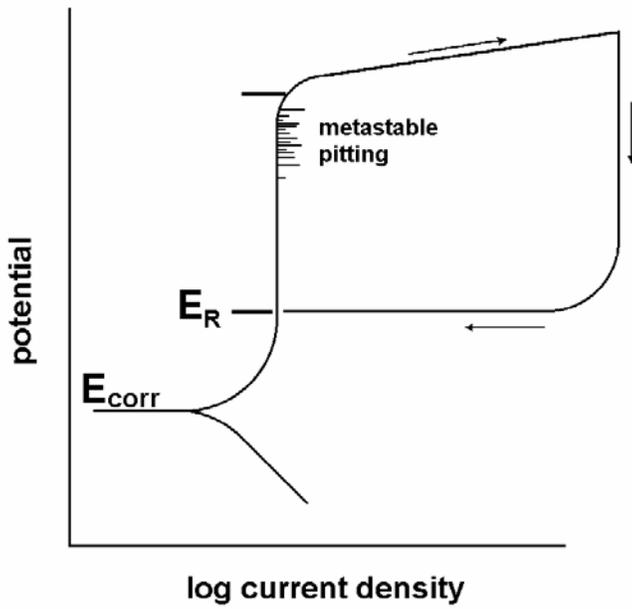


Figure 4-Susceptible zone for localized corrosion determined by corrosivity of the environment and corrosion resistance of the metal.

## Susceptible Zone for Localized Corrosion

### “?” Zone

Correlate with Repository Conditions

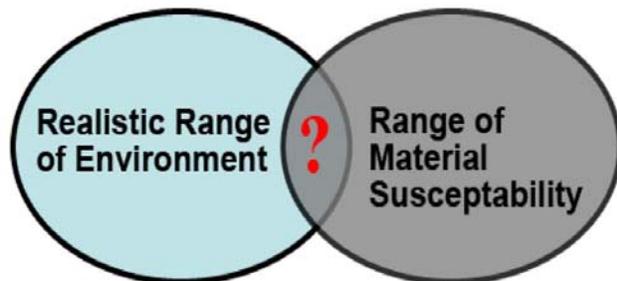
How do these form?

When, where, how much?

Will environments persist?

Can they reform?

“?” Defines the Susceptible Zone



### Additional Requirements for Corrosion

- Water must contact waste package
- Water must remain on waste package
- Corrosive species must be present to form electrolyte
- Material must be susceptible to corrosion under these conditions
- Conditions must persist over sufficiently long time

Figure 5-Factors affecting localized corrosion processes

## Factors Affecting Localized Corrosion Processes

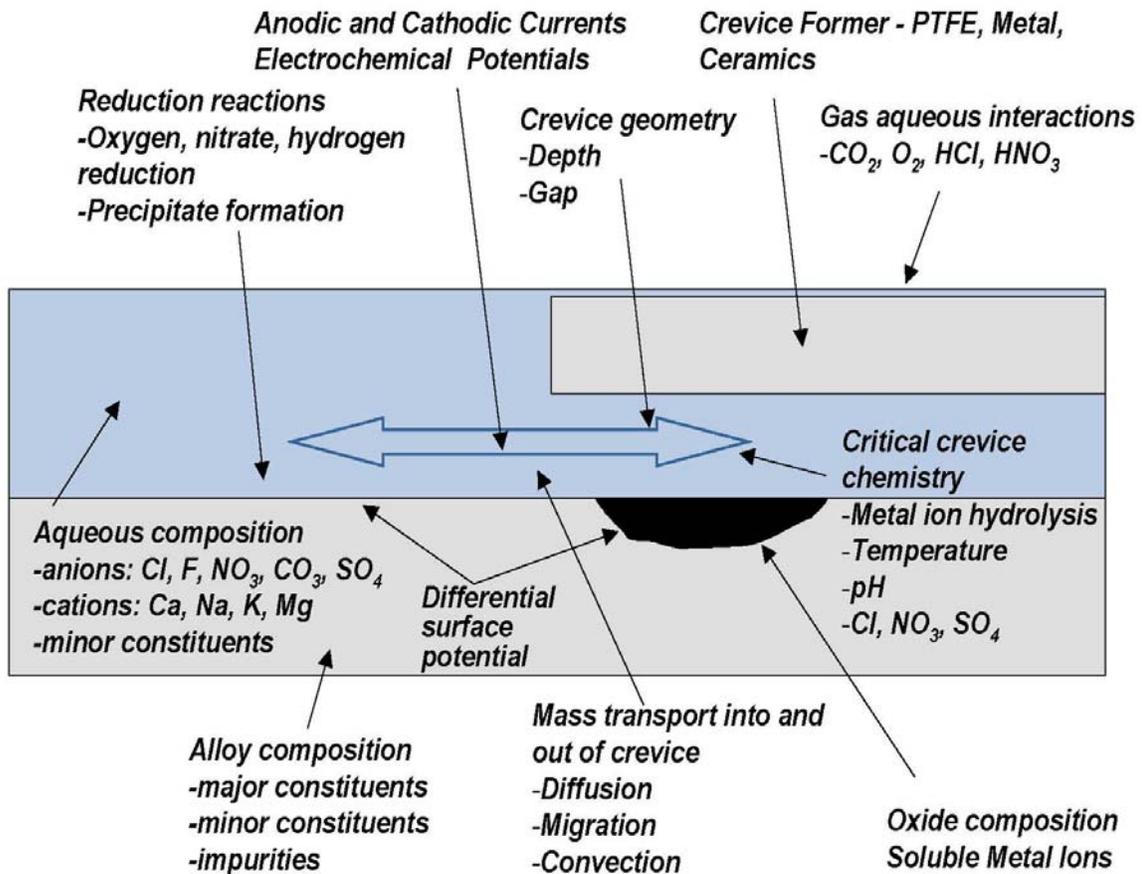
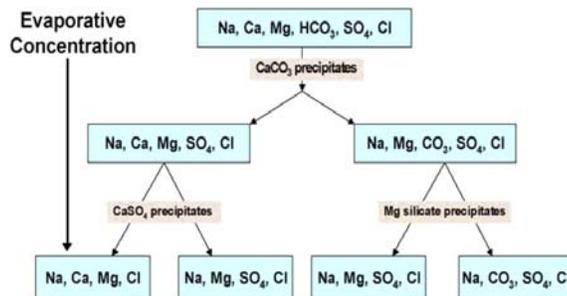
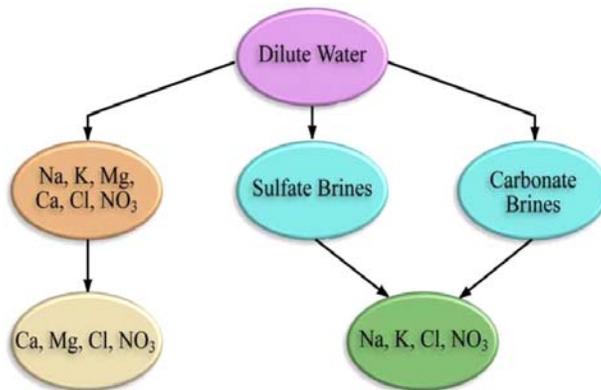


Figure 6-Application of chemical divide methodology to determine the aqueous solution types resulting from the concentration of dilute waters.

## Aqueous Solution Types



- **Ambient Waters:**
  - Dilute solutions
  - Na-Ca-Mg-HCO<sub>3</sub>-CO<sub>3</sub>-Cl-NO<sub>3</sub>-SO<sub>4</sub>
  - Near neutral pH
- **Waters can be concentrated**
  - Modified during movement
  - Thermal-chemical processes
- **Modifications on waste package surface**
- **Chemical and electrochemical processes**

Figure 7-Aqueous solution chemistry principles applied that pertain to repository environments on metal surfaces.

# Solution Chemistry Principles

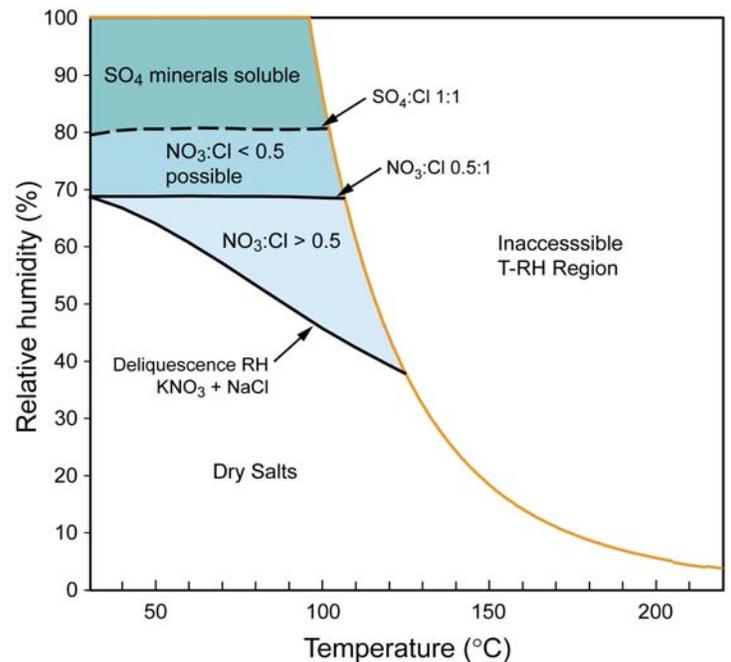
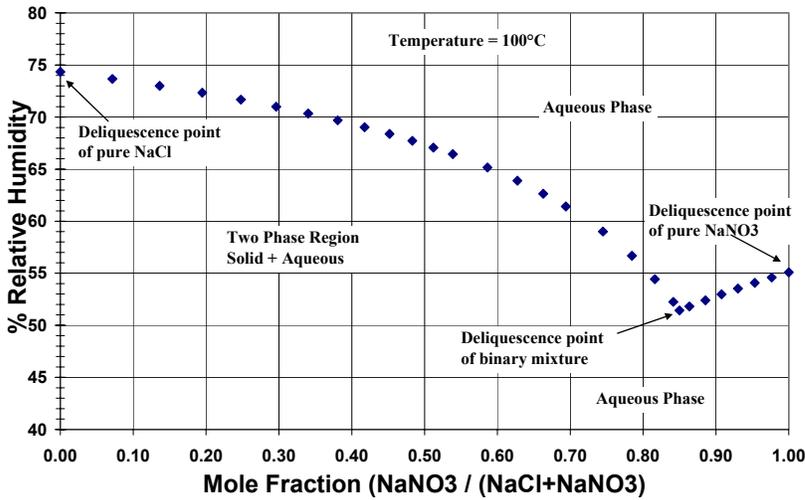
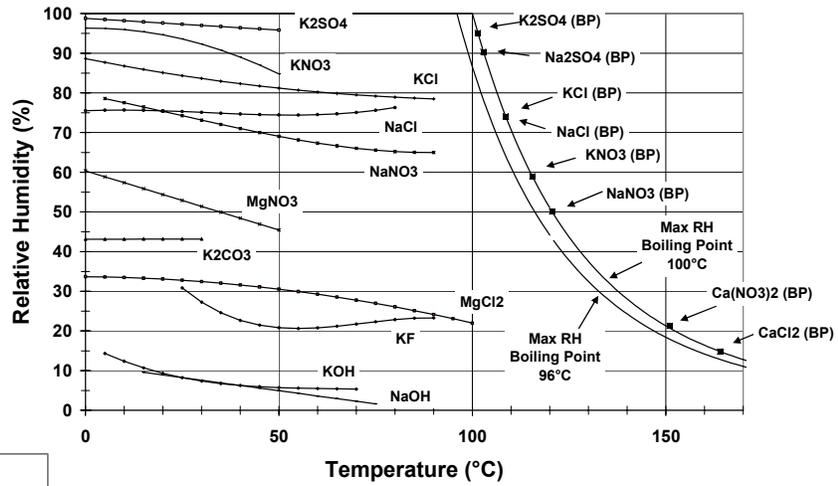
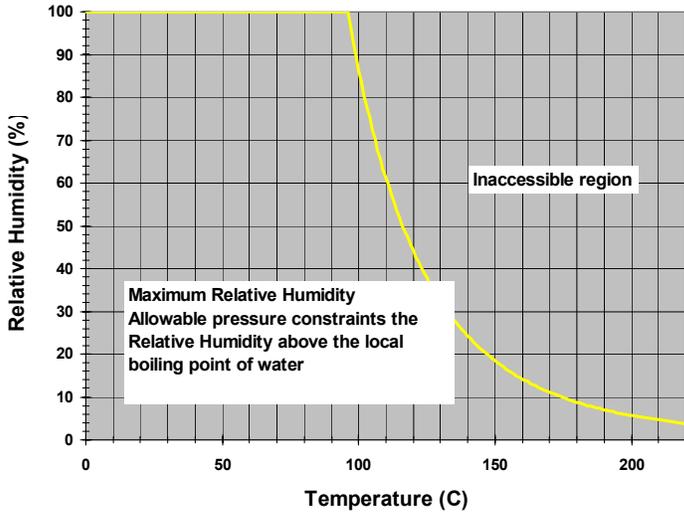
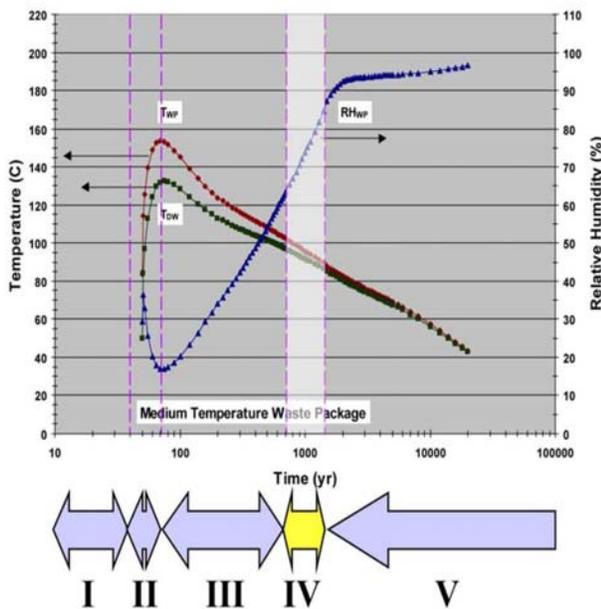


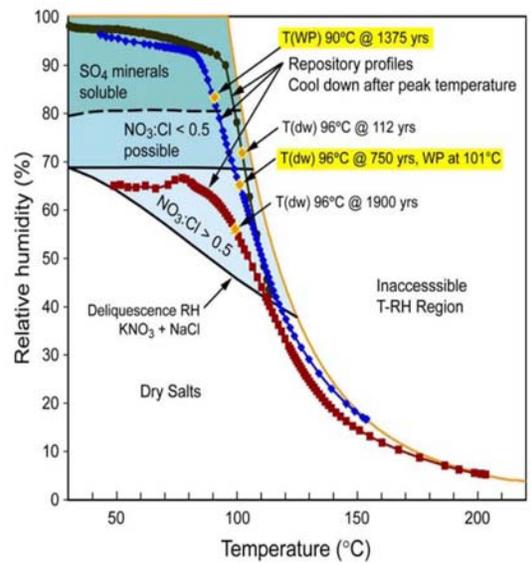
Figure 8-Combination of the temperature-relative humidity behavior and solution chemistry behavior for the time evolution of environments on waste package surfaces.

## Period IV Analysis of T-RH-Solution Composition



Drift wall 96°C at 750 years;  
 Waste Package at 101°C;  
 Relative Humidity 65%

Critical Corrosion Temp 90°C  
 at year 1375; Relative Humidity 85%

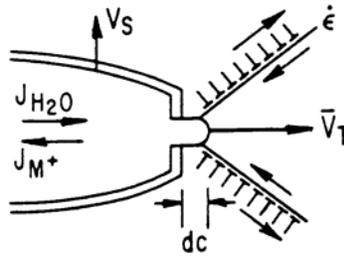
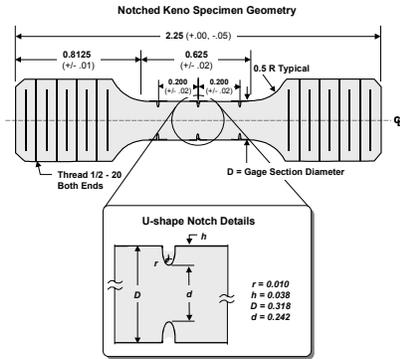


The Temp-RH at any time fixes the possible waters. Can follow the trajectory with time.

Number of non-corrosive solutions; Sodium chloride with low nitrate solutions can be corrosive

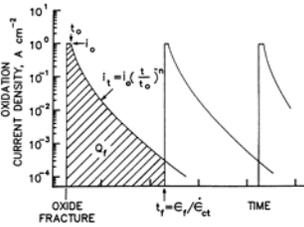
Figure 9- Montage of stress corrosion cracking factors.

# Stress Corrosion Cracking



- Important Factors**

  - Residual stresses**
  - Corrosive environment**
  - Alloy stability: aging**
  - Welds of particular interest**



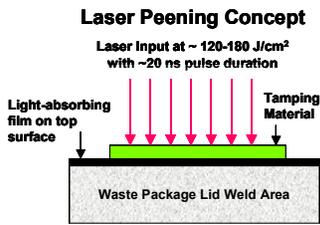
$$v = \frac{dx}{dt}; \bar{v}_{av} = \frac{Q_1}{ZtF} \frac{M}{t_1}$$

FOR HIGH  $\dot{E}_{ct}$  AND/OR LONG  $t_0$  :

$$\bar{v}_{av} = \frac{M}{2tF} i_0$$

FOR LOW  $\dot{E}_{ct}$  AND/OR SHORT  $t_0$  :

$$\bar{v}_{av} = \frac{M}{2tF} \frac{i_0 t_0^n}{(1-n)E_{ct}^n} \dot{E}_{ct}^n = f(n) \dot{E}_{ct}^n$$



Through-Wall Stress in Laser Peened Areas

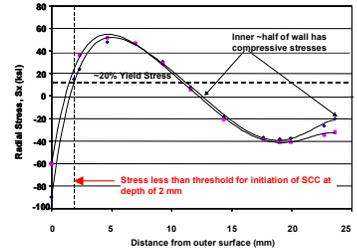
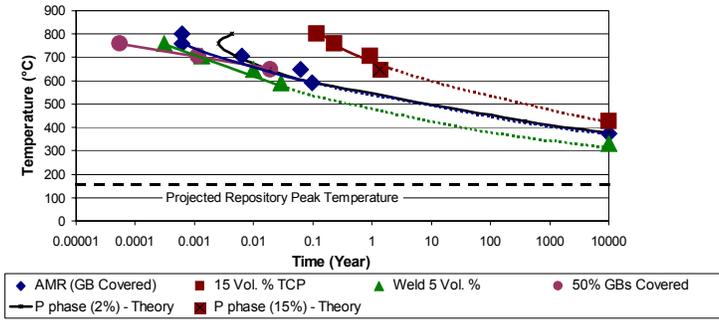


Figure 10- Montage of long term aging of alloys factors.

# Long Term Stability of Alloys

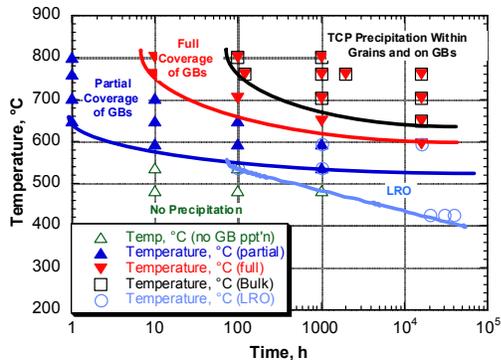


**Important Factors**

**Aging and long range ordering can affect corrosion resistance**

**Time-temperature-composition**

**Bulk alloy and welds**



As-welded Alloy 22 (Gas-Tungsten-Arc-Weld, GTAW)

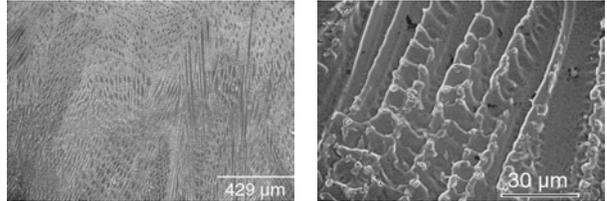
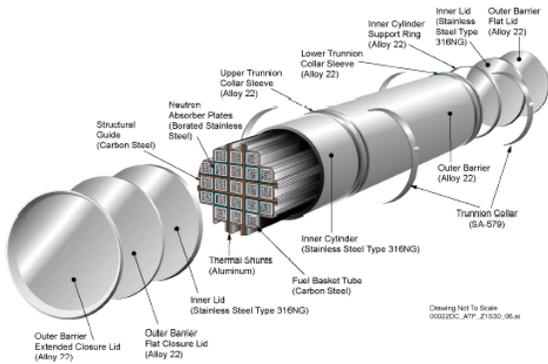


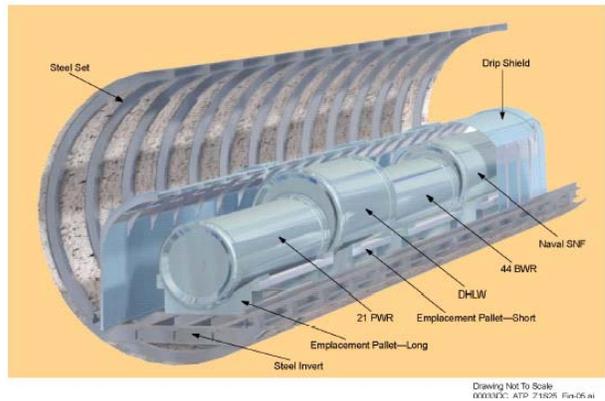
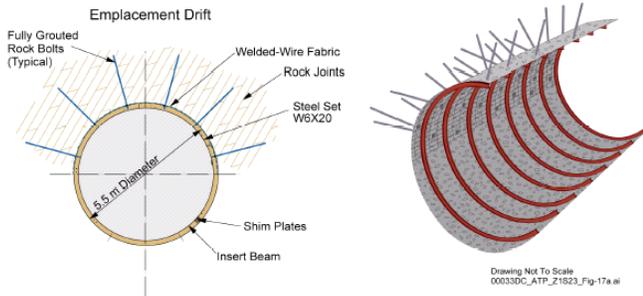
Figure 11-Montage of design and fabrication factors.

## Design and Fabrication Processes



Some Important Factors

- Materials of construction
- Metallurgical structure
- Residual stresses
- Welds of particular interest



## SELECTED RESEARCH OPPORTUNITIES

This report identifies research opportunities in both basic and applied areas. For each of the workshop topic areas, an overarching goal is presented along with selected research opportunities identified from the DOE Corrosion Workshop. Comments and findings are presented from the workshop for each topic areas in separate sections. The topic areas include:

- Life Prediction and Evolution of Corrosion Damage
- Evolution of Corrosive Environments
- Localized Corrosion
- Passivity
- Stress Corrosion Cracking
- Materials Stability and Aging
- Advanced Materials and Fabrication
- Methods and Tools

### Life Prediction and Evolution of Corrosion Damage

#### **Goal**

Quantum advances in state-of-the-art methodologies for life prediction and cumulative damage for highly corrosion resistant materials.

This is a primary theme expressed throughout the corrosion workshop and other gatherings of corrosion/materials experts. This is a special time for major advances, and the Yucca Mountain Repository provides an excellent platform for progress that can greatly affect a broad range of industry, government and public. The directions and approach for progress are clear, and a concerted-coordinated effort can realize great gains.

The goal of the Predictive Modeling portion of the workshop was to identify long-term research and technology development topics that could dramatically improve methodologies for predicting long-term materials performance and ultimately service life. Three general classes of reliability techniques exist. Two are “statistical” based and are often termed (1) probabilistic risk assessment (commonly used with nuclear power plants), and (2) traditional (or experimental) assessments. The third class of techniques is referred to as *computational reliability*, and is based on physical models and probability theory.

The computational-reliability methodology is the focus of the topic area section on Life Prediction presented later in this report. The common elements that an analytical toolset based on the computational reliability techniques must contain are identified.

The context is a presentation of goals to achieve a fully developed predictive capability using this technique. There are opportunities for major advances in life prediction, and a number of significant scientific issues still exist that were the subject of the other workshop topical sessions. Specific analytical tools have been identified whose advancement could produce much more effective and widely accepted predictive capability.

Selected research opportunities from the DOE Corrosion Workshop include:

- Improved (more robust) deterministic models for predicting the accumulation of corrosion damage
- Precise definition of the evolving environment and changes in material properties and characteristics
- Improved methods to validate the evolving process models; possibly using suitable less corrosion resistant analogs

- Develop and apply novel-experimental methods/equipment to support combinatorial and large designed experiments; large-array micro potentiostats; in order to interrogate and define multi-species environmental space at elevated temperatures, and to examine a wide compositional space for Ni-Cr-Mo and Ti alloys.
- Determination and validation of model input parameters
- Identify and develop suitable analogs for ALLOY-22 in long-term performance upon which corrosion phenomena can be effectively studied in laboratory time scales
- Methodologies to achieve more efficient computation times; transition to more computationally efficient mathematical frameworks and models (e.g., fully parallel)
- Application of cognitive techniques (e. g., neural networks) to identify relationships within databases (data mining)

### **Opportunity**

Develop a corrosion life performance model for passivity and localized corrosion of highly resistant alloys (Alloy 22 and Ti) capable of predicting damage evolution. Desirable elements within the damage evolution model would include intact film; single pit and crevice, local breakdown/repair; multiple, interacting events; crevice; local deposit; layer deposit (porous, ionic conductive, mixed ionic and electronic; and transition from localized corrosion to stress corrosion crack.

## **Evolution of Corrosive Environments**

### **Goal**

Develop an extensive knowledge base to include the relevant experimental data that would enable development of a robust model capable of predicting the evolution of aqueous solutions on metal surfaces.

The evolution of corrosion damage is determined by the combination of the corrosivity of the environment (evolving and potentially changing over time) and the corrosion resistance of the metals of construction. Advances to robust computational and experimental methodologies that enable the determination of the evolution of corrosive environments on metal surfaces over time are required in order to realize major advances to the determination of performance in real systems and over long times.

Understanding the evolution and trajectory of water compositions on metal surfaces is central to the determination of corrosion performance over the long-term. The work should focus on concentrated, multi-species solutions in the 80-150 C range. The directions and approach for this research are well defined, and a concerted-coordinated effort can realize great gains.

Selected research opportunities from DOE Corrosion Workshop:

- Enhanced thermodynamic databases for concentrated and high temperature solutions: activity coefficients, vapor pressures, gas solubility, ion/ gas mobility
- Silicate and brine interactions: kinetics of heterogeneous reactions, silicates/ brines at elevated temperatures
- Formation and stability of aqueous solutions on metal surface: condensation, vaporization, sorption, gas-liquid-solid interactions on metal surface
- Processes that lead to formation and control the environments in corrosion scale, dust, deposits, crevices
- Behavior in thin films and porous products/deposits
- Anodic stifling, e.g. formation of solid Mo and W compounds with time.
- MIC: determine corrosion response compared to abiotic behavior; effect of organic species; and then effect or behavior in thin layer electrolytes

## **Opportunity**

Combine expertise of geochemistry/hydrology with electrochemistry and corrosion experts. Develop an extensive experimental base and a robust model for the evolution of aqueous solutions on metal surfaces under relevant conditions. Coordinate with research on passivity and localized corrosion.

## **Localized Corrosion**

### **Goal**

Extend the knowledge base for highly corrosion resistant alloys such as Alloy 22 and titanium in thin electrolyte films. Enhance the theoretical and experimental foundations to enable a robust model for the time evolution of damage from localized corrosion. Include the processes that control corrosion stifling and arrest by repassivation.

Localized corrosion remains a most important damage process to be understood, predicted and controlled. Highly corrosion resistant metals are susceptible to damage in extremely harsh environments. There is a sound, scientific framework for understanding localized corrosion; however, there are also great opportunities to advance the state of knowledge. A more comprehensive knowledge of the relationship between alloy composition and complex environments is obtainable through the combination of emerging experimental, analytical and modeling methods.

An electrochemical approach to localized corrosion susceptibility based upon potential difference ( $\Delta E$ ), i.e. the difference between the corrosion potential ( $E_{corr}$ ) and the repassivation potential ( $E_{repass}$ ) is well founded in corrosion science. Where localized corrosion cannot be ruled out, further development of the understanding of propagation, stifling and arrest, and repassivation mechanisms can have a great impact on determination of the evolution of damage. Combined applications of Fault Tree-Analysis methodology and Damage Evolution procedures provide a promising framework for progress.

Research gaps and opportunities generally lie in the categories of improved understandings and conceptual knowledge in the areas of propagation and either repassivation or stifling of local corrosion. Other opportunities were for advanced tools to measure such phenomena, especially in thin electrolyte films, and models or predictive capabilities to predict behavior over time. Selected research gaps and opportunities identified at the DOE Corrosion Workshop include:

- Dissolution kinetics, propagation laws; and their extension to thin films
- Stifling, arrest, and repassivation mechanisms
- Examine propagation and stifling due to cathode limitations, anode/cathode separation, cathode areas and anode limitations, e.g. competition between neighboring local corrosion sites
- Identify the metallurgical “culprits” in local corrosion/aging
- Identify role of solid solution alloying
- Characterize alloy/film compositions in pits governed by kinetics
- Address specific environmental issues: effects of extrinsic (nitrate,  $Pb^{2+}$ ,  $F^-$ ) and intrinsic (S) species on local corrosion; organic acids
- Combinatorial and/or designed experimental approach to characterize a broad range of concentrated, multi-species solutions
- Understand cooperative interactions during local corrosion that may play a key role in stabilizing local corrosion

- Evolution of the corrosion potential ( $E_{\text{corr}}$ ) and repassivation potential for crevice corrosion ( $E_{\text{crev}}$ ) with time and as a function of alloy and environment

## **Opportunity**

Develop an extensive knowledge base for corrosion resistant alloys in thin electrolyte films that will enable development of a robust model for the time evolution of damage from localized corrosion. Extend experimental data base for corrosion resistant alloys for a wide range of environments as functions of T, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and other relevant species. Also extend to a range of alloy chemistry, microstructure and surface conditions. Include electrochemical measurements and analysis of mixed electrode reaction kinetics. Coordinate with research on passivity and environment. Develop a robust stifling and arrest model.

## **Passivity**

### **Goal**

Develop an extensive scientific foundation of passive film formation, growth and breakdown in corrosion resistant alloys to enable robust modeling of the formation, growth, stability, breakdown and repassivation of passive films including transpassive dissolution.

Stable passive films are the means of corrosion resistance of stainless steels, nickel alloys, titanium, zirconium and other passive metals. Progress in the understanding and long-term prediction of passive metal performance requires a multi-disciplinary set of expertise. Recent progress and advances in analysis of thin films, transport behavior in complex oxides, electrochemistry and computational methods provide an excellent foundation for major advances.

Selected research opportunities from the DOE Corrosion Workshop include:

- Coordinate framework to connect modeling efforts with experimental measurements.
- Create standardized databases on passive film properties to support modeling, data mining.
- Develop multiple length scale modeling efforts from atomistic to performance assessment.
- Develop computationally fast models to integrate over complex evolution path.
- Define reaction pathway and predict multi-layer surface films for passive corrosion in thin aqueous layers
- Link thermodynamics predictions to kinetic observations to characterize the composition, structure of films and in anticipated evolution with time
- Determine the role of pre-oxidized state (thermal treatments, dry/humid oxidation) on passive corrosion
- Create a link between the structure, composition and defect state of surface oxides subsequent electrochemical behavior; understand the influence of specific alloying elements and their distribution; influence of temperature and salinity on these processes
- Define the relationship between the open circuit potential and film stability.
- Identify the nature and source of heterogeneities in the alloy and oxide structure; grain boundary impurities and second phases, inter-metallic precipitates, and other metallurgical features
- Determine failure/repair processes and determine the temporal features of oxide repair events
- Elucidate processes at the oxide/alloy interface: segregation of impurities and other minor constituents; defect structures (vacancies, concentrations of impurities and alloying elements, integrated stresses); chemical evolution of the alloy at the alloy/oxide interface
- Define the chemistry in a thin film or a deliquescent layer in-deposit; chemistry versus bulk environment chemistry and incorporate this knowledge into the understanding of passivity

- Understand cation/anion selective absorption/transport processes
- Quantify the kinetics of oxidant/reduction processes on passive films: influence of passive film properties on oxygen reduction kinetics, kinetics of nitrate reduction

## **Opportunity**

Develop the fundamental foundations to understand passivity of corrosion resistant alloys in thin electrolyte films in order to enable corrosion life performance models for the passivity of highly resistant alloys (Alloy 22 and Ti). Coordinate with research on localized corrosion and evolution of the environment. Link thermodynamic predictions to kinetic observations to characterize the composition, structure of films and the anticipated evolution with time. Ultimately, link the findings to life prediction.

## **Stress Corrosion Cracking**

### **Goal**

Improve the fundamentals associated with stress corrosion cracking by resolving certain critical issues. Extend fundamental understanding towards highly corrosion resistant alloys to enable development of a robust model that is capable of describing the time evolution of damage from stress corrosion cracking.

Extend the capabilities to measure and predict at the low stress corrosion cracking growth rates that are relevant to slow growth over long periods of time. Advance the SCC theory and test methodology for treating slow, growth rate regimes. The control of residual stresses and avoidance of more susceptible microstructures are of key importance to SCC, and these issues are integrally linked with the manufacturing and fabrication processes. This effort requires the integrated efforts of design/fabrication engineers to define material and mechanical conditions and materials/corrosion engineers/scientists to advance modern SCC theory.

Selected research opportunities from the DOE Corrosion Workshop include:

- Improved mechanistic understanding to validate the film rupture model including crack tip strain rates and advancement in alternative models of SCC
- Evaluate the possibility of chemical reaction induced crack growth
- Elucidate environmental degradation mechanisms by unique nanoscale characterization of buried corrosion interfaces and stress corrosion crack tips: crack tip and oxide film
- Examine crack initiation processes, e.g. localized corrosion to crack transition,
- Develop more sensitive tools for utilization in accelerated corrosion that correlates with long term non-accelerated attack; high resolution crack growth measurement in cases where crack growth rate is not accelerated
- Advance tools for determination of local crack tip chemistry and local crack tip hydrogen concentrations
- Develop advanced “damage tolerant approaches” for assessment of stress corrosion cracking

### **Opportunities**

Improve theories of SCC, test methodologies and extend the same towards highly corrosion resistant alloys. Extend the common approaches of materials selection, design, and fabrication for stress corrosion resistance to include a damage tolerant approach for the evolution of stress corrosion damage by cracks should they occur.

## **Materials Stability and Aging**

### **Goal**

Extend current capabilities in computational materials science to more complex alloy systems and applications.

Major gains have been made in this area through the linkage of advanced computational modeling in solid state materials science, controlled exposures (e.g. long-term aging), coupled with careful experimental characterization of structure and composition.

Selected research opportunities from DOE Corrosion Workshop include:

- Extend the modeling of phase evolution to higher component systems, e.g. from Ni- Cr- Mo to Ni- Cr- Mo- W- Fe
- Enhance the kinetic database to understand time-temperature-transformation behavior
- Include geometrical effects on diffusion processes to account for microstructure characteristics
- Extend treatments to welds
- Incorporate effects of cold-work, increased dislocation densities on aging phenomena

### **Opportunity**

Major gains in computational modeling, extension of data base properties, controlled experimental exposures and careful characterization.

## **Fabrication and Advanced Materials**

### **Goal**

Achieve state of the art advances in the structure property paradigm such that the influence of fabrication on structure and the resulting materials behavior can be predicted. Pursue opportunities in advanced materials and material processing that might bring about radical improvements in materials reliability against environmental degradation processes.

Fabrication is a crosscutting issue that affects the corrosion, stress corrosion cracking and mechanical properties; and it has a major effect on the costs. Welds, cold work and forming processes, and surface condition are important considerations.

Selected research opportunities from DOE Corrosion Workshop include:

- Determine the effects of welds on metallurgical stability and performance
- Determine the effects of cold work on corrosion and stress corrosion behavior
- Multiple fabrication steps pertain in many applications, and the cumulative effects of the individual processing steps, govern the performance and cost.
- Advance methods to account for variability from fabrication on performance
- Advance methods to account for an as-fabricated condition (i.e., residual stress distribution, microstructure, and compositional inhomogeneity) on SCC, mechanical failure, and corrosion
- Develop a Damage Evolution approach that is capable of capturing and evaluating the effects of surface condition and fabrication processes on damage evolution.

## **Opportunity**

Promote integrated efforts of design/fabrication engineers to determine the effects of fabrication on structure and composition and relate these to materials performance and corrosion. Multiple fabrication steps pertain, and the cumulative effects of the individual processing steps govern the performance and cost. Develop relationships to understand how these factors affect properties.

## **Methods and Tools**

## **Goal**

Extend and adapt advances in the state of the art surface science, electrochemical and metallurgical approaches to advance the understanding of the corrosion behavior of corrosion resistant alloys and to advance the modeling of damage accumulation. In the areas specified above, many of the required goals are presently difficult to achieve without further developments in experimental methodologies and computational approaches. Close collaboration with experts outside the area of corrosion science is required for advances in this area.

Selected research opportunities from DOE Corrosion Workshop include:

- Develop *in-situ* techniques to examine oxide film in aqueous environment, high temperatures (Raman, polarized ellipsometry, various scanning probe tools).
- Develop high-resolution spectroscopic techniques.
- Develop an oxygen and ion mobility database
- Extend electrochemical measurements in “marginal electrolytes”-- *in situ* techniques.
- Develop imaging methods for high info density measurements, e.g. scanning electrochemical probes.
- Examine canary alloys (metals with less corrosion resistance) and apply combinatorial methods to improve understanding of alloying effects.
- Conduct model testing-studies for model verification, studies aimed at parameter generation.
- Apply and extend *In-situ* IR spectroscopy, *In-situ* synchrotron, Local (AFM based) chemical probes, *In-situ* 3- D neutron imaging, Synchrotron x-ray microtomography, speckle interferometry, electrochemical imaging, sum frequency generation spectroscopy
- Examine thin film micro-fabricated structures to increase sensitivity and localize crack growth
- Develop mechanisms–alloy discovery through the use combinatorial techniques

## **Opportunity**

Advance techniques to increase fundamental knowledge with emphasis on methods that will support the development and validation of predictive models that can forecast damage evolution. Co-opt expertise from areas such as chemistry and physics.

## TOPIC AREA GOALS AND OPPORTUNITIES

Comments and findings from the workshop topic areas are presented in the following sections. Each group provided input in somewhat different formats; however, the common intent was to identify research opportunities for major advances in corrosion science and the long-term prediction of materials performance.

The following topic areas are included:

- Life Prediction
- Evolution of Environments
- Localized Corrosion
- Passivity
- Stress Corrosion Cracking
- Material Stability and Aging
- Fabrication and Advanced Materials
- Methods and Tools

# **Predictive Modeling of Life and Materials Performance**

Digby Macdonald and Jeff Braithwaite with John Beavers,  
Joe Farmer, Russ Jones, John Scully, J. Woods Halley and David Shoesmith

## **Introduction and Background**

The goal of the Predictive Modeling portion of the workshop was to identify long-term research and technology development topics that could dramatically improve methodologies for predicting long-term materials performance, damage accumulation and ultimately service life. To better understand the issues associated with this topic, some background information on how the time-based reliability of complex systems is mathematically calculated is instructive. Three general classes of reliability techniques exist. The first two are “statistical” based and are often termed (1) probabilistic risk assessment (commonly used with nuclear power plants), and (2) traditional (or experimental) assessments. Both of these are typically based on the collection of a large number of samples or observations involving failure data from both field (historical) and accelerated (stress) testing. Metrics include failure rate and mean-time-to-failure. Their prime deficiency is their empirical nature, which means that the resultant findings apply to the existing condition of the system and provide a snapshot of its reliability characteristics at the time of sampling. Extrapolation to other possible environmental conditions and clearly to greatly extended service lifetimes is dubious. Importantly, physics-based analyses are difficult to include in these statistical methods. The third class of techniques is referred to as (3) computational reliability, and is based on physical models and probability theory. The techniques utilize certain random or statistically distributed variables to describe uncertainty in physical models. The prime deficiency is that extensive resources are required to develop the assessment toolset.

The computational-reliability methodology is the focus of this section, and the following discussion is in the context of goals to achieve a fully developed predictive capability using this technique. There are opportunities for major advances in life prediction in corrosive processes, and a number of significant scientific issues still exist that were the subject of the other workshop topical sessions. Specific analytical tools have been identified whose advancement could produce much more effective and widely accepted predictive capability. Some of these developments are quite formidable and long-term in nature. To permit the prime development issues to be understood, a brief philosophical-type discussion is first presented of the common elements that an analytical toolset based on the computational reliability techniques must contain.

## **Elements of the desired predictive toolset**

A number of important technical, philosophical and practical issues exist when attempting to predict the future behavior of complex physico-chemical systems such as waste isolation containers at Yucca Mountain. These issues are not just of academic interest, but can have profound impact on public perception and acceptance. From a strictly technical standpoint, the ultimate solution for materials performance and life prediction would be to develop a completely rigorous and robust analytical toolset that mechanistically accounts for every possible corrosion process and environmental condition that could occur over time in each and all components. The basic mathematical approach that would lead to this highly desirable “bottom-up” capability is relatively straightforward and would consist of the integration of the three computational elements: corrosion process models, a mathematical framework that permits uncertainty/variability to be addressed, and an overarching model for performance assessment that allows system-level failure/reliability to be quantified. The concurrent mathematical integration of these elements would ensure that the myriad of possible degradation and environmental interdependencies are all explicitly addressed.

In the first element, the set of deterministic corrosion process models is required to describe every form of materials degradation (e.g., uniform corrosion, localized corrosion, and environmentally assisted cracking) that would affect a change in the ability to perform the desired isolation function. The degradation models can operate alone or in concert with others to degrade performance, accumulate damage and ultimately cause system failure. Importantly, for this capability to be truly predictive, these materials models must have a physical, mechanistic basis, preferably using first principles. The important feature of determinism is that the solution to the constitutive

equations is constrained to that which is physically meaningful by invocation of the natural laws, which are presumed to hold over the desired time period of interest. Ultimately, predictive description of the microscopic processes leading to corrosion must be based on detailed deductions from the fundamental quantum mechanical laws of nature. Though in corrosion processes this is a formidable task, some very substantial progress in this direction has been made in recent years. For example, by linking continuum finite element calculations with atomistic molecular dynamics calculations and quantum mechanical density functional calculations, a group at the University of Southern California recently simulated an entire stress corrosion cracking process in silicon. Long term success in this direction depends on identification of the rate limiting atomic and electronic events (because the entire system cannot be simulated at the electronic and atomic levels), on refinement of the algorithms which link the calculations at different scales and on improvement of algorithms which scale linearly with the numbers of atoms and electrons (to speed the electronic calculations).

The explicit inclusion of the second toolset element (algorithms to address the uncertainty and variability inherent in many material properties and the operating environment) is also a mandatory toolset element. Even under the most desirable situation, uncertainty and variability will exist (e.g., temperature, alloy composition). To properly illustrate this need, consider the simple case of a containment vessel that is susceptible to three types of localized corrosion. The damaged area increases gradually with time as corrosion proceeds. At some time, a critical amount of damage is reached, and the container will no longer provide its isolating function as desired. A straightforward deterministic calculation would yield a service-life prediction based normally on average properties. However, if the real-world uncertainty is included in the analysis, a distribution of predicted damage sites with specific values (i.e., the “damage function”) can be calculated at each time. The tail of each distribution that is above the critical voided area could represent the probability of failure at that time, which typically occurs at times much shorter than calculated using average values. In high-reliability systems, such as Yucca Mountain, failure may become unacceptable when only a small tail of the distribution exceeds a small critical value. Another very important point to make is that the failure criteria for each area on a container will, in general, be different for each specific location (because of potential differences in the environment, the underlying metal structure, etc.). Therefore, the output from the integrated corrosion model can really only consist of time-based distributions of changes in some metric (e.g., damage area) and not a failure probability, unless the property distributions across the surface can be effectively described. The key enabler of this needed capability involves the development and use of very efficient algorithms that permit parameter uncertainty and variability to be wrapped around the deterministic corrosion process models.

Two needs exist that require the integration of the output from the deterministic/uncertainty analysis with a system-level performance assessment model (3<sup>rd</sup> element). Firstly, because corrosion is the environmentally induced degradation of metals, a precise spatial and time-based definition of the environment is critical. The bane of corrosion engineering is that often such definitions are not available. The performance assessment model must therefore have a highly sophisticated ability to predict the localized and time varying environmental conditions. The corrosion evolutionary path (CEP) is a related term that involves the identification of the variation of environmental parameters that impact the corrosion rate and hence the accumulated damage as a function of time. Included are such parameters as temperature, pH, [Cl<sup>-</sup>], potential, and ionic strength (that affects solubility of oxygen and ion activity coefficients). Contact of the electrolyte film with the corroding surface as a function of time must also be incorporated. The effective definition of the corrosion evolutionary path will require the integration of sophisticated water chemistry/geochemical codes into the performance assessment model for both the adsorbed water films and other relevant environments. An additional need is a comprehensive database for the thermodynamic properties of ionic species in concentrated electrolyte solutions. Secondly, system failure cannot be determined solely based on waste package corrosion behavior. That is, system failure (and thus decreased reliability) only occurs within the context of the system performance itself. That is, specifically for Yucca Mountain, the radionuclide release and transport is affected by many processes in addition to corrosion (e.g., species transport). Besides the environmental model, the performance assessment model must therefore include fully deterministic, age-aware models of all the other relevant processes. As such, a mathematical linkage between critical aspects dealing with scientific understanding for a wide range of potentially relevant degradation modes and complex environments is identified and maintained all the way up to the system level.

## **Critical unresolved scientific and/or technological opportunities**

Two general types of significant technical issues are barriers to progress in life prediction modeling and the development of a more rigorous toolset for prediction: (1) properly formulated deterministic process models and (2) effective integration of the three elements of a comprehensive toolset at length scales that reduce the need for wholesale model abstraction, but yet can be computationally solved. To address both of these issues, a process to use the evolving predictive toolset and supporting experimental studies to guide the toolset development process itself is needed. That is, an improved capability is needed to perform effective sensitivity studies to dramatically improve the utilization of available knowledge and resources. Each of these general deficiencies is discussed separately in this subsection.

### **Formulation of proper deterministic models for all relevant corrosion and environmental processes**

There are a large number of directly coupled environmental, species transport, and materials degradation processes that can occur within the corrosion evolutionary path that need to be characterized at some level (e.g., fundamental, phenomenological, empirical). As examples, consider the following list, each of which can impact component service life:

- General environment as  $f(\text{time})$ 
  - temperature
  - amount of water and moisture
  - water chemistry
- Localized “micro” environment as  $f(\text{time})$ 
  - All the above
- Water and species transport
- Water adsorption
- Corrosion processes
  - general
  - pitting
  - crevice
  - SCC
  - MIC
- Metallurgical effects

The goal is for our understanding to be sufficient to completely formulate robust, validated, deterministic process models that have a physical basis. The other topical sessions in this workshop addressed how to gain this dramatically improved understanding of the majority of these processes and their findings demonstrate the associated significant technical challenges.

### **Code complexity including length-scale discrepancy**

The length scales between the important physical processes and the dimensions of the engineered components vary widely. As an example, consider general atmospheric corrosion where electrochemical processes are occurring in adsorbed water layers that are  $< 10$  nm thick. However, the engineered components have dimensions of interest on the m, cm and mm scale. Clearly, corrosion processes cannot all be modeled at the nm level because millions of finite elements would be required to cover non-uniform conditions that can occur on large or complex engineered structures. But, even when these “sub-grid” nm processes are rolled up in constitutive equations at, for example, a  $\mu\text{m}$  level, convergence of the numerical solution can be achieved only when the time steps are sufficiently small. This situation will dramatically impact computational requirements. Clearly, the entire corroding system cannot be

modeled with atomic resolution at the sub-nanometer level because systems on a cm scale involve numbers of atoms of the order of  $10^{23}$ . The key to microscopic prediction must thus be the identification of rate limiting processes which depend on atomic and electronic dynamics and which can be modeled precisely from first principles. The current practical limits for atomic calculations are about  $10^6$  atoms and for electronic calculations, about  $10^3$  electrons. By identifying rate limiting steps, the atomic and electronic calculations can be limited to calculations of these feasible orders of magnitude (which are increasing yearly) if they are correctly linked to finite element calculations on larger scales. There is currently a great deal of work in several fields on such multi-scalar calculations and the corrosion community should be able to profit from the advances. Recently Vashista, Kalia and coworkers put together a code and carried out such a multi-scalar simulation of a stress corrosion cracking event in silicon using linked computers in California and Japan and implementing finite element (FE) and molecular dynamics (MD) codes developed at USC with DFT codes developed by a Japanese team [Rachid, et al., 2002]. Such calculations, involving thousands of parallel processing links, represent the future potential for truly predictive corrosion science as well as studies using more phenomenological and more easily implemented models which are currently available and in use. The computational demands are then truly compounded by the coupling with the performance assessment model code that is required for proper environmental definition, species transport behavior, and transfer of corrosion damage results. For the desired code execution, the performance assessment model calculations must be performed as a function of time with the corrosion voiding properties of each component also changing as a function of time, as specified by the integrated corrosion model. Finally, there is the computational impact of including uncertainty around the deterministic calculations

An incentive related to computational speed exists for developing composite numerical/analytical algorithms; in which as much as possible of numerical computational functions are replaced by approximate analytical solutions. The decision that has to be made is whether the loss in predictive precision is justified by the gain in speed. A good example of where this has been done is in describing the potential distribution down a crevice that is coupled to processes occurring on the external surfaces. The numerical solution of Poisson's equation is a very lengthy process, because of the small steps required. However, high speed, approximate analytical solutions have been developed that yield results that are imperceptibly different from those given by the lengthy numerical codes. As a second example, the deterministic Coupled Environment Fracture Model (CEFM) was originally developed as a numerically-driven code for calculating crack growth rate for Inter Granular Stress Corrosion Cracking (IGSCC) in Boiling Water (nuclear) Reactor (BWR) primary coolant circuits [Macdonald, Lu, Urquidi-Macdonald and Yeh, 1996]. Later, an approximate analytical solution was developed to the problem, resulting in a decrease in the computational time by a factor of  $10^5$  to  $10^6$ , without significant loss of accuracy. [Engelhardt, Macdonald and Urquidi-Macdonald, 1999.]

The issue of the level of detail that is required in a physical model for each type of relevant corrosion process that is being included is often overlooked. The simple answer to this question is that sufficient detail should be included to capture the physics of the system at the relevant length scale. An alternative would be the use of somewhat empirical "abstraction" models, but then the ability to include process interdependencies (i.e. environment/ corrosion/ transport) is lost and, in some cases, so is the mandatory physical basis. It is clear, then, that modeling and in particular deterministic modeling is always a compromise between what is desired and what is possible. However, work that is ongoing will ensure that computational techniques become faster and more efficient leading to the ability to incorporate greater detail into models and hence to make more precise prediction, provided that the theoretical basis remains valid.

### **Sensitivity studies driven by system-level requirements**

The question of how to most efficiently deploy limited resources is a third major challenge that must be addressed. In general, a system-requirement driven (top-down) approach is the most effective. However, some degree of incompatibility exists between this and the needed bottom-up, rigorous approach desired for the toolset itself. Some aspects of the conflicting needs associated with ongoing decisions related to resource allocation are presented below. The cost of acquiring reliable data typically increases with component complexity. That is, it is cheaper to purchase, test and analyze discrete engineered components in the laboratory than the entire system in an operating, service environment. At the system level alone, confidence is limited, because the population often cannot be properly sampled. Unfortunately, testing cannot only be performed at the materials or component level, because of the increasing level of uncertainty associated with unknown effects (e.g., environmental) and interdependencies.

Similarly, there has been an increasing reliance on computer simulations to augment physical experimentation. However, in addition to trying to characterize the uncertainty in relevant parameters, such as environment and material properties, the analysts must also account for the uncertainties introduced by the mathematical abstraction inherent in the simplified process models. As such, proper attention to verification and validation of the analytical models becomes critical.

A balance must be obtained between the information gained from testing and modeling at various levels of system indenture, the resources required for performing testing and developing models, and the uncertainties introduced in predicting system performance. The ability to logically combine information from these various areas as well as the organization, characterization, and quantification of this myriad of uncertainties are critical aspects that the chosen model development approach must include. Importantly, although the ultimate objective is to obtain accurate predictions, real merit exists for simply obtaining more robust solutions than are presently possible (i.e. just improving our confidence in the estimates of useful life).

The advantages and limitations of using a top-down analytical approach for determining optimum allocation of resources can be illustrated by considering how Bayesian statistical techniques can be incorporated into the system-level analytical framework. The prime advantage of the Bayesian methodology is its demonstrated ability to improve the efficiency of the development process [Gelman, Carlin, Stern and Rubin, 2000; Robinson, 2001]. This gain is possible, because of its required system perspective, the effective use of sensitivity studies and engineering judgment, and the direct mathematical incorporation of information from many different types and levels of sources. Specifically, hierarchical Bayesian methods are particularly suited to this latter capability, in that relationships between test articles can be explicitly included in the analysis. Classical Bayesian methods assume that the articles under test are not related in any manner, even though the articles may be identical.

In particular, the use of the modern hierarchical methodology will permit relevant expert opinion, materials aging, field reliability data, and laboratory failure data to be codified and merged. For example, if laboratory experiments and detailed mathematical simulations are too expensive, empirical models based on data from field measurements and/or component and subsystem testing can drive model refinement. In addition, this methodology has the capability to address both failures due to aging effects and random failures due to unaccounted for latent defects. An example of this approach is the development of Artificial Neural Networks to calibrate/validate deterministic models [Macdonald, and Urquidi-Macdonald, 1995]. ANNs are ideal for this purpose, because they do not contain any preconceived physical or mathematical (functional) model and, when operating in the pattern recognition mode with supervised learning, are capable of defining highly non-linear, coupled relationships between the dependent and independent variables in the database for a complex system. The great advantage of this method, besides not being constrained by preconceived dependent/independent variable relationships, is that the process is not dependent on the results of a single study or even whether that single study measured the dependent variable as a function of all of the independent variable, provided that the database is sufficiently large. Finally, it is important to distinguish an ANN from an Expert System; the latter contains preconceived rules (the “opinions” of experts), which may or may not be true (unlike the natural laws that are used in a deterministic model, which are universally true). Thus, the danger with an expert system is that dependent/independent variable relationships may be obscured by the preconceived rules.

In developing a modern hierarchical methodology, initial estimates of how corrosion affects service life are formulated primarily using expert opinion and engineering judgment. This paper-type study effectively replaces the first stage of detailed model-development activities. The resulting and typically empirical equations obtained by this method are input into some level of performance assessment model. The apparent sensitivity of the system service life to specific materials degradation processes can then be determined. This type of system-level analyses provides more quantitative understanding about which types of materials aging processes probably contribute most strongly to system failure. Additionally, the sensitivity study results are coupled with additional expert opinion to improve the initial model formulations. This information is then analyzed to identify aspects of materials aging where an enhanced definition/quantification would provide optimal benefit at minimal cost. To aid the model refinement process, results from accelerated-aging studies at the component level can be used in conjunction with traditional lab and field degradation data.

Critically, resources must be focused into very selected and specifically identified areas to develop the deterministic “physics of failure” basis required for a truly predictive capability. The information produced by the

deterministic models is combined with data from a broad range of related sources, including (1) experimental results from the literature and previous investigations, (2) laboratory materials experiments, (3) laboratory “component level” testing, and (4) historical field-aging data from relevant subsystems with similar designs. This collective knowledge base is then used to refine and improve the initial “skeleton” model and this process is iteratively continued. Often, the translation from the materials physics model to the improved skeleton model requires higher-level performance assessment model simulations and/or the inclusion of expert opinion.

Importantly, if this type of iterative refinement loses focus, the process will tend back towards the simple bottom-up rigorous solution and thus the development process may become unacceptably costly and time consuming. To avoid this situation, significant attention must be paid to keep the scope and detail of the material model refinement to a minimum by performing frequent iterations with the system-level performance assessment model. That is, the system-level model will be used to reveal the changes in (system) sensitivity after the new (skeleton) models are employed.

Although the identification of a high-level process to develop the desired analytical capability is conceptually straightforward, achieving success certainly is not. The formidable nature of this activity is the result of several factors including the “soft” reliance on expert opinion (not receptive to rigorous analysis), the existence of a wide range of diverse requirements that must be incorporated, and the need for the toolset to have a very computationally efficient framework.

### **Summary position**

Recognizing its formidable nature, a “bottom-up” rigorous corrosion model should still be pursued. However, it is recognized that, even with the composite analytical/numerical codes that result from the needed “top-down” system-driven analyses, greatly enhanced computational power will be required eventually to capture all of the significant aspects of relevant corrosion phenomena.

### **Research opportunities**

The primary opportunities for long-term research are associated with (1) formulation of proper deterministic models and associated quantification of needed modeling parameters, and (2) the identification, development and validation of a new analytical strategy with an improved computational framework for predicting long-term service life of engineered structures. The specific aspects of each of these topical areas that were discussed at the workshop are described in this section. Other topical sessions in this workshop were structured to address the mechanistic underpinnings, identify novel techniques to better characterize the corrosion mechanisms, and identify information required in a proper environmental definition. Importantly, the primary output from all of these related activities flows directly into the enhanced lifetime prediction models. Given this, the intent of this section is to focus primarily on those aspects that specifically relate to predictive modeling. Nevertheless, before the specific gaps in modeling are discussed, a few specific needs that were identified in the modeling session and involve the other topical areas are worth noting:

- The phase space of susceptibility to local corrosion based on fundamental models.
- Induction time until initiation of localized corrosion given actual time-based environmental changes, in addition to oxide aging and micro-structural evolution.
- Prediction of corrosion propagation that includes the corrosion evolutionary path with transient nature of local chemistry and ohmic potential drop along with stifling (delayed repassivation) and arrest of localized corrosion.
- Further refinement of theories to enable prediction of initiation and propagation as a function of environment and alloy and that can span length scales

## **Corrosion-process models and model parameters**

The core of the desired predictive toolset consists of deterministic, physics-based models of the relevant corrosion and environmental processes. Of note, the computational efficiency and complexity considerations of the overall mathematical framework must be taken into account in the formulation of these models. Factors include the large number of physical and chemical processes that are involved in corrosion reactions, the differences between component and process length scales, the large number of required computations that often will be multi-dimensional, and the need to sometimes include moving boundaries. Taken together, these factors will probably force the ultimate use of continuum-level models in which the real mechanistic processes occur at a length scale much smaller than that associated with any finite elements used. Nevertheless, the ultimate goal is to develop deterministic models that capture the mechanistic essence of the damaging processes, that require minimal calibration, and that can be used (possibly within the continuum models) to predict the evolution of corrosion damage over the requisite time to within the required engineering accuracy.

In addition to the opportunities associated with specific aspects of deterministic model development, two non-traditional types of activities were identified that should be considered in more detail:

- Create the opportunity and resource environment that will encourage the development of new deterministic models for predicting the accumulation of corrosion damage, and
- Identify how to properly validate these process models, possibly by using suitable, less corrosion-resistant analogs for which corrosion phenomena can be effectively studied in laboratory time scales.

## **Specific deterministic process models**

General corrosion: An example of a deterministic model for general corrosion is the General Corrosion Model. This model is based on the Mixed Potential Model that was previously developed for calculating corrosion potentials and general corrosion rates of Type 304 SS in Boiling Water Reactor primary coolant circuits [Macdonald, 1992]. Under simplified aggressive conditions, it yields reasonable values for the accumulated damage and a corresponding average corrosion rate. There are a number of ways in which this model can be significantly improved. First, the passive film is assumed to comprise only of the barrier layer and no account is taken of the formation of the outer layer via the precipitation of oxides, hydroxides, and oxyhydroxides at the barrier layer/solution interface. The outer layer may also contain alien species (e.g., mineral salts) that are incorporated as it forms on the surface. In any event, the formation of the outer layer may result in the corrosion rate being considerably reduced, particularly at long exposure times, by restricting access of the cathodic depolarizer (e.g., O<sub>2</sub>) to the surface, or by inhibiting the dissolution of the barrier layer, or both, thereby leading to a reduction of the accumulated damage. This is a possible explanation of the steady decrease with exposure time in the corrosion rate of passive metals in many applications. A second aspect that requires attention involves the role of the barrier layer in the kinetics of the cathodic reactions. Thus, current charge transfer theory posits that the transfer of charge carriers across a passive film occurs by direct or indirect quantum mechanical tunneling of electrons or electron holes, the probability of which is a very sensitive function of the potential profile and barrier layer thickness. Thus, any realistic calculation of the tunneling probability, and hence of the exchange current density, for a redox reaction (e.g., O<sub>2</sub> reduction), will require significant revision of current charge transfer theory.

Localized corrosion: The theory for passivity breakdown, in the form of the Point Defect Model [Macdonald, 1999] and the prediction of accumulated localized corrosion damage in the form of Damage Function Analysis [Macdonald, Engelhardt, Jayaweera, Priyantha and Davydov, 2003] have been developed and tested. However, the current theory addresses only constant environmental conditions and hence is not ideally suited for calculating the nucleation rate of pits along a corrosion evolutionary path where the conditions change with time. The road to generalizing the models to accommodate variable conditions has been examined and defined, and no major impediments to modifying the current theory to accomplish that task have been identified. Furthermore, methods have been developed recently for examining the role of aggressive species, such as Cl<sup>-</sup>, in great detail and, when applied to passivity breakdown on nickel in chloride-containing solutions, confirmed that chloride ion catalyses the ejection of cations from the barrier layer with the concomitant generation of cation vacancies. Because Alloy-22 is a nickel-based alloy, albeit one whose passive film at low voltages is n-type in electronic character, rather than p-type, as is that on nickel, it is expected that the mechanism of passivity breakdown will be the same,

but this needs to be demonstrated experimentally. It is important to note that the passive film on Alloy-22 becomes p-type at voltages above about 0.6 V<sub>she</sub>, a voltage that appears to be inaccessible under open circuit conditions. Also, while the current, “coupled environment” models for pit (and crack) growth are highly deterministic and are well founded in electrochemical, dilute solution, and mass transport theory [Engelhardt, Macdonald and Urquidí-Macdonald, 1999], they need to be rendered more sophisticated by the inclusion of concentrated solution theory, for example. Perhaps the greatest needs are the development of firm theoretical bases for prompt repassivation (meta stable pitting) and, in particular, delayed repassivation (“stifling”). That delayed repassivation, which describes the death of stable pits, has a profound impact on the development of localized corrosion damage is clearly evident from simulated damage functions [Macdonald, Engelhardt, Jayaweera, Priyantha and Davydov, 2003]. There is also the need to incorporate and cope with initiation of corrosion at microstructural heterogeneity’s.

Environmentally Assisted Cracking: The key aspects relative to a predictive capability for environmentally assisted cracking are covered in the Stress Corrosion Cracking section of this report. No additional relevant information on this subject was identified in the modeling sessions.

### **Modeling parameters: kinetic, physical, thermodynamic and environmental**

A critical, but sometimes overlooked, requirement is that all the parameters associated with the final predictive models must be precisely characterized, including those that contain uncertainty. Often, this process is much more difficult and resource intensive than the formulation of the models themselves. All of the deterministic models require that values for various model parameters be determined by independent experiment or calculation, if possible. If that is not possible for any given parameter, then the value may be determined by calibration of the model against other dependent variables and independent variable combinations. For example, all but one of the parameters contained within the Point Defect Model, which yields the metastable pit nucleation rate, may be determined using electrochemical impedance spectroscopy. In addition to the obvious kinetic, physical property, and environmental parameters, thermodynamic properties for many species may also have to be re-determined experimentally, particularly those involved in complex equilibria involving mineralogical species at elevated temperatures and at high concentration.

The specific opportunities that have to be explored in concert with the model development process involve how to properly quantify these model input parameters. One potentially attractive option involves the application of cognitive techniques (e.g., neural networks) to identify dependent-independent variable relationships within existing and future empirical databases (data mining). The use of Artificial Neural Networks operating in the pattern recognition mode and trained under supervised learning protocols could lead to the identification of mechanistic information, that may otherwise be missed because of the multivariate nature of the problem, and complex, non-linear relationships between the dependent and independent variables. These relationships need to be carefully defined by using the most advanced cognitive techniques. Once defined, the relationships need to be used to assess various existing, deterministic models for predicting the dependent variable and to guide the modification and development of more advanced models. The artificial neural networks may be used themselves to predict damage; their advantage in the empirical sense being that they do not contain any preconceived mathematical or physical model. Finally, artificial neural networks are powerful tools for assessing the relative importance of various independent variables and hence for recognizing where emphasis should be placed in experimental programs and model development.

### **System-driven analysis strategy and improved computational framework**

With the clear recognition that a rigorous “do it all” predictive toolset that includes all process models and needed parameters will be difficult to fully attain, an alternative code development approach must be defined and implemented that will allow the necessary deterministic process models to be identified, efficiently formulated, and then subsequently incorporated into a mathematical framework that can be solved using modern computing resources (i.e. a much more computationally efficient, fully parallel code). (1) The first driver involves prioritization of the needed work using an “importance analysis.” With this approach, decisions are based on the probability and potential severity of the related consequence at the accessible environment. That is, compromise of

selected barriers must be allowed to permit a consequence to occur. (2) The capability must exist to incorporate relevant information from all available sources (e.g., scientific discovery, natural analogs, field observations).

The final system-level consideration is the need for a more computationally efficient mathematical solution framework. Solving this deficiency is the true key to the required mathematical integration of the detailed corrosion process, species transport, and environmental definition models that, in turn, will permit both the explicit inclusion of interdependencies and a time variant response. By explicitly addressing the significant corrosion process interdependencies, some of the sources of non-conservative assumptions in the current life-prediction models would be eliminated. Otherwise, empirical-type abstraction models will still have to be used. Also of importance, this advancement could reduce the need to constantly invoke the approach of applying some of the very conservative assumptions which would permit much more realistic assessments.

### **Potential Impact of the Research**

Advancements in life prediction and materials performance modeling can benefit the Yucca Mountain Repository and several other DOE and DoD activities that involve effective predictive lifetime models for complex systems (e.g., aircraft, weapons). The primary benefit of improved life prediction modeling is a dramatically increased confidence in the ability of engineered structures and systems to perform their intended function. The implementation of a new, more effective approach could lead, in the end, to substantially reduced technology development, service analysis and characterization, and component fabrication costs. For example, if the lifetime analyses show that the design is overly conservative, substantial capital costs may be realized, because the use of lower cost materials may be justified.

### **References for Predictive Modeling of Life and Materials Performance**

Engelhardt, G.R., D.D. Macdonald and M. Urquidi-Macdonald, *Corrosion Science*, 41, 2267, (1999).

Engelhardt, G.R., D.D. Macdonald and M. Urquidi-Macdonald, “*Development of Fast Algorithms for Estimating Stress Corrosion Crack Growth Rate*”, *Corrosion Science*, 41, 2267-2302, (1999).

Gelman, A., J. Carlin, H. Stern and D. Rubin, *Bayesian Data Analysis*, Boca Raton, Chapman and Hall/CRC, (2000).

Macdonald, D.D., *Corrosion*, 48(3), 194, (1992).

Macdonald, D.D., G.R. Engelhardt, P. Jayaweera, N. Priyantha and A. Davydov, “*The Deterministic Prediction of Localized Corrosion Damage to Alloy C-22 HLNW Canisters*”, *Proc. European Corrosion Fed*, in press (2003).

Macdonald, D.D., P.C. Lu and M. Urquidi-Macdonald, “*The Use of Neural Networks in the Prediction of Damage in Water Cooled Nuclear Reactors*”, *Proc. International Symposium on Plant Aging and Life Prediction of Corrodible Structures/95*, 1-7, (1995), NACE International, Houston, TX.

Macdonald, D.D., P.C. Lu, M. Urquidi-Macdonald and T. K. Yeh, “*Theoretical Estimation of Crack Growth Rates in Type 304 Stainless Steel in BWR Coolant Environments*”, *Corrosion*, 52(10), 768-785, (1996).

Belkada, Rachid; Ogata, Shuji; Shimojo, Fuyuki; Nakano, Aiichiro; Vashishta, Priya; Kalia, Rajiv K., “*Mechanisms of Stress Corrosion Cracking in Si: A hybrid Quantum-Mechanical/Molecular-Dynamics Simulation*,” *Materials Research Society Symposium - Proceedings*, 750, 2002, p 531-536, and unpublished reports

Robinson, D., “*Hierarchical Bayes Approach to System Reliability Analysis*,” SAND2001-3513, Sandia National Laboratories, Albuquerque, NM, (November 2001).

## Evolution of Corrosive Environments

Rob Kelly with Greg Gdowski, Steve Dexter, Roger Newman, Joe Payer, Peter Scott

### Introduction

The evolution of corrosion damage is determined by the combination of the corrosivity of the environment (evolving and potentially changing over time) and the corrosion resistance of the metals of construction. Advances to robust computational and experimental methodologies for the determination of the evolution of corrosive environments on metal surfaces over time are would lead to the realization of major advances in the determination of performance in real systems and over long times.

### Background: Corrosive Environments Approach by the Yucca Mountain Project

For Yucca Mountain, the approach to determining the possible corrosion environments on the waste packages is to combine results from thermal-hydraulic-chemical modeling for a range of scales (mountain, near field, drift) with thermodynamic calculations of the geochemistry and experimental measurements of solution composition as a function of evaporation. In the limit, this approach would lead to an infinite number of solution compositions to be investigated with regards to corrosivity if each ion was considered an independent variable.

To surmount this challenge, the chemical divides concept [Garrels, 1967; Eugster, 1978] can be used to group solution into categories based on chemical similarity described by a small number of major ions. The power of this standard approach is that the evolution of a solution during evaporation can be predicted with knowledge of the initial dilute water composition. The chemical divides approach and the geochemistry of multi-species solutions can be used for evaluating the plausible extremes of the chemical composition of the aqueous solutions that develop on the waste package [Gdowski, 2001].

Testing in environments has focused on the use of concentrated simulated waters. Evaporative concentration effects have been simulated by increasing concentrations of the species. In addition, solutions with substantially lower and higher pH have been studied [Estill, 1998]. Testing is conducted over a range of temperatures. The boiling point of pure water at the elevation of Yucca Mountain is 96°C; however, concentrated salt solutions can exist at considerably higher temperatures. Coordinated evaporative concentration and evaporative drip corrosion tests have been conducted in which simulated waters are dripped onto hot metal specimens to better define plausible extremes of the environments that develop on waste package and drip shield surfaces.

Summary comments regarding the environments relevant at Yucca Mountain include:

- Fully immersed conditions on metal surfaces are not relevant to waste package performance. Waste packages are placed in the unsaturated zone of rock some 300 meters above the water table. Rather than full immersion, the environment comprises thin layers of moisture on metal surfaces and episodic dripping onto some waste packages for some of the time.
- It is expected that after an initial dry period of tens of years during emplacement of waste packages and following the repository heating to above boiling after closure, the repository cools and relative humidity rises in the disposal drifts.
- Aqueous solutions can be expected to form on the waste package at relative humidity substantially less than saturation due to the presence of deliquescent salts and/or capillary condensation on dust and particulates. These conditions will lead to formation of aqueous solutions at temperatures above the boiling point of pure water at the elevation of Yucca Mountain (96 C).
- As the temperature of the surface decreases, the relative humidity increases, more water condenses on the surface, and dilution of the aqueous solution on the waste package occurs. The relative concentrations of the dissolved salts change as less deliquescent salts become increasingly soluble.

- It is highly unlikely that a low pH (*i.e.*, less than pH 3) aqueous solution can be maintained on the waste package in contact with the gaseous environment surrounding it due to the limits on the system pressure. The acid gases (*e.g.*, HCl, HNO<sub>3</sub>) would have to be maintained at pressures well above those attainable in the repository in order to maintain the pH of the solutions at low values.
- The metal surfaces can be covered by dust and particulates. Deposits of salts and minerals in the water can form as well as the accumulation of any prior corrosion products.
- Crevice corrosion effects from scale, rock and metal contact are to be considered.

A technically sound approach to the problem of determining the environment on the waste packages is to define the physical/chemical bounds of environments that can be expected. This approach involves considering known physical and chemical processes, inherent variability throughout the repository, and uncertainties in quantitative determination of the coupled processes that affect the environment. A comparison of the corrosion performance bounds to the environment bounds guides the determination of corrosion damage evolution over time.

## **Opportunities for Advances in the Determination of the Evolution of Environment**

### **Realistic extremes of environments and interactions with corrosion rates**

There are interdependencies between the corrosion rate evolution and realistic extremes of environments. Understanding those interactions is the foundation upon which any scientifically valid prediction of damage evolution must be built. Aspects of the interrelationship include:

- Character of the three likely waste package surface conditions
  - Moist dust from condensation
  - Wet mineral deposits from dripping and evaporation
  - Crevices in which accumulation of species can occur
- Effects of the evolution of the temperature and relative humidity
  - Establishment of the true deliquescence points for the three surface conditions
  - Establishment of the relative contributions of transient chemistries to the steady state, *i.e.*, determination of the role of episodic dripping on waste package environment evolution
- Plausible extremes of chemistry of thin electrolyte layers under the three surface conditions including the contributions of:
  - *Acid gas release*  
If acids were to form in solution during the corrosion process at Yucca Mountain, it is expected that they would quickly volatilize due to the fact that the mountain “breathes,” *i.e.*, it is a constant pressure system. Therefore, an understanding of the fate of volatile acids (HCl, H<sub>2</sub>SO<sub>4</sub>) and the sorption of CO<sub>2</sub> is of interest with regards to the effects on the surface chemistry.
  - *Microbial influences*  
Microbial effects on corrosion are well known [Stoeker, 2001], including the ability of microbes to thrive under extremes of temperature and salinity. The effects are due to changes in the local chemistry due to microbe metabolism and the regions of physical occlusion their colonies create on surfaces. Determination of the extent to which microbes could affect the plausible extremes of environments is of interest to establish the effects on the overlap with the windows of susceptibility of the materials of construction.
  - *Oxidizers present and effects*  
Passive materials exhibit increasing corrosion potentials with time due to a decrease in the passive current density [Kelly, 2002]. One aspect of material susceptibility is the concept of a critical potential above which stable localized corrosion can be sustained [Dunn, 2000]. What bounds the maximum corrosion potential ( $E_{\text{corr}}$ ) is the combination of this passive current density evolution with kinetics of the cathodic reactions [Hoare, 1975]. The latter depend on the nature and concentration of the oxidizers present. Characterization of the surface chemistry in terms of its oxidative power is important to predicting the evolution of corrosion damage.

## **Transport measurement and modeling related to corrosion**

The ease with which mass and charge can be transported often exerts a controlling effect on the location and rate of electrochemical reactions, and thus on the spatial distribution and severity of the corrosion damage evolution. Measurement of transport in thin electrolyte is notoriously difficult, and modeling of the controlling processes with relevant boundary conditions is in its infancy. Modeling and measurement necessarily interact; accurate boundary conditions are needed for accurate models, and modeling results can serve as intelligent guides for measurements by identifying areas of the relevant parameter space within which large changes occur. In practice, modeling and measurement are iterated to best characterize the corrosion situation. Specific opportunities for advances are:

- Measurements of conductivity and chemical composition under the three surface conditions are needed to quantify the effects of important system parameters (e.g., temperature, relative humidity).
- Measurements of electrode kinetics are needed under the appropriate conditions, including surface condition, temperature, relative humidity, and mass transport.
- The most advanced science-based models of thin electrolyte layers in contact with gaseous atmospheres and subsequent atmospheric corrosion [Graedel, 1996] have necessarily used oversimplified electrochemical boundary conditions and have considered one spatial dimension (that perpendicular to the surface). Progress in such modeling requires progress in the application of realistic electrochemical boundary conditions, including transient effects. In addition, lateral interactions will be critical at Yucca Mountain; during some time periods, wetting will occur on limited surface regions. The ability of these limited-area cathodes to provide support for localized corrosion will likely be rate-controlling.
- Transport parameters are a strong function of concentration and temperature. Only a few current corrosion mass transport models deal with non-ideal transport parameters [Gartland, 1996; Anderko, 2004]. Although object-oriented design computing has made implementation of non-ideal parameters possible [Stewart, 1999], issues remain with regards to defensible “interpolation” between known points. In addition to the need for computational implementation, data are needed that are applicable to the conditions at Yucca Mountain.
- The coupling of electrochemical and chemical conditions within thin electrolyte layers to those of crevices is required to fully characterize the corrosion situation for each of the three surface conditions. The thin electrolyte layer outside the crevice represents the source of the cathodic reaction primarily responsible for any corrosion growth within the crevice, but the extent to which that area can be effectively coupled to the crevice will be determined by the transport conditions.
- During the time period of interest, many of the likely crevice locations will be undergoing heat transfer. The heat transfer processes need to be coupled to the mass transport in order to determine the extent to which the time evolution of the chemistry/corrosion are affected. Although heat transfer modeling is at least as mature as mass transfer modeling, the coupling of the two with highly nonlinear boundary conditions represents a special challenge to computational codes.

## **Thermodynamic and physical properties of concentrated, mixed-ion solutions**

A robust database of thermodynamic, physical and transport properties for the conditions of high temperature, concentrated and multi-species solutions is required for analysis and modeling. Parameters of interest are activity coefficients, boiling points, density, viscosity, diffusivity of water and ions, and solubility. The temperature dependence of these parameters, as well as any strong environmental dependence, also needs to be characterized. Currently, there is no generally accepted theoretical framework that quantitatively can predict all of these properties over the range of dilute solution to precipitation. This knowledge is particularly important when dealing with heat transfer conditions on both the boldly exposed and creviced surfaces.

Experimental measurements of relevant parameters in concentrated, mixed-ion solutions are lacking, both because of the lack of validated experimental tools as well as the lack of a theoretical framework that can rationalize and predict property values.

## **Opportunities to Advance State of Knowledge of Corrosion Environments**

### **Improved Understanding of Concentrated, Multi-Species Solutions at Elevated Temperature**

There is a tremendous opportunity for better understanding of the physical chemistry of concentrated solutions. The impact of such understanding on corrosion science would be tremendous, as in a variety of cases, such conditions exist (such as in cracks, pits, and crevices) [Turnbull, 1983]. Dilute solution theory clearly breaks down in thin electrolyte layers during drying, but no generally accepted theory exists to extend to near saturation conditions to predict thermodynamic and physical properties. In addition, accurate measurements of thermodynamic and physical properties are needed to provide a database for modeling. A subtopic would be the mechanisms by which microbes can alter the plausible extreme environments. The influence of microbes on corrosive environments is an area ripe with opportunity for advances to fundamentally sound science.

### **Fundamental Understanding of “Time-of-Wetness”**

The temporal dependence of thin film electrolytes is often characterized by “time-of-wetness (TOW)” [Jung, 2002]. Although definitions have been standardized [Morcillo, 2002; G-84, 1999], a strong, fundamental understanding does not exist of TOW with regards to its physical meaning as well as its relation to initiation and propagation of corrosion in a thin layer to rationalize alternate immersion aggressiveness. There is a need to better understand what might be considered a trivial question: “When is a surface sufficiently wet to allow corrosion reactions to occur?” Not only is there a highly limited fundamental framework on which to place measurements, but the measurement of time-of-wetness is poorly defined, although standards exist for measurement of TOW.

Time-of-wetness makes intuitive sense; corrosion will occur when the surface is wet. Paradoxically, intuition fails when the definition of “wet” is tackled. Quantification of the influence of relative humidity and surface chemistry on the ability of anodic and cathodic sites on a metal surface is poor. A practical application of such knowledge would be a quantitative understanding of the increased aggressiveness of alternate *vs.* full immersion. Alternate immersion testing represents a poorly characterized corrosion situation, but one that is often preferred in practice because of its significant acceleration of attack. In fact, in some cases, alternate immersion is required for the attack to occur [Craig, 1987; Buchheit, 1995]. A scientific understanding of “time-of-wetness” would represent a quantum leap in corrosion science. Better accelerated tests could be developed, decreasing overall testing time for new materials or surface treatments.

In order to achieve such understanding, especially with regards to the initiation and propagation of corrosion in a thin layer, a number of aspects of TOW must be attacked. Mass transport of gaseous species in the system needs better characterization. Gases of importance include oxygen as well as CO<sub>2</sub>, which will strongly influence pH in thin electrolytes, as well as any pollutant gases such as SO<sub>2</sub>, NO<sub>x</sub>, and chlorine-containing species [Leygraf, 2000]. The effects of crevices on the TOW are also of importance, with aspects including the geometry of the crevice (gap, depth), the nature of the crevice (metal-metal, metal-deposit, metal-polymer), and the surface energies of the crevice surfaces.

### **Local Corrosion Initiation and Propagation in a Transient, Thin Electrolyte Film**

The vast majority of localized corrosion studies have used potentiostats to control the electrochemical conditions on the boldly exposed surface. However, actual localized corrosion rarely has such an “infinite cathode;” cathode limitations are particularly relevant to thin electrolyte layers. There is a great need to clarify the factors that control localized corrosion under such conditions in order to determine to what extent experiments and theories developed for full immersion must be modified for such restricted geometries.

Transients in the electrolyte thickness and composition are often due to heat transfer effects. Heat transfer will affect evaporation, precipitation, and chemical dissolution of corrosion products, as well as influencing the chemical properties relevant to mass transport. Incorporating heat transfer effects into the understanding of corrosion in thin electrolytes would have a substantial impact on many areas of technology.

## Occluded Site Chemistry Computational Toolsets

Further development of computational toolsets is for the treatment of occluded site chemistry with:

- complex, concentrated electrolytes departing from dilute ideal binary electrolyte behavior with respect to transport and solubility
- complex (*i.e.*, non-Tafel, non-linear), environment-dependent interfacial kinetics
- precipitation/solid products within the occluded site
- sub-crevices that alter transport within a occluded site
- incomplete separation of anodes and cathodes such as occurs in a crevice that becomes isolated from the boldly exposed surface due to drying of the outer surfaces

## In-situ, real-time measurements

In-situ, real-time measurements of ionic content (including pH), potential, conductivity without affecting crevice gap for gaps < 10 microns. Much of the chemical sensor community is working on miniaturization of chemical sensing of solution composition to make it compatible with microelectronics fabrication [Lin, 2000; Tang, 2002]. One driver for this is the desire to lower the expense of manufacture to make such sensors attractive to the large-scale consumer applications (e.g., biomedical sensing). It should be possible to leverage such work to make sensors that can be placed on surfaces or within tight crevices characteristic of the conditions under which Ni-Cr-Mo alloys corrode.

## Predictive Capabilities

The ability to accurately predict both transient and steady state chemical composition of electrolytes under heat transfer conditions. The opportunity here is to take advantage of the increases in computational power. The conceptual model and descriptive mathematics of transient properties are not intractable. The solutions to the descriptive models using realistic boundary conditions are computationally challenging. The modeling is not amenable to parallel computing because the processes are so tightly coupled. Instead, raw computing power combined with highly computationally-efficient differential equation solvers is required. In addition, there is an opportunity to take advantage of the ability of object-oriented programming to handle inputs of differing degrees of information (e.g., if a great deal of information is known about the transport properties of chloride, but less is known about sulfate) which will certainly be the case. Many of the advances can occur through careful coupling of state-of-the-art codes for the different processes.

## References for Evolution of Corrosive Environments

Anderko, A., N. Sridhar and D.S. Dunn, "A General Model for the Repassivation Potential as a Function of Multiple Aqueous Solution Species", *Corrosion Science*, 46(7), 1583-1612, (2004).

Buchheit, R.G., F.D. Wall, G.E. Stoner and J.P. Moran, "Anodic Dissolution-Based Mechanism for the Rapid Cracking, Preexposure Phenomenon Demonstrated by Aluminum-Lithium-Copper Alloys", *Corrosion (Houston)*, 51(6), 417-28, (1995).

Craig, J.G., R.C. Newman, M.R. Jarrett and N.J.H. Holroyd, "Local Chemistry of Stress-Corrosion Cracking in Aluminum-Lithium-Copper-Magnesium Alloys", *Journal de Physique, Colloque*, (C3), C3-825/C3-833, (1987).

Dunn, D.S., G.A. Cragolino and N. Sridhar, "An Electrochemical Approach to Predicting Long-Term Localized Corrosion of Corrosion-Resistant High-Level Waste Container Materials", *Corrosion (Houston)*, 56(1), 90-104, (2000).

Estill, J.C., S. Doughty, G.E. Gdowski, S. Gordon, K. King, R.D. McCright and F. Wang, "Long-Term Corrosion Testing of Candidate Materials for High-Level Radioactive Waste Containment", High-Level Radioactive Waste Management, Proceedings of the International Conference, 8th, Las Vegas, Nev., May 11-14, 1998, 669-673, (1998).

Eugster, H. P. and L.A. Hardie, in Lerman, A. (ed.), Lakes: Chemistry, Geology, Physics, Springer-Verlag, New York, (1978).

Garrels, R.M. and F.T. Mackenzie, in Gould, R. F., (ed.), Equilibrium Concepts in Natural Water Systems, Ch. 10, Am. Chem. Soc., Advances in Chemistry, (1967).

Gartland, P.O., "Modeling of Crevice Processes", Proceedings of Corrosion/96 Research Topical Symposia, Denver, Mar., 1996, 311-339, (1996).

Gdowski, G.E. T.J. Wolery and N.D. Rosenberg, "Waste Package Environment for the Yucca Mountain Site Characterization Project", Materials Research Society Symposium Proceedings, 713, (Scientific Basis for Nuclear Waste Management XXV), 29-36, (2002).

Graedel, T.E., "GLIDES Model Studies of Aqueous Chemistry. I. Formulation and Potential Applications of the Multi-Regime Model", Corrosion Science, 38(12), 2153-2180, (1996).

G84-89(1999)e1, "Standard Practice for Measurement of Time-of-Wetness on Surfaces Exposed to Wetting Conditions as in Atmospheric Corrosion Testing", American Society For Testing and Materials, Philadelphia, (1999).

Hailey, P. and G. Gdowski, "Thermogravimetric Thin Aqueous Film Corrosion Studies of Alloy 22; Calcium Chloride Solutions at 150°C and Atmospheric Pressure", Materials Research Society Symposium Proceedings (2002), Volume Date 2003, 757(Scientific Basis for Nuclear Waste Management XXVI), 765-770, (2003).

Hoare, J. P. (1975), "A Kinetic Study of the Rest Potential on a Platinum|Oxygen Diaphragm Electrode", The Journal of Physical Chemistry, 79(20), 2175-2179, (1975).

Jung, Sungwon, Y. Kim, H. Song, S. Lee and Y. Kho, "Atmospheric Corrosion Monitoring with Time-of-Wetness (TOW) Sensor and Thin Film Electric Resistance (TFER) Sensor", Corrosion Science and Technology, 31(5), 383-387, (2002).

Kelly, R.G., J.R. Scully, R.G. Buchheit and D.W. Shoesmith, Electrochemical Techniques in Corrosion Engineering, Marcel Dekker, 86, (2002).

Leygraf, C. and T. Graedel, Atmospheric Corrosion, John Wiley & Sons, Inc., New York, (2000).

Lin, J., "Recent Development and Applications of Optical and Fiber-Optic pH Sensors", TrAC, Trends in Analytical Chemistry, 19(9), 541-552, (2000).

Morcillo, M., E. Almeida, B. Chico and D. de la Fuente, "Analysis of ISO Standard 9223 (Classification of Corrosivity of Atmospheres) in the Light of Information Obtained in the Ibero-American Micat Project", ASTM Special Technical Publication, STP 1421 (Outdoor Atmospheric Corrosion), 59-72, (2002).

Rosenberg, N.D., G.E. Gdowski and K.G. Knauss, "Evaporative Chemical Evolution of Natural Waters at Yucca Mountain, Nevada", Applied Geochemistry, 16(9-10), 1231-1240, (2001).

Stewart, K.C., "Intermediate Attack in Crevice Corrosion by Cathodic Focusing", Ph.D. Dissertation, University of Virginia, (1999).

Stoecker, J.G., Ed., A Practical Manual on Microbiologically Influenced Corrosion, Vol. 2, NACE, International, Houston, TX, (2001).

Tang, T.B., E.A. Johannessen, L. Wang, A. Astaras, M. Ahmadian,, A.F. Murray, J.M. Cooper, S.P. Beaumont, B.W. Flynn and D.R.S. Cumming, *“Toward a Miniature Wireless Integrated Multisensor Microsystem for Industrial and Biomedical Applications”*, IEEE Sensors Journal, 2(6), 628-635, (2002).

Turnbull, A., *“The Solution Composition and Electrode Potential in Pits, Crevices, and Cracks”*, Corrosion Science, 23(8), 833-70, (1983).

## Localized Corrosion

John Scully, Hugh Isaacs and Roger Newman with Rudy Bucheit,  
Rob Kelly, Nancy Missert, Joe Farmer, Steve Dexter and Jerry Frankel

The following research opportunities were identified in the area of localized corrosion. Opportunities generally lie in the categories of improved understanding and conceptual knowledge in the areas of crevice corrosion propagation especially in thin electrolyte films (e.g., in the absence of an infinite cathode) as well as both repassivation and stifling of local corrosion. There is also the need for advanced tools to measure such phenomena, especially in thin electrolyte films, and models or predictive capabilities to predict behavior over time. These latter issues are discussed in a separate section regarding techniques and methods.

### **Overview of Localized Corrosion Research Opportunities**

It is generally recognized that there is a shortage of information concerning the localized corrosion (specifically crevice corrosion) of any corrosion resistant material in thin electrolyte films, especially those environments containing particulate matter or under deposits that might act as reactive, ion selective and semi-permeable crevices. In addition, it is clear that the overall topics of crevice repassivation in realistic crevices after long propagation times, and stifling due to corrosion products or cathodic starvation are research gaps. They also provide areas where there is an opportunity to determine if, despite high temperatures and possible global chemistries containing high concentrations of halides, that crevice corrosion just cannot be sustained in very thin electrolyte films or moist dusty layers. Therefore, research opportunities include improved understanding of anodic dissolution kinetics and propagation behavior in pits and crevices with emphasis on understanding the impact of deposits, solution species, surface films, external cathode conditions and alloy composition on stabilization, propagation, repassivation and stifling. Advances in the understanding of the effects metallurgical factors such as alloy composition and intermetallic formation on local corrosion in the Ni-base system are also required. These issues are of particular importance because of concerns over either long term aging and/or fabrication.

One of the biggest needs and fertile areas for research is in the area of local corrosion stifling and arrest mechanisms. It is recognized that several aspects of exposure in a repository type situation, e.g. thin electrolytes, non-immersed conditions, and episodic wetting, likely impose additional restrictions to crevice propagation that render stifling and/or repassivation more likely than in full immersion. In addition, evolution of damage depths and morphologies should be understood better in crevices under conditions of cathodic starvation, in the case of resistant alloys, and with highly acidic critical crevice solutions. It was also recognized that there are specific unresolved issues that affect local corrosion behavior such as the effects of extrinsic environmental variables (microbes, nitrate,  $Pb^{2+}$ , etc.) and intrinsic metallurgical (S) species on local corrosion of Ni-base materials.

The following topics are presented below:

- Critical Threshold Conditions for Corrosion (Initiation and) Propagation
- Anodic Dissolution Kinetics and Propagation Behavior in Pits and Crevices
  - Solution composition effects and properties of films formed in crevices
  - Pits and crevices governed by alloy composition
- Computational Understanding of Critical Crevice Solution Chemistries that Enable Localize Corrosion Propagation
- Local Corrosion Stifling and Arrest Mechanisms
- Metallurgical effects in local corrosion/ aging
  - Role of major solid solution alloying on local corrosion
  - Role of metallurgical phases
- Specific environmental species on local corrosion: extrinsic (e.g. nitrate,  $Pb^{2+}$ ,  $F^-$ ) and intrinsic (e.g. S)
- Effects of Microbiological Activity on Localized Corrosion

## **Critical Threshold Conditions for Corrosion (Initiation and) Propagation**

The anodic kinetics within corrosion cavities control the propagation, and, according to one view, the ‘initiation’ (as opposed to ‘nucleation’), of localized corrosion. That is, a small cavity on a metal surface has a certain geometry that sets the initial boundary conditions for mass transport; the anodic reaction in the local environment must be able to sustain sufficient chloride concentration by inward electromigration and acidity (via cation hydrolysis) in the face of outward diffusion of the aggressive environment [J.R. Galvele, 1976]. Sufficient acidity and depassivating anion (i.e., chloride) concentration form a critical crevice chemistry. This simple approach lends itself to a graphical representation defining stable and unstable steady states for localized corrosion [N. J. Laycock and R.C. Newman, 1997]. Another factor to consider is the potential inside the crevice, which will be lower than the external surface potential owing to IR drop from current flow between the active crevice interior and external cathodes. The lower potential can either stabilize the attack by moving the potential into the active range or destabilize the attack by consuming part of the driving force for dissolution.

But this is not a static picture: consumption of metal changes the cavity geometry, and may for example undercut the passive surface [P. Ernst, N.J. Laycock, M.H. Moayed and R.C. Newman; N.J. Laycock, S.P. White, J.S. Noh, P.T. Wilson and R.C. Newman, 1998]. Alternatively, corrosion products or precipitates might provide a crevice-like geometry and/or an ion-selective membrane action. A simple view of such complexities is that they alter the effective diffusion length associated with the cavity; the longer this length, the more stable the corrosion and the lower the potential required to stabilize it, other things being equal. For these reasons a more robust critical potential is required rather than relying on the long-term validity of a single short term repassivation potential for localized corrosion  $E_{r,crev}$ . In other words, the repassivation potential represents a situation where the critical crevice chemistry is not maintained given the particular details of the crevice and transport conditions. To the extent that the critical local environment requires or implies chloride enrichment and high acidity, that enrichment requires a minimum overpotential referred to the open-circuit potential of the metal in the local environment.

Solid-solution alloying enters the above argument via anodic dissolution kinetics and critical solution chemistry for passivation. The difference in behavior between two alloys that are both well above their critical temperatures for localized corrosion (e.g., 304 vs. 316) can be understood by comparing the dissolution kinetics in the worst possible local environment. The difference in local environment dissolution kinetics correlates perfectly with the difference in critical potential, both for chloride solutions where Mo has a large effect, and for bromide solutions where it has little or no effect [Newman, 1985]. A more interesting and complicated situation occurs when passivation intervenes, which can occur even in the most aggressive/concentrated local environment; this has been covered in one model for the CPT and CCT of high-alloy materials [Laycock and Newman, 1998]. Now one should consider the dependence of the generalized critical temperature for localized corrosion on alloy composition and cavity geometry. For a particular temperature, as Mo is added to an alloy, passivation is introduced at more and more concentrated local chemistries. For pit initiation on a smooth metal surface in a bulk electrolyte, this soon renders pit initiation impossible at any potential and the CPT is increased. For initiation of corrosion under a deposit, the propagation rate required to sustain the necessary local chemistry is so low that a near-saturated metal salt solution is no longer required; 10 percent or even 1 percent of saturation may suffice. This domain of crevice stability needs to be mapped as it is critical to the slow rates of propagation that may occur under dense deposits.

It has been identified that threshold potentials and temperatures remain technique- and condition-dependent, and resulting metrics such as  $E_{r,crev}$  can depend on geometric and mass transport factors. Crevice studies show that the diffusion length formed by the crevice former governs  $E_{r,crev}$  instead of the depth of corrosion attack [Kehler, Ilevbare and Scully, 2001]. A universally versatile threshold parameter that is not experimental technique dependent is needed. It is desirable to move beyond a critical potential for repassivation towards a set of readily obtainable parameters derived from lab testing that hold for a variety of geometries and mass transport situations. This would be analogous to a set of Galvele-type criteria instead of one critical potential [Galvele, 1976]. For these situations, it would be worth mapping the domain of crevice corrosion stability even when the propagation rate required to sustain the necessary local chemistry is low. There is uncertainty over the electrochemistry of low-propagation rate crevice corrosion and long diffusion/migration lengths. The open circuit potential in the pit electrolyte is very conservative, but it represents the most conservative potential threshold in the limit of extreme mass transport limitations.

## **Anodic Dissolution Kinetics and Propagation Behavior in Pits and Crevices**

### **Growth Rates and Propagation Laws**

The anodic dissolution behavior of highly corrosion resistant materials, like Alloy 22, in crevices is important for several reasons. Foremost, the anodic behavior in conjunction with geometric and chemical factors governs crevice stability. Secondly, these phenomena govern growth rates, propagation laws, repassivation and stifling. For a thick waste canister, considerable propagation is required for failure by penetration. The mere initiation of localized corrosion, especially for an alloy like Alloy 22, will not constitute failure. Consideration of localized corrosion propagation and stifling is required for a full prediction of failure.

The anodic behavior of localized corrosion of Alloy 22 at elevated temperatures appears similar to stainless steels and Ni alloys and is critically related to maintaining the critical concentrated environment required for localized corrosion to propagate by active dissolution. The alloy composition, solution concentration, corrosion products, and potential at the dissolving interface determine the rate of dissolution. The fundamental understanding of dissolution kinetics of complex multicomponent alloys is not well developed. [Landolt, Matlosz and Sato, 1999]. When the concentration drops below a critical value, repassivation takes place. When the concentration exceeds the solubility of the lowest solubility component, salt films precipitate. [Gaudet, Mo, Hatton, Tilley, Isaacs and Newman, 1986]. The dissolution and repassivation kinetics of Fe-Cr alloys in pit solutions have been investigated. [Steinsmo and Isaacs, 1993]. Localized corrosion studies on Alloy 22 are rare, but those published appear consistent with this behavior. [Kehler, Ilevbare and Scully, 2001]. Still, a direct method to quantify this model and note its limitations are required. One particular uncertain aspect is the influence of Mo at the 10-12 wt. percent level; a hypothesis is that new mineral-type species (molybdenum containing phases) provide the means for deterministic stifling.

When stable crevice or pitting corrosion occurs in stainless steels and other alloys such as Ti and Al, propagation rates have been explained by ohmic, mass, and charge transfer controlled models [Vetter and Streblow, 1974]. Localized corrosion growth kinetics typically conform to a power law,  $d = Kt^n$ , where  $d$  is depth,  $t$  is time,  $0 < n < 1$ , and  $K$  is a constant [Hunkeler and Bohni, 1981]. It can be shown that single hemispherical pits grown under either ohmic or mass transport control at the anode produce  $t^{1/2}$  propagation rates and dissolution current densities that decay with  $t^{-1/2}$  power [Frankel, 1998]. Note that such a relationship prevails at high applied potentials when there are few other restrictions on localized corrosion growth because the potentiostat can serve as an infinite cathode. However, a variety of exponential growth rates characterized by an effective  $n < 0.5$  are often observed in crevices grown naturally without a potentiostat [Romanoff, 1957], [Marsh, Taylor, Bland, Westcott, Tusker, Sharland, 1985].

Moreover, dependency of the  $n$  value on cathode area, deposits and the properties have been observed. The reason for natural long-term crevice propagation with  $n < 0.5$  could be due to additional restrictions and limitations compared to lab experiments or to stifling and/or repassivation phenomena. Limited long term experimental data and lack of real-time propagation information hinder this analysis. Both fundamental and technologically useful data regarding the origins of propagation behavior are lacking in the case of Ni-Cr-Mo alloys. It is unclear what fundamental parameters govern growth laws and what factors govern temperature dependency of crevice growth. For instance, the roles of alloying additions, deposits, and solution chemistry are unknown. In limited potentiostatic studies, potential, bulk solution chemistry, and alloy composition all affected crevice propagation rates in Alloy 22, suggesting neither pure ohmic nor pure mass transport control of crevice propagation [Kehler, Ilevbare and Scully, 2001].

Finally, and especially in thin electrolyte layers, the supply of cathodic current may be insufficient to support growth of a conventional hemispherical pit or crevice site. The geometry of corrosion has been found to change in response to cathodic starvation, propagating in such a way that the dissolving area stays constant or decreases. Thus, effects at the cathode are important factors in determining both crevice stability governed by maintenance of critical crevice solutions as well as the geometric shapes of damage and propagation laws. Only a few studies have been performed in this area and they were on stainless steels [Laycock and White, 2001].

Moreover, several additional aspects relating to the dissolution of metals at local corrosion sites need particular attention to both fundamentally understand crevice corrosion and to construct propagation laws. The first is the role of alloying elements present in Ni alloys. The second is the effect of solution composition including oxyanions, sulfur, and  $Pb^{2+}$ . The third factor includes physical and chemical properties of films and corrosion products and their effect on crevice stabilization and repassivation. These issues and others concerning alloy composition are discussed below.

### **Dissolution kinetics in pits governed by solution composition effects and properties of films formed in crevices**

An aspect is the critical concentration for reformation of a passive film and its dependence on local pH, chloride concentration, and water activity, which are influenced by the concentration and secondary solvation of dissolved cations [Burgess, 1978]. Non-halide anions are important. Stable oxyanions are generally considered to protect passivity to and assist repassivation, but unstable sulfur anions increase dissolution kinetics [R.C. Newman, 1982]. Electrochemistry in concentrated salts with complexation must be better understood.

The presence of corrosion product remnants on the active surfaces is also known to facilitate the repassivation processes by retarding dissolution, but persistent solid products within the zone of localized corrosion may reduce the mass transfer efficiency or buffer the halide concentration and delay the repassivation process. Indeed, a previously unexplored aspect of crevice corrosion includes “reactive” crevices, where the products of corrosion or the crevice former itself function as chemical buffers or ion selective membranes. Extensive corrosion product formation within the zone may increase polarization resistance and enable the concentration at the interface to drop below the critical concentration. The products of W dissolution are particularly insoluble in acidic environments. Mo products must also be understood. For instance, the amount of solids found in pits in 304SS is similar to the amount in 316SS, but with much higher Mo content (as well as W) in the latter, it appears that new solids may be generated and play a part in blocking pit growth through their ohmic barrier effect. Little is known about these solids. These products could exclude chloride from the metal solution interface. Thus, there is the opportunity to study the inhibiting and/or stabilizing effects of a variety of corrosion products and films in the crevices on Ni-Cr-Mo-Fe alloys.

### **Dissolution kinetics in pits and crevices governed by alloy composition**

The presence of Mo is known to reduce the dissolution kinetics of stainless steels [Newman and Franz, 1984], [Kaneko and Isaacs, 2002], but less work is available regarding Ni alloys and effects of Mo, W, and other elements. Fe ions dramatically reduce Ni electro-deposition rates [Hessami and Tobias, 1989] and a similar kinetic effect is expected during dissolution of Ni-base alloys containing Fe. Solid solution alloying elements would be expected to affect metal-metal bond strength [Marcus, 1994] which could alter the ease of bond severance as seen in Ti [Yu and Scully, 2001]. Other alloying elements probably act in a similar way, and the effects of Mo, W, Fe and Cr on crevice corrosion electrochemistry are of interest in both concentrated chloride and less aggressive environments.

Time-dependent changes in alloy composition and structure at localized corrosion sites may alter electrochemical properties during crevice propagation in several ways. Changes in the composition and electrochemical properties of dissolving pits and crevices may (a) affect anodic dissolution kinetics, which could evolve towards either more or less susceptible conditions, (b) alter or focus the area of dissolution and therefore the geometry of damage, or (c) increase or decrease the rate of local cathodic reactions. The latter effects are seen in crevices of Ti Grade 12 (Ni + Mo) and Ti Grade 7 (Pd) versus other Ti alloys [He, 2003]. Here, proton discharge in the crevice is catalyzed consuming protons. Subsequently, rapid repassivation occurs and  $n$  approaches zero. Different cathode effects inside the crevice must be considered in the case of Ni-base alloys where the passivation potential is more positive than reversible hydrogen depending on alloying content. There is also a need to understand congruent and non-congruent dissolution of alloys in slowly and rapidly dissolving situations. One of the challenges here is to extend dealloying science towards systems for which all components may dissolve albeit at different rates. Previous work is almost exclusively in noble metal systems where one alloy component is thermodynamically stable, at least as a bulk element. Quantification of these factors in the changing environment

associated with the localized dissolution is necessary to enable prediction of the stifling or stabilizing of localized corrosion as well as to define the processes determining propagation /repassivation criteria and critical thresholds.

There is also the general need to understand and quantify hydrogen uptake in halide induced acid-pits and cracks in corrosion resistant metals. In general, corrosion resistant materials acquire the hydrogen concentrations that trigger environment assisted cracking via local hot spots such as pits and crevices as opposed to bulk or global hydrogen charging. The latter is precluded because of unfavorable electrochemical conditions in bulk electrolytes that lack sufficient proton activity, ohmic voltage drop and hydrogen overpotential, the long solid state diffusion lengths associated with cracking via bulk charging, slow solid state diffusivities in f.c.c. Ni-base alloys and high critical hydrogen concentrations required for cracking. Thus, hydrogen embrittlement susceptibility is governed by local crack tip, pit or crevice uptake. There is a growing body of evidence that extraordinarily high local dissolved hydrogen concentrations can be produced locally in the pits and crevices of stainless steels [Switzer, 2003]. These alloys have low solid state hydrogen transport rates considering both ideal lattice and trap effected transport. The locally high absorption of hydrogen in the local uptake situation can accumulate since locally accumulated hydrogen is not readily diluted into the bulk of the alloy. In the case of Ni-Cr-Mo alloys, extremely acidic critical crevice solutions are likely. However, high interfacial potentials inside crevices may preclude significant hydrogen overpotentials, but not conditions for concurrent dissolution and hydrogen production possible at hydrogen underpotentials.

### **Computational Understanding of Critical Crevice Solution Chemistries that Enable Localize Corrosion Propagation**

Parametric control and quantification of the factors discussed above on localized dissolution kinetics is necessary to properly characterize electrochemical kinetics of alloy dissolution that could serve as inputs into a mass transport code capable of defining crevice chemistries. A series of well planned experiments should be conducted to investigate the electrochemical corrosion properties of Ni-Cr-Mo-Fe alloy alloys in crevice environments. An input to such models would be the fundamental dissolution properties of the Ni-base alloy which serve as electrochemical boundary conditions. These experiments would be inputs for modeling of critical crevice chemistry maintenance, and the results would provide information on conditions under which crevice stifling can occur due to non-maintenance of critical crevice solution chemistries [Kehler and Scully, 2001; Lillard and Scully, 1994]. However, codes that can predict crevice solution chemistries must be improved to accommodate well-supported electrolytes, precipitation and buffering, ion selective transport in deposits, isolated crevices (i.e., no external cathode) and a crevice with a thin layer of solution outside over the cathode area. Chemistry change and potential distribution models must be capable of considering conditions (a) when anodes and cathodes are not well separated, (b) in thin electrolyte films, under water droplets, or in moist dusty oxides with particulate matter, (c) with time dependent cathode sizes such as produced by episodic dripping and water layer thickness change, (d) when interactions between multiple pit and crevice sites exist, (e) under reactive crevice formers, where the crevice former is not inert but may buffer acidification or facilitate mixing of some species but not others. Computational codes should eventually move from 1-D to 2-D and account for corrosion site shape evolution. Such knowledge would enable the prediction of propagation /repassivation phenomena. Moreover, it could establish fundamentals-based repassivation criteria under a variety of circumstances, including physical and chemical variations in crevice former, anodes and cathodes as well as variations in alloy dissolution properties.

### **Local Corrosion Stifling and Arrest Mechanisms**

Assuming that initiation and propagation is possible, another opportunity is in the area of the understanding of local corrosion site stifling and arrest. Conceptually, stifling concepts are still emerging because of an historical lack of attention to this research area. Nevertheless, some stifling concepts can readily be proposed. A great benefit would be the ability to technically justify that stifling has indeed occurred in many engineering situations. In this section, stifling refers to a decline in rate of penetration and arrest refers to a stop in penetration, e.g. repassivation.

Stifling represents a reduction in propagation rates brought about by progressive reduction in corrosion rate. Repassivation phenomena either stem from the inability to maintain a critical chemistry for depassivation in acid pit or crevice corrosion phenomena or inability to maintain the necessary potential drop (the two phenomena are coupled in the case of Ni-Cr-Mo-Fe alloys) [Lillard and Scully, 1994]. Propagation rates that slow with time at a faster rate than the effective diffusion length or impedance path increases with time due to crevice deepening or

deposit formation can lead to stifling [Kehler and Scully, 2001]. Repassivation and stifling in natural corrosion systems without a potentiostat (e.g., infinite cathode) can arise from several causes including (i) external cathode limitations and cathodic starvation, (ii) inability to maintain a critical chemistry for stable crevice propagation due to anodic dissolution rate limitations brought about by a variety of causes such as formation of a salt film or, in this case, a highly insoluble tungstate film, change in surface alloy composition due to incongruent dissolution or some other cause, (iii) disruption in the geometric and physical conditions required to sustain the occluded site, and/or (iv) evolution in the metallurgical properties in the active crevice over time. For instance, the local cathodic reaction rates inside crevices could increase over time in some materials due to exposure of cathodically active intermetallics or replating of elements that support cathodic reactions. Alteration in anode cathode separation could occur to the point where the critical depassivating chemistry is not maintained.

Thus, there is a need to conceptually define stifling and repassivation criteria, investigate fundamental aspects of the criteria and model both crevice chemistry evolution and cathode area and specific cathode properties as a function of electrolyte characteristics, especially in thin, aqueous layers. The electrochemistry of crevice site dissolution should be investigated under cathodic starvation conditions by characterizing anode dissolution kinetics and crevice chemistry when mediated by finite cathode area, cathode reaction rate limitations, or alloy surface film or alloy composition evolution. There is also the need to conduct analysis of current and potential distribution within the crevice and external to the crevice during propagation of local corrosion. This requires consideration of crevice corrosion and cathode behavior under thin electrolyte layers, in moist dust, or thick particulate layers. These studies would improve understanding of the conditions leading to cathodic starvation. In addition, the fundamental electrochemical kinetics of the oxygen reduction reaction on Ni-base alloys must be understood in thin electrolytes as a function of composition, valence state of the oxide, oxide thickness as well as on distributed metallurgical phases and last, but not least, under particulate matter.

To date, limited studies have been conducted to address these stifling and arrest phenomena. If this research gap was understood better, there could be a rational technical basis to propose crevice stifling and repassivation should the  $\Delta E$  criterion suggest that crevice corrosion could occur in the case of a buried Ni-base alloy in a dusty humid condition with episodic dripping. The stability of crevice corrosion propagation and ultimately damage evolution of structures undergoing crevice corrosion under such circumstances requires this information.

### **Metallurgical effects in local corrosion/ aging**

Metallurgical effects can be divided into the effects of global solid solution alloy composition, microchemistry (e.g., metalloid and heavy metal impurity effects), metallurgical depletion and segregation, and metallurgical heterogeneities such as intermetallic phases. Metallurgical effects are particularly relevant to the case of long-term exposure of warm engineering components where initial solution annealed conditions might be altered over time. Each is discussed below.

### **Identify role of major solid solution alloying on local corrosion**

Solid-solution alloying enters the above argument concerning crevice chemistry maintenance via *anodic dissolution kinetics* and *critical solution chemistry for repassivation*. It also affects stifling criteria as discussed above through the formation of corrosion product films, etc. As mentioned above, it has been shown that the effect of alloying (at temperatures well above the critical temperatures for localized corrosion, e.g. 304 vs. 316) can be determined by comparing the dissolution kinetics in the worst possible local environment. Perfect agreement is obtained with the displacement in critical potential for chloride solutions where Mo has a large effect, and for bromide solutions where it has little or no effect [Laycock and Newman, 1997]. A more interesting and complicated situation occurs when passivation intervenes, even in the most aggressive/concentrated local environment; this is the UMIST model for the CPT and CCT of high-alloy materials [Salina-Bravo and Newman, 1994]. Now, consider the dependence of the CT (generalized critical temperature for localized corrosion) on alloy composition and cavity geometry. For a particular temperature, as Mo is added to a stainless steel alloy, passivation at more and more concentrated local chemistries. On a smooth metal surface in a bulk electrolyte, this soon renders pit initiation impossible at any potential and the CPT is now greater than our test temperature. Mo and W are known to have beneficial effects on corrosion resistance of Ni-Cr-Mo-Fe alloys [Kehler and Scully, 2001; Lillard, Jurinski, and Scully, 1994].

It is desirable to understand the kinetics of dissolution of Ni-Cr-Mo alloys in concentrated crevice-type environments in order to understand the effect of alloying elements on suppression of active dissolution rates in concentrated acid solutions representative of crevices as well as their effect on the critical solution chemistries for depassivation. The kinetic rates of solid solution alloy dissolution in pits or crevices must be obtained experimentally as a function of surface composition because their effects cannot readily be predicted based on fundamental theories. In other words, experimental E-I behavior across electrochemical interfaces can not be forecast from first principles. Because of this gap, the effects of major and minor alloying elements on local corrosion initiation, stabilization-propagation or arrest of crevice corrosion cannot be readily forecast. Stabilization criteria have emerged via crevice corrosion models [Oldfield and Sutton, 1978; Oldfield and Sutton, 1980] that embrace the critical crevice chemistry concept [Galvele, 1976; Galvele, 1981; Gravano and Galvele, 1984], as well as considering the possible need for ohmic drop [Pickering, 1989; Pickering, 2001] or both chemistry change and ohmic drop [Gartland, 1996] in order to achieve crevice corrosion stabilization.

These models all require electrochemical kinetics as inputs to the computational code. Ideally, input of a range of E-I data for a range of alloys into such codes could yield an understanding of the exact beneficial alloying element concentration desired or maximum detrimental impurity level tolerated to avoid crevice corrosion at specific temperatures, potentials, halide contents and diffusion lengths (i.e., crevices under a given set of conditions). Therefore, crevice electrochemistry including E-I dissolution kinetics as a function of alloying content must be understood. The impact of such alloying elements on crevice corrosion can only currently be accessed through empirical rules based on large databases for a variety of alloys using an inflexible metric such as the relationship between PREN and critical crevice temperature [Sedriks, 1996]. Unfortunately, as discussed above, any metric such as crevice temperature or threshold potential is a function of the experimental method.

An improved understanding of the effects of alloying elements on dissolution kinetics could be obtained if evaluated in conjunction with a computational mass transport code that can handle a range of crevice geometries (e.g. transport conditions). Such an approach would ultimately enable alloy design involving specific alloying element choice tailored to a specific set of circumstances. The criteria for alloying content would not be from lessons learned but instead could then be based on knowledge of the alloying content and dissolution overpotential required to achieve the critical crevice solution chemistry and also the potential for passivation under the given set of conditions (specified by the user). This would require a detailed and precise understanding of the effects of alloying content on electrochemical properties in acid solutions. None of these issues can be explored properly by testing just the C22 alloy. A carefully chosen matrix (or continuum) of less resistant alloys needs to be developed. This needs to be more extensive but along the lines employed previously [Lillard, Jurinski and Scully, 1994] starting with binary Ni-Cr alloys and continuing through Ni-Cr-Mo-Fe alloys. To the extent that localized corrosion can be predicted from acid-dissolution kinetics, these could be sputter-deposited thin films, which can be prepared with nearly linear lateral composition gradients using co-sputtering techniques. Combinatorial and/or designed experimental approaches may be required to elucidate combined and possibly synergistic effects or abrupt transitions in behavior with Mo or W concentrations.

## **Identify the role of metallurgical phases**

Improved mechanistic understanding is required of metallurgical phase formation, alloying element partitioning in solidification, and heat affected zone regions typified by dendritic and interdendritic microstructures. In aged and welded Ni-Cr-Mo alloy systems, several phases develop and have been observed to affect  $E_{r,rev}$  [Heubner, Altpeter, Rockel and Wallis, 1989]. However, the precise role of microstructure is unknown.

The role of metallurgical phases on initiation, propagation and stifling is not well understood in most alloy systems including Ni-Cr-Mo-Fe alloys. In the area of initiation, the microstructural defects that serve as the local corrosion initiation site and the critical defect size (character or condition) responsible for local corrosion stabilization are unknown for many engineering alloys. Progress has been made in some alloy systems (e.g., Mn(Fe,Cr)S inclusions in stainless steels, S-phase  $Al_2CuMg$  in precipitation age hardened Al alloys) but the need remains to define and understand the metallurgical culprit responsible for localized corrosion initiation in the case of nickel base super alloys. Moreover, existing reports do not elucidate the exact roles of the metallurgical phases in the initiation, propagation, nor stifling stages. The need exists to explore metallurgical effects on all three stages of crevice corrosion.

Second phases including carbides and intermetallics can be formed under certain thermal conditions in Ni-Cr-Mo-Fe alloys [Sedriks, 1996]. Aging at intermediate temperatures (approximately 600-800°C) leads to the precipitation of carbides as well as a  $\mu$  phase that nucleates from the carbides at the grain boundaries [Summers, Shen, Rebak, 2001; Rebak, Koon, Dillman, Crook and Summers, 2000]. In addition, alloying additions such as Mo and W used to enhance corrosion resistance and strength can form carbides and intermetallics. For 625, carbides can be found in the form MC or  $M_6C$  where M is Ni, Nb, or Mo. The intermetallic  $Ni_3Nb$  can also form. This could be detrimental since beneficial alloying elements such as Mo are depleted from solid solution. Precipitation of topographically close-packed phases (TCP) such as the  $\sigma$ ,  $\mu$  and P phases can also occur in these high nickel alloys [Cieslak, Headley, Romig, 1986; Cieslak, Knorovsky, Headley, Romig, 1986]. The  $\mu$  phase consists of Ni, Mo, Cr, W, and Fe and the  $\sigma$ ,  $\mu$  and P phases can contain up to 30% Mo [Raghaven, Mueller, Vaughn and Floreen, 1984]. Mo and W are more soluble at temperatures above 1000°C than at lower temperatures [Rebak and Crook, 2000]. Therefore, solution heat treatment and water quenching (or furnace cooling) is thought to ensure retention of these elements within the single-phase FCC structure and studies of aging and phase stability on solution heat treated alloy 22 show that formation of P or  $\sigma$  phases is unlikely at 200°C for over 10,000 years [Wong, 2003]. However, welding and fabrication processes may promote formation of these phases and associated alloying element depletion in the weld metal and at grain boundaries in the heat affected zones of welds. In fact, during solidification of welds, Mo and W can partition to interdendritic regions leaving dendrites depleted in these elements [Cieslak, Headley and Romig, 1986; Cieslak, Knorovsky, Headley and Romig, 1986]. The TCP phase precipitation is promoted by such partitioning and W and Mo are subsequently depleted because of the concentration of these elements in the  $\sigma$ ,  $\mu$  and P phases. Intergranular precipitation is also possible leading to Mo depletion near boundaries. Little fundamental information is known about crevice corrosion properties in these complex microstructures, the metallurgical culprits, the structure property relationships pertinent to crevice and pitting corrosion, or metallurgical mitigation strategies.

In addition, a long standing question is the critical defect size needed for local corrosion and the density of such sites. A more sophisticated effect is the role of clusters of metallurgical sites on local corrosion stabilization. Evidence is emerging that suggests that cooperative interactions between corrosion sites may be required to stabilize and spread local corrosion under certain conditions such as at low potentials and chloride contents. There is the need to define conditions that trigger interactions. Are interactions (positive and negative) between multiple pit sites sufficiently understood to define the role of clusters of microstructural defects (as might occur in material processing and/or fabrication) in stabilizing pitting? Can alloys be designed take into account these considerations and to resist stabilization by controlling the clusters of the critical defects?

### **Specific environmental issues: effects of extrinsic (nitrate, $Pb^{2+}$ , $F^-$ ) and intrinsic (S) species on local corrosion**

Addition of non-chloride anions introduces these ions to the rapidly dissolving surface of a pit nucleus. The roles of other halide ( $Br^-$  etc.) and non-halide oxyanions on local corrosion of stainless steels have been studied [Ernst, et al., 1999] but understanding is lacking in the case of nickel base super alloys. Nitrate has peculiar effects that suddenly arise (at least in stainless steel) when there is precipitation of an anodic salt film; the suggestion is that nitrate only becomes electroactive in a low-water-activity environment [Newman, 1986]. Reduction of nitrate under the salt film leads to passivation. Such an interpretation explains why pitting occurs in an intermediate range of potentials in chloride-nitrate media and can be anodically passivated. Sulfate acts a little differently than nitrate; it is a buffer ( $pK_a = 1.9$ ) and also tends to form less soluble and aggressive salt films than chloride. It is critical to understand the effects of these inhibitors on crevice corrosion in Ni base alloys (most literature is on stainless steels) and at low rates of propagation of localized corrosion (long effective diffusion length), where it is not self-evident whether or not they will be effective. There is a parallel, mechanistically, between the effects of decreasing temperature, increasing Mo content and increasing inhibitor concentration: the unifying feature is the onset of passivation in the local environment. But if the propagation rate is very low, the criteria for maintaining active dissolution may be less stringent.

Concerning intrinsic microchemistry effects, it is known from studies of Al alloys that solid-solution alloying with low-melting-point metals degrades passivity in both acid and alkaline solutions. The activators act via the metal surface, not the oxide, probably by peptizing the developing polymeric oxide network at the surface. To some extent such effects can be reproduced by adding the cation of the activator to the solution, and this is the basis for one theory regarding the effect of lead (Pb) on the corrosion and SCC of Ni base alloys. Where the effect persists above the  $Pb/Pb^{++}$  equilibrium potential, one can appeal to lead's well-known tendency to undergo underpotential

deposition on fcc metals. Much more work is required on this topic, using the Al base systems as a guide or working model. An alternative or complementary approach would be to explore the similarities and differences between Pb and S effects.

Combinatorial and/or designed experimental approaches may be required to elucidate combined and possibly synergistic effects of concentrated, multi-species solutions on crevice corrosion electrochemistry. The exact composition of non-chloride anions will depend on microbiological activity as discussed below.

### **Effects of Microbiological Effects on Localized Corrosion**

An interesting aspect of the localized corrosion issue is the possible mediation of the bulk environment composition by bacteriological action [Little, 2003] and other microbiological effects. MIC tests have never been run in thin (less than 50 microns) film electrolytes. The environmental conditions needed include thin film deliquescent brines of the organic and inorganic chemistries expected and temperatures from 100 C up to the boiling point of the brine. The microbes used in these tests should ideally be identified as being present in the service environment and capable of growing in hot brines. Alternatively, organisms culturable from other sites with warm to hot brines may be used. Of specific interest are:

- Concentrations of naturally produced inhibiting compounds such as nitrates and phosphates. What will be the ratio of their concentrations to chlorides, and sulfides? What will be the effect of the initial colonizing microbes on the concentrations (or activities) of these ions in thin films?
- Production of sulfides. This species is believed to be a key factor in the corrosivity. How much sulfide can be produced in these thin film electrolytes as a function of temperature?
- Thickness of biofilms and microbial communities within biofilms. Under realistic service conditions, will biofilms grow thicker than the expected deliquescent salt films? How might such growth affect the limitations on corrosion propagation rate imposed by a thin film electrolyte?
- Mitigation with inhibitors. For example,  $\text{CaNO}_3$  is injected into oil reservoirs to inhibit sulfide production. Would this approach work in a thin film electrolyte, and what methods for delivery of the  $\text{CaNO}_3$  or other inhibitors could be used?

MIC tests done under realistic environments will be necessary to determine whether microbes will be able to alter global chemistries in thin electrolyte films containing multi-species to create conditions within which initiation and/or propagation of localized corrosion can occur. It is critical to run MIC tests using realistic thin film electrolytes and organisms with demonstrated capabilities to grow in specific environments at high temperatures.

### **References for Localized Corrosion**

Burgess, J., Metal Ions in Solution, John Wiley, New York, p. 20, (1978).

Cieslak, M.J., G.A. Knorovsky, T.J. Headley and A.D. Romig, *Metallurgical and Materials Transactions*, 17A, 2107-2116, (1986).

Cieslak, M.J., T.J. Headley, A.D. Romig, Jr., *Metallurgical and Materials Transactions*, 17A, 2035-2047, (1986).

Ernst, P., et al. in *Passivity of Metals and Semiconductors*, Passivity VIII, Jasper, Canada, (1999).

Ernst, P., N.J. Laycock, M.H. Moayed and R.C. Newman, "*The Mechanism of Lacy Cover Formation in Pitting*", *Corrosion Science*, 39, 1133, (1997).

Frankel, G.S., *Journal of Electrochemical Society*, 145, 2186-2198, (1998).

Galvele, J.R., *Corrosion Science*, 21, 551-579, (1981).

Galvele, J.R., *Journal of Electrochemical Society*, 123, 464, (1976).

Galvele, J.R., *Journal of Electrochemical Society*, 464-474, (1976).

Gartland, P.O., *Research Topical Symposium, Corrosion '96*, National Association of Corrosion Engineers, 311-339, (1996).

Gaudet, G.T., W. T. Mo, T. A. Hatton, J. W. Tester, J. Tilley, H. S. Isaacs and R. C. Newman, *AIChE J* 32, 949, (1986).

Gravano, S.M. and J.R. Galvele, *Corrosion Science*, 24, 517-534, (1984).

He, X., “*Effects of Temperature, Impurities and Alloying Elements on the Crevice Corrosion of Alpha Ti Alloys*”, Ph.D. Thesis, University of Western Ontario, London, ON, (Nov. 2003).

Hessami, S. and C.W. Tobias, *Journal of Electrochemical Society*, 36, 3611, (1989).

Heubner, U.L., E. Altpeter, M.B. Rockel and E. Wallis, *Corrosion*, 45, 3, (1989).

Hunkeler, F. and H. Bohni, *Corrosion*, 37, 645-650, (1981).

Kaneko, M. and H.S. Isaacs, *Corrosion Science*, 44, 1825, (2002).

Kehler, B.A., G.O. Ilevbare and J.R. Scully, “*Crevice Corrosion Behavior of Ni-Cr-Mo Alloys: A Comparison of Alloys 625 and 22*,” *Proceedings of the National Association of Corrosion Engineers Research Topical Symposium on Localized Corrosion, Corrosion 2001*, Houston, Texas, *Corrosion/2001*, editors G.S. Frankel and J.R. Scully, 30-64, (2001).

Kehler, B.A., G.O. Ilevbare and J.R. Scully, “*Crevice Corrosion Stabilization and Repassivation Behavior of Alloys 625 and 22*,” *Corrosion Journal*, 57(12), 1042-1065, (2001).

Kehler, B.A., G.O. Ilevbare and J.R. Scully, *Corrosion*, 57, 1042, (2001).

Landolt, D., M. Matlosz, and Y. Sato. Editors, [Fundamental of Electrochemical Deposition and Dissolution](#), The Electrochemical Society, Pennington NJ, PV 99-33, (1999).

Laycock, N.J. and R.C. Newman, “*Localized Dissolution Kinetics, Salt Films and Pitting Potentials*”, *Corrosion Science*, 39, 1771, (1997).

Laycock, N.J. and R.C. Newman, “*Temperature Dependence of the Pitting Potential for Austenitic Stainless Steels Above Their Critical Pitting Temperature*”, *Corrosion Science*, 40, 887, (1998).

Laycock, N.J. and S.P. White, “*Computer Simulation of Single Pit Propagation in Stainless Steel under Potentiostatic Control*”, *Journal of Electrochemical Society*, 148, B264, (2001).

Laycock, N.J., S.P. White, J.S. Noh, P.T. Wilson and R.C. Newman, “*Perforated Covers for Propagating Pits*”, *Journal of Electrochemical Society*, 145, 1101, (1998).

- Lillard, R.S. and J.R. Scully, "*Modeling of the Factors Contributing to the Initiation and Propagation of Crevice Corrosion of Alloy 625*," Journal of Electrochemical Society, 141, 3006-3015 (1994).
- Lillard, R.S., M.J. Jurinski and J.R. Scully, "*Crevice Corrosion of Alloy 625 in Chlorinated ASTM Artificial Ocean Water*," Corrosion Journal, 50(4), 251-265, (1994).
- Little, B.J., "*A Perspective on the Use of Anion Ratios to Predict Corrosion in Yucca Mountain*," Corrosion, 59 8, 701-704, (August 2003).
- Marcus, P., Corrosion Science, 36, 2155, (1994).
- Marsh, G.P., K.J. Taylor, I.D. Bland, C. Westcott, P.W. Tusker and S. Sharland, "*Evaluation of the Localized Corrosion of Carbon Steel Overpacks for Nuclear Waste Disposal in Granite Environments*," in Scientific Basis for Nuclear Waste Management IX, Materials Research Society, Pittsburgh, PA, 421, (1985).
- Newman, R.C., Corrosion Science, 25, 341, (1985).
- Newman, R.C., Corrosion Science, 26, (1986).
- Newman, R.C. and H.S. Isaacs, Corrosion, 38, 261 (1982).
- Newman, R.C. and ME. Franz, Journal of Electrochemical Society, 131, 223 (1984).
- Oldfield, J.W. and W.H. Sutton, Br. Corrosion Journal, 13, 175-199 (1978).
- Oldfield, J.W. and W.H. Sutton, Br. Corrosion Journal, 175-199, 15, (1980).
- Pickering, H.W., "*The Significance of the Local Electrode Potential within Pits, Crevices and Cracks*", Corrosion Science, 29, 325-341 (1989)
- Pickering, H.W., "*Status of the IR Mechanism for Describing Crevice Corrosion*, in Localized Corrosion, Proceedings of the Topical Research Symposium, eds. J.R. Scully, G.S. Frankel, CORROSION 2001, 103-127 (2001).
- Raghaven, M., R.R. Mueller, G.A. Vaughn and S. Floreen, Metallurgical and Materials Transactions A (1984).
- Rebak, R.B., N. E. Koon, J. R. Dillman, P. Crook and T. S. Edgecumbe Summers, Corrosion, Paper 181, Houston, TX: NACE International, (2000).
- Rebak, R.B. and P. Crook, Advance Materials & Processes, (February 2000).
- Romanoff, M., "*Underground Corrosion*", National Bureau of Standards, Washington DC, Circular 579, (1957).
- Salina-Bravo, V.M. and R.C. Newman, Corrosion Science, 40, (1994) 67.
- Sedriks, A.J., Corrosion of Stainless Steels, New York: John Wiley & Sons, (1996).
- Steinsmo, U. and H. S. Isaacs. Journal of Electrochemical Society, 140, 643 (1993).
- Summers, T. S. Edgecumbe, T. Shen, and R. B. Rebak, Ageing Studies and Lifetime Extension of Materials, New York, NY: Kluwer Academic/Plenum Publisher, 507, (2001).

Switzer, M.A., “*Use of Crevice Scaling Laws to Investigate the Local Hydrogen Uptake in Rescaled Model Pits*,” a Master Thesis Presented to SEAS, University of Virginia, (August 2003).

Vetter, K.J. and H.H. Streblov, in *Localized Corrosion*, edited by R.W. Staehle, B.F. Brown, J. Kruger and A. Agrawal, NACE International, (1974).

Wong, F.M.G., “*Summary of Alloy 22 Aging and Phase Stability Studies*”, in DOE OCRWM/BES Corrosion Workshop Bethesda, MD: LLNL, (2003).

Yu, S.Y. and J.R. Scully, *Journal of Electrochemical Society*, 148, B68-B78, (2001).

## Passivity

D.W. Shoesmith and C.R. Clayton with T. Devine, S. Dexter, A. Gewirth,  
J.W. Halley, C. Orme, D.D. Macdonald, John R. Scully and J. H. Payer

The following research opportunities were identified in the area of passivity.

- Link thermodynamic predictions to kinetic observations to define a reaction pathway for materials degradation
- Determine the role of the preoxidized state (thermal treatments, dry/humid oxidation) and its subsequent influence on passive corrosion
- Develop an understanding of the relationships between passive film structure/composition, the defect properties of thin oxide films and the electrochemical/corrosion behavior they exhibit
- Define the relationship between open circuit potential and film stability
- Identify the nature and source of heterogeneities in the alloy and oxide structure; grain boundary impurities and second phases, intermetallic precipitates.
- Determine the nature of film fracture/repair events and their potential to cause the accumulation of corrosion damage.
- Determine the importance of the segregation processes at the alloy/oxide interface
- Define the chemistry in thin aqueous films or deliquescent deposits.
- Determine the influence of exposure environment on the chemistry of the oxide/solution interface.
- Quantify the kinetics of oxidant reduction processes on passive films.

For each topic, a research goal, the scientific/technological opportunity and relevance and impact are presented.

### **Link thermodynamic predictions to kinetic observations to define a reaction pathway for materials degradation**

#### **Research Goal**

Perform a reaction pathways analysis based on thermodynamic expectations on the alloy corrosion process over the expected timeframe of the service life/exposure period. This will provide an alternative to predictions based on short times relative to the long service lives and where there is a lack of a natural analog for the engineered alloys. The purpose of such an analysis would be to determine the reasonableness of material's degradation pathways observed experimentally in accelerated tests, and to provide a reaction pathway to validate, as far as is possible, the model extrapolations necessary to assess long and realistic lifetimes.

#### **Scientific/Technological Opportunity**

For the spent fuel waste from this goal can be achieved by the comparison of laboratory observations from accelerated tests to the geochemical evolution observed for natural uranium ore deposits. Such a comparison compensates partially for the inability to make experimental observations on a meaningful timescale, and establishes a justifiable experimental pathway along which to extrapolate in performance assessment models. In the absence of appropriate natural analogs, such a procedure cannot be used for engineered metallic materials.

The laws of thermodynamics demand that chemical transformations must evolve along a path towards enhanced stability. For a passive metal/alloy this evolution (metal to metal oxide) is kinetically controlled by the properties and behavior of the passive film, and how they change with time, since the oxide separates the unstable metal/alloy from the redox driving force of the environment. If predictive models are to show that this evolution is

slow enough to guarantee the durability of engineered structures on the required timescale, then it must be demonstrated that the material is on an appropriate evolutionary pathway.

Thermochemical modeling of the oxide film, using approaches such as [Kaufman, 2001], will provide a map of stable (or metastable) oxide phases. In general the oxide phases are a function of many variables including temperature, metal composition, solution composition and the ratio of available metal to solution volume. One commonly used representation of such calculations is the Pourbaix diagram, which calculates equilibrium redox potentials ( $E_h$ ) as a function of system pH. These thermodynamic calculations essentially solve many simultaneous differential equations describing the competing equilibrium reactions between solution, metal and oxide species. While first developed for single component metals, such calculations have been, and are currently being, extended to three [Beverskog and Puigdomenech, 1999] and five component alloys, respectively. Further developments are required to predict the consequences of exposure to more complicated and concentrated solutions as well as the expected behavior when the aqueous phase is limited in volume, as will commonly be the case when only thin aqueous layers are present.

### **Relevance and Potential Impact**

These calculations are important for long-term predictions of performance. Since there is often an absence of performance data accumulated on the application service life time scale, these thermodynamic predictions linked to kinetic observations provide one of the few procedures to validate model predictions. Since such calculations rely heavily on the reliability of thermodynamic data for such reactions, the development of these reaction pathways models will also identify the relevant database and hence, guide experimental efforts to enhance thermodynamic databases. This last feature expands the impact of such calculations to a broader range of applications beyond the Yucca Mountain project. It is also anticipated that surface analytical techniques will provide an essential short-term guide to the probable ranges of speciation that such calculations will provide. This will enable much longer-term models to be developed and justified.

## **Role of the Preoxidized State (thermal treatments, dry/humid oxidation) and its Subsequent Influence on Passive Corrosion**

### **Research Goal**

Determine the role of preconditioning of the surface of a passive metal before it is exposed to harsh environmental conditions on the subsequent behavior. Metal surfaces can be exposed to dry and humid air oxidation conditions and to elevated temperatures before wet conditions occur. This pre-exposure condition represents a starting point for eventual corrosion processes. In industrial applications, passive metals are often “passivated” by chemical treatments prior to service. Modifications to the corrosion processes of passive metals after preconditioning and once wet conditions are established are fruitful areas for research advances. The possibility also exists for intermittent states (i.e., switches between dry, humid and wet conditions) throughout the service life.

### **Scientific/Technological Opportunity**

For passive metals, the key difference resulting from prior exposure to dry and humid air exposure is the possibility of the incorporation of water into the outer oxide layers and its influence on the redistribution of species dissolved at the oxide/solution interface. Under dry conditions, the redistribution of alloying elements can only occur by ionic/defect transport within the oxide as a consequence of oxide growth and a slow subsequent evolution in oxide film properties. One would expect these processes to lead to an increase in oxide film impedance due to the slow annealing out of the ionic defects within the oxide that support film growth. Some evidence exists to show that this occurs and is responsible for the limitation on oxide thickness observed after short periods of thermal oxidation at temperatures below 200°C.

For aqueous immersion conditions, irreversible loss of dissolved elemental species from the surface is possible, a process that would sustain corrosion. Under humid vapor conditions, however, the loss of alloying elements is not feasible, but their redistribution via hydrated states is. Such a process could accelerate the conversion

of the alloy to thermodynamically stable oxide/hydrated oxide phases and, in so doing, deplete the alloy of those elements essential for subsequent corrosion protection. By controlling the defect properties of the oxides the preconditioning phase could influence the sustainable electric field within the oxide once it is exposed to dissolved oxidants in wet exposure environments.

These effects are of interest for stainless steels and more corrosion resistant nickel alloys. The preconditioning processes could especially influence the subsequent corrosion performance of titanium alloys since evidence exists to suggest the defect properties of the oxide are involved in the rate of corrosion in the presence of fluoride and in the efficiency of the absorption of hydrogen which could potentially lead to embrittlement [Hua et al, 2004].

The effects of “macro” surface films on engineered structures such as scale formed during mill treatment and the oxides covering welded areas are noted in the fabrications section.

### **Relevance and Potential Impact**

Since passivity can be viewed as a dynamic steady-state balance between film growth and film dissolution, both processes controlled by the defect properties of the oxide, then the state of the pre-grown oxide could have a very significant effect on subsequent corrosion processes and rates. A clear characterization of the relationship between passive film structure and composition and their effects on protective properties and corrosion processes would be a significant advance in determination of materials performance.

## **Develop an understanding of the relationships between passive film structure/composition, the defect properties of thin oxide films and the electrochemical/corrosion behavior they exhibit**

### **Research Goal**

Develop a common understanding of the compositional, structural and defect properties of oxide films and their influence on electrochemical/corrosion properties of materials. This understanding should encompass behavior in extreme environments created by a combination of salinity and high temperatures. The possibility of ennoblement of the underlying alloy surface, as a consequence of the incongruent segregation of alloying elements to the film, should also be investigated.

### **Scientific/Technological Opportunity**

A significant amount of effort has been expended on the determination of the composition and structure of passive films on a wide range of materials [Clayton and Olefjord, 1995; Marcus and Maurice, 2000; Schmuki, 2002] using an extensive array of surface analytical probes. While much understanding has been generated and the general features of passivity identified, much of the data is probe-specific and considerable effort will be required to produce a more comprehensive understanding of film properties independent of the measurement tool used. Also, since the growth and passive corrosion behavior of oxide films, as well as their susceptibility to breakdown, is known to be controlled by defect processes, a similar, but not quite so extensive an effort, has been devoted to the experimental study and development of theories to describe these properties [Macdonald, 1999; Bojinov et. Al., 2001]. However, a general unified understanding of passive films based on a synthesis of the results from these approaches has not been achieved.

Key issues include the following: (i) determination of the nature and function of the key defect(s) controlling film growth, and how this changes with changes in alloy composition; (ii) elucidation of the interactions between different defects and how they control film growth processes and the resistance to corrosion (as measured by properties such as film impedances and passive dissolution currents); (iii) determination of the interaction between defects and aggressive species present in the exposure environment (e.g., F<sup>-</sup>, Cl<sup>-</sup> and small highly polarizable cations such as Mg<sup>2+</sup>) which will determine the likelihood of localized corrosion processes.

Major experimental challenges persist for the study of thin passive films. One of these is the present reliance on ex-situ techniques often conducted under high vacuum conditions. Their use leads to unavoidable ambiguities in the film properties determined as a consequence of the transfer process from controlled electrochemical/corrosion environments to the high vacuum chamber of the analytical instrument. There is a very clear need to develop new techniques and improved methodologies to compliment those presently available. By contrast, the defect properties of films are more easily probed in-situ (by techniques such as electrochemical impedance spectroscopy (EIS) and photoelectrochemical methods), but require complex models for their interpretation. This combination of experimental limitations and model complexity presently severely limits the ability to accurately correlate compositional and defect properties.

## **Relevance and Potential Impact**

The development of a general unified understanding of passive films, which relates their compositional and defect properties, will provide a conceptual basis upon which to validate models developed to predict long term materials performance. The development and application of in-situ techniques will remove many of the uncertainties presently associated with the use of ex-situ vacuum methods.

## **Define the relationship between Open Circuit Potential and Film Stability**

### **Research Goal**

Determine the quantitative relationships between open circuit corrosion potential and the defect/compositional properties of passive oxide films in the various exposure environments of interest. The influence of various aggressive oxidants in saline environments and at elevated temperatures on these relationships should also be determined.

### **Scientific/Technological Opportunity**

The open circuit potential is a key parameter in the experimental study of materials passivity and susceptibility to localized corrosion, and in the development of models to predict passive corrosion behavior and susceptibilities to localized corrosion. It is the primary parameter used to define the state of a corroding surface, and its significance as the potential of coupling of the anodic and cathodic reactions involved in corrosion is well known. However, its interpretation in terms of the properties of the corroding surface is not well characterized making its application inevitably empirical.

With passive materials, changes in potential (applied or open circuit) are accompanied by changes in surface properties (e.g., composition, oxide thickness and defect density) that influence both anodic and cathodic kinetics. For complex alloys (such as the Ni-Cr-Mo Alloy 22) the changes in film properties with potential are complex. Available evidence based on electrochemical experiments suggests that at the negative potential end of the passive region oxide film properties are controlled by anion defects (i.e., oxygen vacancies) whereas at the positive end of this range, prior to the onset of transpassivity, these properties are controlled by cation defects (i.e., vacancies and/or interstitials) [Bojinor et. al., 2001]. Thus, as the potential increases throughout the passive region the impedance (and, hence, the corrosion) properties of the oxide first improve, as the concentration of anionic defects decreases and then degenerate as the concentration of cationic defects increases. The quantitative evolution of these two trends is critical in determining both the passive behavior and the susceptibility to localized corrosion of a specific material. To date such a characterization of defect properties has been conducted for only a few materials. This evolution of properties with potential would be expected to depend on a range of influences such as the composition and structure of the substrate material and the nature and composition of the exposure environment (e.g., pH, temperature, ionic composition).

## **Relevance and Potential Impact**

These influences, and their effect on corrosion kinetics, especially the kinetics of the cathodic reaction essential to sustain corrosion, are not well understood. Their characterization is crucial in the development of improved understanding of passive metals and their localized corrosion behavior over the intended service life. The goal is to move toward the development of more deterministic models to predict both long-term passive behavior and localized corrosion susceptibility and to move from partially empirical treatments. The benefit is more accurate prediction of long-term corrosion behavior.

The characterization of the corrosion potential in terms of material and environmental properties is a key in many corrosion applications. More generally, a clear understanding of the passive film parameters which control open-circuit potential will provide a reliable scientific basis upon which to judge material susceptibility to localized corrosion processes, thereby making material's selection discussions much more reliable. Presently, these decisions are primarily made on the basis of empirical-based critical potential measurements.

## **Identify the Nature and Source of Heterogeneities in the Alloy and Oxide Structure; Grain Boundary Impurities and Second Phases, Intermetallic Precipitates.**

### **Research Goal**

Identify and characterize the nature, source and distribution of heterogeneities in the alloy and oxide film structure and composition. Issues to be clarified include: the relationship between local crystallinity in the oxide film and that of the substrate; local variations in oxide film thickness and their relationship (if any) to the properties of the substrate; whether grain boundaries represent sites of enhanced reactivity; the distribution of impurities either initially present in the substrate alloy or accumulated during exposure; the consequences for film properties of the presence of macroscale inhomogeneities such as inclusions and secondary phases.

### **Scientific/Technological Opportunity**

A possibility with passive films is that they will not be laterally homogeneous, and the variations in composition and structure observed as a function of depth will be further complicated by additional variations across the surface of the alloy. The scale of these lateral variations could range from microscopic to macroscopic depending on their nature and the forces that form them.

At the microscopic level, the grain structure of the substrate alloy could influence the film growth process as recently observed for Ti, for which it has been shown that the oxide film thickness varies from grain to grain depending on its crystallographic orientation [Schultze and Schweinsberg, 1998]. On a slightly larger scale, the presence or development of grain boundaries in crystalline oxides introduces the possibility of pathways with resistance to charge transfer processes (ionic and/or electronic) orders of magnitude lower than that in the oxide film itself. As a consequence, the high impedance properties of the film could be, at least partially, bypassed. One example would be the recently demonstrated nanocrystallinity of Cr<sub>2</sub>O<sub>3</sub> films on Cr, Fe-Cr and Fe-Cr-Ni surfaces [Marcus and Maurice, 2000] when the potentially enhanced reactivity in grain boundaries is suppressed by the accumulation of Cr(OH)<sub>3</sub> [Marcus and Maurice, 2000].

These effects manifest themselves on single crystals and in relatively pure materials and for commercial alloys are likely to be swamped by the effects caused by the presence of macroscale heterogeneities, such as the presence of inclusions and secondary phases in the substrate. Mechanical and metallurgical processes such as cold-rolling and welding are likely to exacerbate these variations by introducing local stresses and/or the formation of secondary phases, which would distort the local film structures and compositions.

## **Relevance and Potential Impact**

This understanding of metallurgical features on the passive-film oxide structure would benefit the determination of fabrication processes and the development of materials and processing specifications for greater

corrosion resistance and reliability. More generally, these studies would provide a firmer understanding of the defect sites that might eventually prove to be the sites for initiation of localized corrosion.

## **Determine the nature of film fracture/repair events and their potential to cause the accumulation of corrosion damage.**

### **Research Goal**

Determine the nature, frequency and consequences of metastable film breakdown/repair events. In particular, the long-term potential for the accumulation of corrosion damage due to an on-going series of these events is to be determined. These studies should be conducted over a wide range of aggressive conditions of salinity and temperature, including the effects of “shock” conditions; i.e., rapid changes in wetting and temperature.

### **Scientific/Technological Opportunity**

One possible mechanism by which the passive properties of an oxide film could be bypassed is the occurrence of physical film breakdown events. If the site at which breakdown occurs does not repair itself (by re-growth of a passive film), then localized corrosion ensues. However the loss of local passivity is often temporary and a sequence of noise or metastable breakdown events is observed in current and/or potential measurements, especially under saline conditions. The characteristics of these events are likely to vary significantly with the exposure environment, especially with ionic solution composition (i.e., salinity and the concentration of small highly charged cations such as  $Mg^{2+}$ ) and temperature. High temperatures and wetting/drying cycles could significantly influence such events.

The characteristics of these events have been clearly related to alloy composition and microstructure. In some cases, they have been associated with the temporary localized loss of passivity at impurity, inclusion and secondary phase locations in the substrate material. Examples would be inclusions in stainless steels [Ilevbare and Burstein, 2001] and impurity-stabilized secondary phases (e.g.  $Ti_xFe$ ) in titanium [He et al., 2004]. In other cases, their origin is either unknown [Kobayashi et al., 2000] or uncharacterized. Inevitably, the study of such events has been relatively short term (a few hours) and conducted under controlled room temperature conditions. The potential for the long-term accumulation of corrosion damage due to an on-going series of these events has not been investigated. It is necessary to identify the features in the oxide at which such events occur and to determine whether there is any relationship to the compositional and microstructural properties of the substrate. It is also important to probe the local chemistry within these sites to determine how this influences the metal dissolution/site repassivation process and whether the properties of the resulting film vary significantly from those of the original passive film prior to breakdown.

A key issue that will determine the rate of accumulation of damage is how the nature, frequency and size of events evolve with time. Two limiting processes appear possible. If re-growth of the oxide occurs at the alloy/oxide interface (via defect transport processes) then the stress build-up associated with the growth process might be expected to lead to the continuing occurrence of these events. By contrast, if re-growth occurs at the oxide/solution interface, then stress build-up would be avoided and the sequence of such events would be expected to die out. The first process would depend on conditions at the alloy/oxide interface and the occurrence of events would be expected to continue at a rate determined by the development of conditions at this interface and how they are affected by alloy properties. The second process would be expected to be much less dependent on the alloy/oxide interfacial properties since oxide re-growth (and, hence, damage accumulation) would be more dependent on facile transport through the defective site.

### **Relevance and Potential Impact**

The nature of film fracture and repair events is central to the long-term performance of passive metals. Further understanding would benefit life prediction and particularly the processes and damage evolution from localized corrosion with consideration of film break down, stifling and arrest processes.

## **Determine the Importance of the Segregation Processes at the Alloy/Oxide Interface**

### **Research Goal**

Determine the long-term changes in interfacial conditions at the alloy/oxide interface and whether the enrichment of alloying elements and/or impurities is beneficial or detrimental. In particular, the fate of S is of interest since this impurity could degrade passivity. Since surface segregation of S, at sites such as grain boundaries, may lead to a loss of local passivity [Marcus and Maurice, 2000], the resulting possibility of the initiation of localized corrosion should also be studied.

### **Scientific/Technological Opportunity**

A key feature of passive film growth, which is commonly ignored, despite its potential to significantly influence passivity, is the evolution of alloy composition at the alloy/oxide interface. The incongruent segregation of alloying elements to the oxide (at the alloy/oxide interface) as well as their incongruent dissolution from it (at the oxide/film interface) has been observed to lead to compositional variations at the alloy/oxide interface that can be either beneficial or detrimental to passivity.

In high purity alloys the beneficial enrichment of alloying elements such as Ni and Mo may occur at the alloy/oxide interface [Clayton and Olefjord, 1995]. Alternatively, in commercial alloys, passive corrosion could result in the enrichment of impurities such as S and N [Marcus and Maurice, 2000; Marcus, 1995]. Available evidence suggests N enrichment produces a beneficial effect by reaction with Ni and Mo possibly to produce mixed Ni-Mo nitrides [Lu et al., 1983], the free energy of formation of the mixed cation nitride being significantly lower than that for the individual nitrides. By contrast, S enrichment is generally thought to be disruptive. Surface S appears to weaken metal-metal bonds, thereby lowering the activation energy for anodic dissolution, and to disrupt passive film growth by hindering M-OH bond formation [Marcus and Maurice, 2000; Marcus, 1995]. The key observation is that the continuing build-up of S at the alloy/oxide interface can lead to de-passivation due to a loss of film adhesion. The presence of Mo, however, tended to counteract the deleterious effect of S by facilitating its removal via the dissolution of Mo-S-Mo clusters [Marcus and Maurice, 2000].

Most of these observations are based on experiments with stainless steels and NiFe alloys. The work should be extended to a wider range of alloys and in particular to alloys with high Mo content. The effect of Mo to provide protection against S surface segregation and loss of passivity remains to be investigated. However, the achievement of such protection would involve the dissolution of Mo, with the resultant loss of a major component of the passive film.

### **Relevance and Potential Impact**

The identification and quantification of the influence of key impurities will allow the specification of alloy properties and chemical compositions for specific applications. This will allow the optimum alloy composition to be specified and to balance the requirements of both performance and cost.

## **Determine Passive Behavior in Thin Aqueous Films or Deliquescent Deposits.**

### **Research Goal**

Determine passive behavior for the chemical and physical conditions within thin aqueous films and within electrolyte layers with solid particulate. The study should concentrate on defining the difference from environmental exposure conditions in thin films of electrolyte and those prevailing in bulk aqueous systems. The goal is to define the influence of these environments on the chemical and physical properties of thin, passive oxide films.

## **Scientific/Technological Opportunity**

The performance of passive metals in thin moisture layers as opposed to fully immersed conditions is relevant in a wide range of applications, and passivity in these thin moisture layers has not been extensively studied. For these applications, the question of when aqueous conditions can be established and maintained becomes a key issue. Also, the possibility for the formation of deliquescent deposits introduces an additional environment within which the chemistry could vary significantly from that encountered if the engineered materials were fully immersed in an aqueous environment. In the case of thin films or small droplets of aqueous brines the hydrophobicity of the oxide/aqueous environment is an issue, since no systematic understanding of whether and how these brines will wet the mixed cation oxide surface is available. This issue is important since the ionic currents and species concentrations, and hence the relevant electrochemistry, are expected to be considerably different in non-wetting droplets and wetting thin films.

The chemistry within non-wetting droplets, thin wetting films and inert and deliquescent deposits will be affected by a wide range of influences including capillary action, selective ion absorption processes, the truncated range of transport processes and the limited lateral coupling range for potential anodic and cathodic reactions. Capillary action will dictate the extent of wetting within deposits and solids, and selective absorption processes could disturb key ion ratios (e.g.,  $[\text{NO}_3^-]/[\text{Cl}^-]$ ) important in determining corrosion susceptibilities and rates [Suleiman et al., 1994]. The lack of a bulk aqueous environment would limit the loss by transport of dissolved metal cations from, while facilitating the transport of oxygen to, the alloy surface. These transport limitations coupled to the lateral resistances associated with thin aqueous layers will have a significant influence on the distribution of anodes and cathodes and could be critical in determining the importance of lateral variations in corrosion processes and rates.

## **Relevance and Potential Impact**

Since the great majority of surfaces on the waste package/drip shield will be exposed to these conditions of limited water, these environmental issues are likely to be critical in determining the durability of engineered structures. The understanding will also be more generally valuable in understanding atmospheric and wet vapor corrosion situations.

## **Determine the influence of Exposure Environment on the Chemistry of the Oxide/Solution Interface.**

### **Research Goal**

Determine the chemistry of the oxide/solution interface and its influence on passive oxide dissolution processes. In particular, the influence of environmental parameters such as the nature and concentration of the exposure environment, including its microbial content, are of interest.

## **Scientific/Technological Opportunity**

Studies of oxide dissolution kinetics have shown that the rate is primarily dependent on the number and nature of the defects in the oxide but also is dependent on the nature and concentration of the exposure environment. From the corrosion perspective the key environmental parameter is the redox potential but many other environmental features including pH, ionic solution composition, and the presence of microorganisms could influence the properties of the oxide solution interface and, hence, the dissolution rate.

Since mixed ion solutions with widely varying compositions and concentrations pertain for many applications, a systematic attempt to elucidate the nature of adsorption/ion exchange/precipitation processes on passive oxides is of interest. Well developed models describing ion adsorption properties on oxide surfaces are available [Stumm, 1992], but their application to passive oxides has not been seriously attempted. Since the oxide/solution interface is in dynamic interaction with the alloy/oxide interface, the simple unrevised adoption of these models is inappropriate. Depending on the point of zero charge of the oxide surface, both anions and cations

can adsorb/ion exchange with oxide surfaces. These interactions could accelerate or suppress oxide dissolution depending on whether they stabilize soluble species (by complexation), facilitate or inhibit ion transfer processes by electrostatic interactions, interact with point defects in the oxide to destabilize oxide film structures, or incorporate into secondary precipitates to produce insoluble deposits. The influence of temperature on the balance between these conflicting processes is likely to be very significant.

The effect of microorganisms on passive film properties and dissolution is known to be complex and recent studies indicate that metals/alloys covered by n-type oxide films react more rapidly than those with a p-type film [Dexter and Maruthamuthu, 2001]. Since the point defect structure of passive films determines the conductivity type and changes with redox conditions, the susceptibility of passive films on Ni-Cr-Mo alloys could be subtly dependent on alloy composition, including the effects of impurities such as Fe. To date the consequences for oxide dissolution are poorly characterized. Also, the influence of microorganisms could vary drastically with the degree of surface wetting since they are known to be sensitive to environmental parameters such as temperature and the availability of water. Particular attention should be paid to the development of biofilms at such sites as welds which contain heat tints which have been found to be sites of preferential biofilm formation in stainless alloys. It should also be borne in mind that extra cellular polysaccharides and proteins comprising the biofilm around microorganisms in some cases may offer corrosion protection and are not necessarily a precursor to localized corrosion.

### **Relevance and Potential Impact**

Passive corrosion can be viewed as a steady-state balance between processes at the alloy/oxide interface and those at the oxide/solution interface. Since the processes at the latter interface will control this steady-state condition, an understanding and quantification of the environmental parameters that influence oxide behavior are important to the conceptual validation of empirically measured passive corrosion rates.

## **Quantify the Kinetics of Oxidant Reduction Processes on Passive Films.**

### **Research Goal**

Determine the electrochemical kinetics of the possible oxidant reduction processes on thin passive oxides and in the presence of inert and deliquescent solids. These studies should cover a wide range of surface wetting conditions, including wetted particulate and deliquescent deposits.

### **Scientific/Technological Opportunity**

If corrosion is to be supported under oxidizing conditions, the kinetics of the cathodic reaction could be critical in determining the passive corrosion rate as well as determining whether or not an alloy is susceptible to stable localized corrosion. The primary oxidant in thin electrolytes in air will be dissolved oxygen but species such as nitrate could also act as oxidants. As a key reaction in many electrolytic and fuel cells, the oxygen reduction reaction has been extensively studied; however, this is not the case for nitrate reactions. For oxygen reduction, it has been clearly demonstrated that the oxides ability to interconvert surface oxidation states (e.g.,  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$  in  $\text{Fe}_3\text{O}_4$ ) and to coordinate oxygen by surface adsorption at these sites is a key feature in the kinetics [Vago et al., 1994]. However, the reduction of both oxygen and nitrate on passive oxide surfaces has received very little attention [Bozec et al., 2001; Okuyama and Haruyama, 1990].

A number of features of the passive film could influence the cathodic reduction of oxidants including, film thickness, structure, composition and dielectric properties: (i) for sufficiently thin films, electron tunneling could support electron transfer; (ii) for passive films (or barrier layers within such films) of normally anticipated dimensions (1-5 nm in thickness), the ability to support a cathodic process may also depend on potential-induced ionic space charges which could potentially influence the surface adsorption processes involved in the cathodic reaction as well as influencing the secondary conductive properties of the oxide involving the defect structure; i.e., the coupling of ionic and electronic transport processes. Since these oxide features will evolve with time and potential, begin with a thermally oxidized starting condition (see the section on defect structure/open circuit potential), and is dependent on alloy and oxide composition, the kinetics are expected to be complex; (iii) For

crystalline and/or fractured films, there exists the additional possibility of enhanced conductivity in grain boundaries and/or enhanced transport of the oxidant within flaws; (iv) when a deposit is present, transport ( $O_2$ ) and transport/adsorption ( $NO_3^-$ ) processes could make the reaction dependent on the properties (porosity, number density of possible adsorption sites) of the deposit.

### **Relevance and Potential Impact**

A characterization of the kinetics of the cathodic reaction(s) involved in corrosion as a function of oxide characteristics is an important component of any model developed to predict either passive or localized corrosion behavior. For Cr-containing alloys, such as Alloy-22, the cathodic reaction could prove to be the key one controlling overall corrosion behavior.

### **References for Passivity**

Beverkog, B. and I. Puigdomenech, "Pourbaix Diagrams for the Ternary System of Iron-Chromium-Nickel", Corrosion 55, 1077-1087, (1999).

Bojinov, M., G. Fabricius, P. Kinnunen, T. Laitinen, K. Makela, T. Saario and G.Sundholm, "Electrochemical Study of the Passive Behaviour of Ni-Cr Alloys in a Borate Solution – A Mixed-Conduction Model Approach", J. Electroanal.Chem, 504, 29-44, (2001).

Clayton, C.R. and I.Olefjord, "Passivity of Austenitic Stainless Steels", in Corrosion Mechanisms in Theory and Practice, edited by P.Marcus and J.Oudar, Marcel Dekker, New York, 175-199, (1995).

Dexter, S.C. and S.Maruthamuthu, "Response of Passive Alloys with n-type and p-type Passive Films to Manganese in Biofilms", Corrosion2001, NACE International, Houston, TX, Paper No. 01256, (2001).

He, X., J.J. Noel and D.W. Shoesmith, "High Temperature General Corrosion of Grade-7 Titanium", submitted to Electrochimica Acta, (2004).

Hua, F., K. Mon, P.Pasupathi, G.Gordon and D.W.Shoesmith, "Corrosion of Ti Grade-7 and Other Titanium Alloys in Nuclear Waste Repository Environments", Corrosion 2004, New Orleans, March 28-April 1 (2004), Paper 04689, NACE International, Houston, TX, (2004).

Ilevbare, G.O. and G.T. Burstein, "The Role of Molybdenum in the Inhibition of Pitting Corrosion in Stainless Steels", Corrosion Science, 43, 485-513, (2001).

Kaufman, L., CALPHAD 25, 141, (2001).

Kobayashi, Y., S.Virtanen and H. Bohni, "Microelectrochemical Studies on the Influence of Cr and Mo on Nucleation Events of Pitting Corrosion", Journal of the Electrochemical Society, 147, 155-159, (2000).

Le Bozec, N., C. Compere, M.L 'Her, A. Laouenan, D. Costa and P.Marcus, "Influence of Stainless Steel Surface Treatment on the Oxygen Reduction Reaction in Seawater", Corrosion Science, 43, 765-786, (2001).

Lu, Y.C., R. Bandy, C.R.Clayton and R.C. Newman, Journal of the Electrochemical Society, 130, 1774, (1983).

Macdonald, D.D., "Passivity – The Key to our Metals-based Civilization", Pure and Applied Chemistry, 71, 951-978, (1999).

Marcus, P., "Sulfur-Assisted Corrosion Mechanisms and the Role of Alloyed Elements", in Corrosion Mechanisms in Theory and Practice, edited by P.Marcus and J.Oudar, Marcel Dekker, New York, 239-264, (1995).

Marcus, P. and V. Maurice, "*Passivity of Metals and Alloys*"; in Corrosion and Environmental Degradation, Volume 1, edited by M.Schutze, Wiley-VCH, New York, 131-170, (2000).

Okuyama, M. and S. Haruyama, "*The Cathodic Reduction of Oxygen on Stainless Steels in a Neutral Solution*", Corrosion Science, 31, 521-526, (1990).

Schmuki, P., "*From Bacon to Barriers: A Review on the Passivity of Metals and Alloys*", Journal of Solid State Electrochemistry, 6, 145-164, (2002).

Schultze, J.W. and M. Schweinsberg, "*From pm to km: Scaling Up and Scaling Down of Electrochemical Systems with TiO<sub>2</sub> and ZrO<sub>2</sub> Passive Films as an Example*", Electrochimica Acta, 43, 2761-2772, (1998).

Stumm, W., Chemistry of the Solid-Water Interface, John Wiley and Sons, New York, (1992).

Suleiman, M.I., I.Ragault and R.C.Newman, "*The Pitting of Stainless Steel under a Rust Membrane at Very Low Potentials*", Corrosion Science, 36, 479-486, (1994).

Vago, E.R., E.J. Calvo and M. Stratmann, "*Electrocatalysis of Oxygen Reduction at Well-defined Iron Oxide Electrodes*", Electrochimica Acta, 39, 1655-1659, (1994).

## Stress Corrosion Cracking

R.H. Jones and J.A. Beavers with Peter Scott, Frank Wong, Larry Kaufmann, Jeff Braithwaite, and John. R. Scully

The following research opportunities were identified in the area of stress corrosion cracking (SCC):

- Understand crack initiation processes in Stress Corrosion Cracking and factors governing transitions from localized corrosion to SCC initiation and propagation
- Improve mechanistic understanding of SCC including alternate mechanisms such as internal oxidation as a viable mechanism
- Analysis of crack tip chemistry, materials and mechanics including internal hydrogen
- Improve understanding of slip/film rupture/dissolution model as it applies to Ni-Cr-Mo alloys
- Develop high resolution crack growth measurement techniques

For each topic, a research goal and impact are presented and the scientific/technological opportunity is described.

### **Crack Initiation Processes in Stress Corrosion Cracking and the Transition from Local Corrosion to SCC**

#### **Research Goal and Impact**

If stress corrosion cracks initiate, they may propagate; therefore, a better understanding of crack initiation processes and the transition from local corrosion to SCC are critical to predicting long term performance of structures where SCC is a viable mode of corrosive attack. Stress corrosion crack initiation can occur at pre-existing surface defects, from pits that form during exposure to the service operation or by prior cleaning operations. Pits can form at inclusions that intersect the free surface, known as heterogeneous pitting, or by general breakdown of the passive film, known as homogeneous pitting. In electrochemical terms, pits form when the potential exceeds the pitting potential. It has been shown in some materials that the SCC and pitting potentials are identical. Cracks can also initiate at surface flaws such as grinding laps and other surface imperfections. Crevices can also lead to crack initiation through the development of localized chemistry that induces pitting.

Surface defects associated with welds or crevice corrosion are also possible locations where cracks are likely to initiate. Whether they will grow into short cracks and ultimately into long cracks, growing at stage II velocities, is not known, especially for alloys that are resistant to pitting and crevice attack. Laboratory tests have demonstrated that long cracks in compact tension samples, tested in repository relevant environments but at relatively high cyclic stress, do grow but whether a pit will transition into a crack or whether the short crack will grow to be a long crack with stage II velocities requires further evaluation. Moreover, the geometric, metallurgical, mechanical and (electro) chemical factors governing whether a local corrosion site will transition into a stress corrosion remain unclear for most alloys. However, such understand would improve the fundamental foundations of corrosion science in this area and also serve as model inputs to predictive models that seek to incorporate more than one corrosion mode in assessments of corrosion damage accumulation.

#### **Scientific opportunity**

The transition from an initiation process to a growing crack is not well understood and likely is quite complex. There is some evidence that this transition is controlled by the same parameters that control crack growth, i.e., electrochemistry at the base of the pit, chemistry of the material, a metallurgic ally susceptible condition and stress or strain rate at the base of the pit. The transition of a pit to a crack requires a change in geometry from a hemispherical shape for ideal pit geometry to a planar shape for the crack. How this transition occurs is not clear but it has been clearly demonstrated in a number of materials [Jones, 2003]. The transition from a surface flaw or defect to a crack often does not require as significant a change in shape since these flaws often have a more planar geometry. Once a planar geometry is established, crack growth does not immediately achieve Stage II growth kinetics and the crack growth rate may differ for short cracks compared to long ones owing to chemistry and electrochemistry differences. There is a limited amount of data on the growth rate of stress corrosion cracks in

austenitic stainless steels that shows that the growth rate begins slowly and increases in velocity until it achieves the stage II velocity [Jones, 1997; Jones, 1994]. The scientific opportunity exists to minimize stress corrosion crack growth through better understanding of the factors governing initiation and transition to propagation.

## **Improved Mechanistic Understanding of SCC**

### **Research Goal and Impact**

Improve the mechanistic understanding of SCC in Ni-Cr-Mo alloys to advance the slip dissolution/film rupture model and develop alternative models. In the current SCC models, it is assumed that any stress corrosion cracks that initiate will propagate through the wall thickness at a fairly constant rate. No account is given for slower crack growth rates or for crack stifling because the models do not incorporate a crack stifling mechanism. An improved mechanistic understanding of SCC may facilitate the development of better methods to validate crack growth models and therefore improve our predictive capability.

### **Scientific Opportunity**

The slip/film rupture/dissolution model has been successfully applied to predict SCC behavior in a number of alloy-environment systems where passive films are present, including stainless steels in light water reactor environments [Andresen, 1994]. In the model, slip dissolution refers to the process of dislocations emerging at the surface of the crack tip and the rupture of the passive film by this process. Corrosion of the exposed non-passivated metal contributes to the crack extension. Film rupture refers to the process by where strain at the crack tip causes the “brittle” passive film to rupture thus allowing the unfiled metal to corrode. The crack advances by anodic dissolution (corrosion) at the crack tip while the crack walls and the free surface are protected from corrosion by the passive film, maintaining the crack-like geometry. A number of factors establish the rate of crack advance including the mechanical properties of the film, the rate of repassivation of the film, the creep rate of the metal at the crack tip and the kinetics of the corrosion reactions. However, there are significant opportunities to improve and advance this model in order to predict stress corrosion crack growth rates. Regarding the charge emitted during unfiled metal corrosion and repassivation following film rupture, recent advances in inventorying the crack tip anodic currents can improve the ability to determine crack growth rates by anodic dissolution [Kolman and Scully, 2000; Kolman, Gaudett and Scully, 1998]. Moreover, establishing the technical basis for stifling of crack growth provides an opportunity to justify decrease in crack propagation whether via stress relaxation during propagation (loss of mechanical driving force), cathode limitations such as in thin film electrolytes, corrosion product buildup in crack wakes and subsequent alteration of electrochemical driving forces or other possible stifling mechanisms. Another possible stifling mechanism is the need for connectivity of susceptible crack paths, this is particularly relevant to IGSCC where susceptible grain boundaries are required [Gaudett and Scully, 1994]. This area is relatively unexplored in corrosion science.

The slip/film rupture/dissolution model to SCC starting within active pits and crevices has room for improvement since the material is already depassivated at these sites and it is unclear how the strain rate at the pit bottom rupture a polymeric type or gel-like film. Thus alternative models of stress corrosion cracking remain quite desirable, plausible and may enable more realistic modeling of long term cracking phenomena.

The issue of the mechanisms by which stress corrosion cracking is accelerated in certain alloy systems by alternate immersion remains unclear. It is clear that alternate wetting and drying shifts the spatial relationships between anodes and cathodes. The implication is that heterogeneous surface reactions that contribute so significantly to local chemistry changes are altered both in rate and location. Chemistry changes that play a key role in SCC are expected to be changed. Moreover, it is known that the nature of oxide films during cycling may differ compared to full immersion. However, the precise mechanisms by which alternate immersion or episodic dripping conspire to increase SCC susceptibility represents an area of corrosion science ripe for advance.

Moreover, improved scientific understanding of SCC mechanisms can also shed light on accelerated testing whether by use of alternate immersion, more aggressive solutions than seen in practical application, temperature

elevation or other cause. Understanding of acceleration factors and mechanisms would enable improved validation of SCC models through short term testing.

## **Crack Tip Chemistry, Material and Mechanics Analysis**

### **Research Goal and Impact**

Further the understanding of the crack tip aqueous chemistry, near crack tip material behavior (e.g., near tip creep behavior and strain gradient plasticity) as well as dissolved hydrogen content to provide the foundation for model improvement, validation or elimination. The improved mechanistic understanding of SCC is important to both the slip dissolution rupture model and alternative models. Validation of the slip dissolution model or development of an alternative model will enable the prediction of SCC velocities under relevant environmental conditions. Currently, laboratory tests must be conducted under more aggressive conditions than expected in the repository because the crack growth rates are at the limit of detection with the most sensitive crack monitoring equipment. A validated model could be used to predict whether stress corrosion cracking will impair performance.

### **Scientific Opportunity**

Crack tip chemistry and material analysis using modern tools provides an opportunity to resolve important issues that shed light on the appropriateness/verification of SCC models as well as refine SCC model input parameters. Verification of stress corrosion cracking (SCC) models will be of considerable benefit to the prediction of performance with respect to this potential failure mode. This verification is possible by matching experimental measurements with predictions of the SCC models. Further verification is possible by examining the crack tip chemistry and microstructure to demonstrate whether slip dissolution in stress corrosion test samples or other reactions such as oxygen uptake and embrittlement have occurred.

Crack tip chemistry and material analysis can be accomplished by three methods: 1) physical measurement of the crack tip solutions and materials, 2) measurement of rescaled crack tip solutions and materials, and 2) modeling of the crack tip chemistry. Physical measurement of SCC tip materials has been made possible by the development of reliable methods for producing cross-section samples of crack tips for high-resolution analytical electron microscopy (ATEM) [Lewis, 1995; Thomas, 2000; Thomas, 2003]. This method has been used on both austenitic stainless steels and nickel base alloys and has revealed chemical reactions at crack tips that were previously not known. One question that could be answered by this analysis is whether oxygen induced crack growth is a factor in SCC. Enhanced chemistry probes enable chemistry measurements with unprecedented resolution at crack tips. Scaling laws [Lee, Reed and Kelly, 2004] have been employed in crevices in order to sample solution chemistries and hydrogen contents from crack tips [Scully, Switzer and Lee, 2004]. Crack tip chemistry modeling would be a valuable tool when coupled with the physical measurement of crack tips to evaluate which environmental species have entered the crack tip. An example is the concern with Pb on stress corrosion of Alloy 22. If lead can be shown to not penetrate to the crack tip then concern about its presence in the environment would be greatly decreased.

Advances have also been made in understanding crack tip mechanics. Stress corrosion cracks are often sharper than blunted crack tip opening displacement calculations indicate. Strain gradient plasticity studies and experimental micro-indentation have improved understandings of local deformations such as may occur near sharp crack tips. These refinements to the understanding of mechanics and deformation behavior at crack tips could improve slip/film/rupture parameters and improve modeling of crack chemistry and electrochemistry.

## **Internal Oxidation as a Viable Mechanism**

### **Research Goal and Impact**

Evaluate the viability of a chemical reaction inducing oxygen reduction, uptake and embrittlement as a viable crack-tip mechanism for SCC. Key issues are the diffusion rate of oxygen at relevant temperatures, and its

relationship to the production significant crack extension. Some critical analysis to be performed are 1) high resolution TEM of laboratory test samples, and 2) modeling crack growth rates based on Alloy 600 data and mechanisms for a broader range of alloys.

### **Scientific Opportunity**

A recent development in SCC of nickel-based alloys is the hypothesis that crack growth occurs by an internal oxidation mechanism (Thomas, Insights 41. Newman, Internal 79). The supporting evidence for this mechanism, as cited by Scott (Scott, Overview 3), is the observation of morphology of nickel separated from chromium oxide formed ahead of resolvable crack tips and the absence of solution impurities in the oxidized grain boundaries. This evidence was observed by high-resolution transmission electron microscopy of stress corrosion crack tips in Alloy 600. Similarities in activation energies of crack growth rates for Alloy 600 over temperatures ranging from liquid water to steam phase is further evidence that an electrochemical reaction may not be involved but that a chemical reaction may be the rate controlling process. There is also a similarity in the activation energy for crack growth of Ni<sub>3</sub>Al tested in air to that of Alloy 600 tested in aqueous and steam environments.

## **High Resolution Crack Growth Measurement Technique**

### **Research Goal**

Develop a high-resolution technique for the in-situ measurement of slow crack growth rates in stress corrosion crack propagation tests. For extremely long lived structures, crack growth rates near the limits of current measurement methods could be of concern. The film rupture-dissolution model has been applied extensively for austenitic stainless steels, and there is a significant database that has been used to qualify this model for these alloys. However, the crack growth rates are sufficiently slow for Alloy 22 and other nickel alloys in relevant environments that it has not been possible to verify whether this model is valid in this instance. The calculations of the constants in the film rupture/slip dissolution model are well developed for 304 stainless steel in 288°C water. It is uncertain that these constants are applicable for alloys with significantly different plastic deformation behavior, such as Alloy 22. Constants specific to Alloy 22 and other nickel alloys for the film rupture/slip dissolution model are needed at relevant temperatures for conditions of very slow crack growth rates. The limited crack growth sensitivity has made it difficult to accomplish this, and consequently there is uncertainty in the application of the film rupture/dissolution model to crack growth for these extremely slow growth conditions.

### **Scientific Opportunity**

Sensitive, accurate measurements of crack growth rates are required for the verification of the slip dissolution model, or alternative crack propagation models for conditions where crack growth is extremely slow. Accurate crack growth rate data also are required for establishing the magnitude and variability of the constants in the models. The electric potential drop (EPD) technique is the most common technique used for the in-situ measurements of crack growth rates. This technique involves the application of a DC or AC current to a test specimen containing a growing crack and the measurement of the voltage drop between contacts placed on the specimen on either side of the crack. As the crack grows, the resistance of the specimen increases, and there is a resulting increase in the voltage drop, according to Ohms law. The technique can be quite sensitive but there are a number of factors that introduce variability and error in the measurement including temperature fluctuations in the specimen, thermocouple effects for any electrical contacts in the measurement circuit, and variations in the gain of the measurement equipment. These issues can be addressed through various control measurements and careful experimental techniques. Andresen does not specifically identify a sensitivity for the reversing DC potential drop technique used in his crack growth research but he claims the ability to accurately measure crack growth rates of  $5 \times 10^{-10}$  mm/s [Andresen, 2001]. While this is highly sensitive, it may be below the sensitivity necessary for establishing the constants under non-accelerated testing conditions. The measured growth rate on 20% cold worked Alloy 22 samples was approximately  $4 \times 10^{-10}$  mm/s, a rate that is near the lower limits of detection. Research is needed to determine whether the EPD technique can be modified to obtain the sensitivity required for application in crack growth modeling for slow growth conditions. Alternative techniques are needed if the limits of the EPD technique result in inadequate accuracy or sensitivity.

Another consequence of testing at the measurement limits for extremely slow crack growth rates is that crack stifling and arrest effects are difficult to detect in experimental measurements. Consequently, cracks that initiate are often presumed to propagate at a constant rate. No credit is given for slower crack growth rates or for crack stifling. This results because the currently available techniques for measurement of crack growth rates have inadequate sensitivity for detection of stifling. With a high-resolution technique for the in-situ measurement of crack growth rates, crack growth models could be verified and stifling could be incorporated in long term damage accumulation models. Accurate measurements of slow crack growth and stifling could be performed to improve the predictive capability of the models.

## References for Stress Corrosion Cracking

Andresen, P.L., P.W. Emigh, L.M. Young and G.M. Gordon, "Stress Corrosion Cracking of Annealed and Cold Worked Titanium Grade 7 and Alloy 22 in 110°C Concentrated Salt Environments," Corrosion/2001, Paper 130, NACE International, Houston, TX, (March 2001).

Andresen, P. L. and F.P. Ford, "Fundamental Modeling of Environment Cracking for Improved Design and Lifetime Evaluation in BWRs.", International Journal of Pressure Vessels and Piping, Vol. 59 (1-3), 61-70, Elsevier Science, New York, NY, (2004).

DOE Report, TDR-MGR-MD-000007 REV00, (June 2001).

Gaudett, M.A. and J.R. Scully, "Applicability of Bond Percolation Theory to IGSCC of Sensitized AISI 304 Stainless Steel", Metallurgical and Materials Transactions A, 25A, 775-787, (1994).

Jones, R.H., ASM Handbook, Vol. 13A, 346, ASM International, Materials Park, OH, (2003).

Jones, R.H. and E.P. Simonen, "Early Stages in the Development of Stress Corrosion Cracks", Materials Science and Engineering, A176, 211, (1994).

Jones, R.H., E.P. Simonen and R.E. Williford, "Early Stages of Intergranular Stress Corrosion Cracking", Corrosion 97, Paper No. 97184, (1997).

Kolman, D.G. and J.R. Scully, "An Assessment of the Crack Tip Potentials of  $\beta+\alpha$  Titanium Alloys During Hydrogen Environmentally Assisted Crack Propagation Based on Crack Tip and Passive Surface Electrochemical Measurement," Corrosion Science, 42(11), 1863-1879, (2000).

Kolman, D.G., M.A. Gaudett and J.R. Scully, "Modeling Anodic Current Transients from Oxide Rupture on Plastically Strained  $\beta+\alpha$  Titanium", Journal of the Electrochemical Society, 145(6), 1829-1840, (1998).

Lee, J.S., M.L. Reed and R.G. Kelly, "Combining Rigorously Controlled Crevice Geometry and Computational Modeling for Study of Crevice Corrosion Scaling Factors", Journal of the Electrochemical Society, 151(7), B423-B433, (2004).

Lewis, N., D.J. Perry and M.L. Bunch, in JMSA Proc. Microscopy and Microanalysis, 550, (1995).

Newman, R.C., T.S. Gendron and P.M. Scott, "Internal Oxidation and Embrittlement of Alloy 600", in Proceedings of the Ninth International Symposium on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, S.M. Bruemmer, F.P. Ford and G.S. Was, Eds, TMS, Warrendale, 79, (1999).

Scott, P.M., "An Overview of Internal Oxidation as a Possible Explanation of Intergranular Stress Corrosion Cracking of Alloy 600 in PWR's", in Proceedings of the Ninth International Symposium on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, S.M. Bruemmer, F.P. Ford and G.S. Was, Eds, TMS, Warrendale, PA, 3, (1999).

Scully, J.R., M.A. Switzer and J.S. Lee, “*Crevice Scaling Laws to Investigate Local Hydrogen Uptake in Rescaled Model Occluded Sites*”, Proceedings of EICM-2, Banff Canada, (September 2004).

Thomas, L.E. and S.M. Bruemmer, 11<sup>th</sup> Environmental Degradation of Materials in Nuclear Systems, Stevenson, WA, 1049, (August 2003).

Thomas, L.E. and S.M. Bruemmer, Corrosion Journal, 56, 572, (2000).

Thomas, L.E. and S.M. Bruemmer, “*Insights into Environmental Degradation Mechanisms from Analytical Transmission Electron Microscopy of SCC Cracks*”, in Proceedings of the Ninth International Symposium on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, S.M. Bruemmer, F.P. Ford and G.S. Was, Eds, TMS, Warrendale, PA, 41, (1999).

# Effects on Aging and Phase Stability

Frank Wong and Lawrence Kaufman

## Introduction

The effects of aging and phase stability of corrosion and stress corrosion processes can be substantial. For example, TCP phase and carbide precipitates that form in Alloy 22 are generally rich in chromium (Cr) and/or molybdenum (Mo) [Raghavan et al., 1984]. Because these elements are responsible for the good corrosion resistance of Alloy 22, precipitation of TCP phases and carbides, especially at grain boundaries, can lead to an increased susceptibility to localized corrosion in the alloy. These phases are brittle, and they also tend to embrittle the alloy [Summers et al., 1999]. They are known to form in Alloy 22 at temperatures greater than approximately 600°C. Progress has been made; however, and there are ample opportunities to improve the determination of metallurgical changes to an alloy at temperatures and time-scales of interest in any application. The lower the temperatures, the slower the rates and the more difficult it is to address the problem experimentally. There is benefit to be gained from improved methods (computational and experimental) to determine the phases that form at the lower temperatures. The kinetics of this precipitation are relevant to both base metal and the weld heat-affected zone (HAZ).

The CALPHAD approach has been applied to the study of statics (stability) and kinetics (aging) of phase formation and evolution in Ni-based alloys. Some examples of applications for Yucca Mountain relevant conditions are summarized here. At equilibrium, Alloy 22, at its nominal compositions and at low temperatures, should exhibit, besides the fcc matrix, long-range order of the Ni<sub>2</sub>Cr-type, complex Frank–Kasper phases (here, the P phase), carbides and silicides. The kinetics of Long Range Order (LRO) formation occurs at relatively low temperatures, and therefore, does not favor the formation of the ordered phase of Ni<sub>2</sub>Cr-type as the phase formation kinetics are primarily driven by diffusion. Alloys homogenized (or annealed) at high temperatures and quenched should not display any deleterious phase. Extrapolation of computationally derived TTT curves (which employ a Ni-Cr-Mo surrogate for Alloy 22) to lower temperatures, which are expected in a repository, indicates that forming the P or oP6 ordered phases from the fcc solid solution is unlikely. Project literature showed that formation of TCP or ordered oP6 phases in Alloy 22 base metal and annealed welds (which are deemed to be similar to base metal) is unlikely at temperatures near 200°C sustained for times in excess of 10,000 years.

Discussions during the BES-OCRWM Corrosion Workshop identified several research goals that would extend fundamental understanding of thermal aging effects on the corrosion performance through the further development of computational and experimental methodologies for aging and phase stability. These research goals are described below.

## **Extension of the Simulation of the Thermodynamics and Kinetic Behavior of Alloys to Higher-Order Component Systems**

### **Scientific and/or technological opportunity**

The current Ni-Cr-Mo ternary alloy database has been shown to conservatively predict the formation of P,  $\sigma$ , and oP6 (ordered) phases in base metal. However, this database does not include W directly, but uses an adjustment to Mo to account for W. It also does not contain Fe, which may affect the formation of the oP6 phase. Ni-Cr-Mo-W-Fe are important elements in Alloy 22.

Gibbs energy and mobility descriptions that have been developed and tested for three component systems, e.g. Ni-Cr-Mo, should be extended to higher-order component systems, e.g., the five component system Ni-Cr-Mo-W-Fe. To properly account for the effects on phase stability of the most important elements, the Ni-Cr-Mo ternary alloy database needs to be expanded to include both W and Fe. Similarly, phase kinetics calculations have been made with DICTRA using the Ni-Cr-Mo database, and it is recommended these be extended to a Ni-Cr-Mo-W-Fe system. Further, kinetic data is needed for a Ni-Cr-Mo-W-Fe system.

### **Relevance and potential impact**

The present models for predicting and simulating formation of the oP6 phase in the Ni-Cr-Mo-W system suggest that while Mo increases the stability, W decreases the stability of the oP6 Phase. It would be useful to determine the effects of Fe on the thermodynamic and kinetic properties so that the time-temperature-transformation characteristics for the fcc/oP6 transformation in the five component alloy could be calculated.

## **Effects On Long-Term Corrosion Performance Of TCP Phase Precipitates**

### **Scientific and/or technological opportunity**

The TCP phases have much different compositions than the matrix phases. The phase fraction versus potential curves for the matrix,  $\sigma$  and P phases could be calculated and measured at selected pH values as a function of temperature. This technique would be applicable to base metal and welds.

### **Relevance and potential impact**

Such calculations would permit an evaluation of the segregation that can be expected in base metal and welds on localized corrosion in this region.

## **Inclusion of Geometrical Effects on Diffusion Processes to Account for Microstructure Characteristics.**

### **Scientific and/or technological opportunity**

Current phase kinetics calculations are based on a simple model of one-dimensional diffusion without considering the geometric effects that should be applied for processes such as grain boundary precipitation. These geometric effects are evident in the microstructural characterization and should be included in these kinetics calculations. Extensions to these models to treat the growth of the  $\sigma$ , P-phase and ordered phases as a planar front are needed. A more realistic geometrical description would include examination of a hemisphere advancing from a grain boundary. Such geometries are implemented within DICTRA and can be applied using the existing Gibbs energy and mobility data.

### **Relevance and potential impact**

Models based on precipitation at a grain boundary could provide a more accurate description of the transformation kinetics and provide some insight into the effects of the grain size on phase precipitation which could be verified experimentally.

## **Computational Thermodynamics and Kinetics Simulations to Determine the Phase Stability of Welds**

### **Scientific and/or technological opportunity**

The problems associated with segregation in welds have been addressed by performing Scheil-Gulliver simulation calculations of weld solidification processes. The results show substantial segregation which are supported by experimental studies. The experimental data that have been generated for welded nickel alloys can be used to define the limits of compositional changes in both the matrix and TCP phases. These compositional limits could be investigated at specific pH and temperature levels by experimental and computational methods. Performing similar types of computational simulations to those on base metal should also be extended to welds.

### **Relevance and potential impact**

Using the Scheil-Gulliver model and the extended five component data base outlined above could provide enhanced predictions of segregation in the weld region which could be used in calculations of the variation of corrosion properties over a range of pH and temperature.

## **Effects of Cold-Work and Increased Dislocation Densities on Aging Phenomena**

### **Scientific and/or technological opportunity**

Because precipitates are present in as-welded microstructures, the kinetics of precipitation is not an issue as it is in the base metal and the heat-affected zone (HAZ) for long-term metallurgical performance. Whether these precipitates are stable and grow or unstable and dissolve with aging at service temperatures is an important issue. For weld regions where stress mitigation techniques are used, these techniques may result in areas of increased cold-work (due to local plastic deformation), and hence, dislocation density. As a result, the increase in dislocation density may result in faster diffusion rates for phase precipitation. Advanced treatments are needed for the effect of such faster diffusion rates at relevant temperatures on phase kinetics.

### **Relevance and potential impact**

Cold work after solution annealing will result in increased dislocation densities in the cold-worked regions. Such an increase in dislocation densities may result in faster pathways for diffusion processes, such as phase precipitation, which, if significant, could alter corrosion performance. The effects of cold work after solution annealing on the phase precipitation kinetics should be determined.

## **Effects Resulting from Heat-To-Heat Variability on Stress Corrosion Cracking Behavior**

### **Scientific and/or technological opportunity**

An analogy was presented from industry experience with Alloy 600. Heat-to-heat variability effects on Alloy 600 was identified as the likely cause of the SCC failures that were examined, but no fundamental understanding of the heat-to-heat variability effects on SCC was developed.

## **Relevance and potential impact**

The suggested analyses could provide a means for characterizing the variability in the performance of the alloys to the heat-to-heat compositional variability.

## **References for Effects on Aging and Phase Stability**

Raghavan, M., R.R. Mueller, G.A. Vaughn and S. Floreen, "*Determination of Isothermal Sections of Nickel Rich Portion of Ni-Cr-Mo System by Analytical Electron Microscop.*", Metallurgical Transactions A, 15A, (5), 783-792, New York, New York: Metallurgical Society of American Institute of Mining, Metallurgical, and Petroleum Engineers, (1984).

Summers, T.S.E., M.A. Wall, M. Kumar, S.J. Matthews and R.B. Rebak, "*Phase Stability and Mechanical Properties of C-22 Alloy Aged in the Temperature Range 590 to 760°C for 16,000 Hours*", Scientific Basis for Nuclear Waste Management XXII, Symposium held November 30-December 4, 1998, Boston, Massachusetts, Wronkiewicz, D.J. and J.H. Lee, eds., 556, 919-926, Warrendale, Pennsylvania: Materials Research Society, (1999).

## Methods and Tools

R. G. Buchheit and N. A. Missert  
with C. R. Clayton, J. R. Scully, H. S. Isaacs, R. G. Kelly,  
T. M. Devine, R. Newman, G. Gdowski, W. Halley, A. Gewirth

## Introduction

To characterize the knowledge gap in localized corrosion, it is interesting to consider pitting of 18Cr-8Ni austenitic stainless steel. A myriad of sophisticated methods and tools have been applied to the problem of passivity breakdown, metastable pitting, pit propagation, pit repassivation. The phenomenology of these processes has been characterized in exquisite detail and essential mechanistic aspects have been described and modeled. It is likely that more is known about pitting of this alloy than any other. Nonetheless, it remains very difficult to predict, using a deterministic approach, when and where pits will initiate, and how fast corrosion damage will accumulate. Similar statements can be made for other important corrosion resistant engineering alloys including those based on aluminum, titanium, nickel, and copper.

The traditional framework for experimental corrosion characterization is formed by techniques drawn from electrochemistry, surface analysis, and metallurgy. This framework, which is shaped by the physics and chemistry of the corrosion process itself, is more useful than ever for addressing the knowledge gap in localized corrosion. It would be a significant accomplishment if the research community were to use this framework to develop a robust knowledge base for the treatment of localized corrosion of passive metals. However, based on foregoing arguments, this knowledge base alone does not enable deterministic modeling of corrosion damage accumulation. It is noted that experimentation in support of deterministic models is more prevalent than ever before. Additionally, there have been great advances in analytical tools that now enable resolution of important chemical and physical phenomena at atomic and near-atomic length scales. This is precisely what is needed to help modelers formulate and parameterize deterministic models for corrosion damage accumulation in Alloy 22 and other corrosion resistant alloys.

In the following section, promising approaches and techniques to address the knowledge gap in localized corrosion for corrosion resistant passive alloys of engineering significance are highlighted.

## Electrochemical Approaches

Electrochemical measurements remain one of the most sensitive analytical techniques in all of materials science and chemistry. Using electrochemical measurements, localized corrosion can be studied at its very earliest stages. Perhaps one of the best examples of this is the measurement and analysis of noise associated with metastable pit formation [Frankel, Stockert, Hunkler and Boehni, 1987]. Combining these approaches with characterization of surface film or corrosion product chemistry or alloy microstructure is a fruitful exercise in the context of corrosion modeling because well described formalisms exist for determining metastable pit initiation rates, pit lifetimes, critical incubation times for stabilization and pit death rates [Williams, Westcott and Fleischmann, 1985]. These parameters can be used to understand global susceptibility to localized corrosion. Similar characterizations can be made for crevice corrosion [Laycock, Stewart and Newman, 1997]. These approaches are attractive because they are probabilistic in nature and can be related to surface treatment and chemistry [Noh, Laycock, Gao and Wells, 2000], environment [Pistorius and Burstein, 1994; Pride, Scully and Hudson, 1994], temperature [Laycock, Moayed and Newman, 1998], and alloy microstructure [Scully, Peebles, Romig, Frear and Hills, 1992]. These relationships can provide a solid foundation for assessing the risk of corrosion damage and forecasting corrosion damage accumulation. Therefore, they continue to form a promising line of research.

Much attention has been given to the extreme corrosion resistance of Alloy 22 and to the fact that if it does corrode it will do so only in extremely aggressive localized environments within pits and crevices. Pit initiation rates, propagation rates and death rates (stifling) will need to be characterized under these conditions. The evolution of chemistry within restricted spaces will also need to be characterized. This will need to include characterization of the electrolyte chemistry, the formation of salt films, hydrated corrosion product films. There are a number of very

good artificial pit and crevice approaches that have been used to support electrochemical and chemical interrogation of occluded cell corrosion processes [Steinsmo, 1993; Kimura, Kaneko and Ohta, 2002]. Because they can be designed with idealized shapes and sizes, artificial pits and crevices can be used to develop models or validate model predictions related to local dissolution rates or occluded environment chemistry [Shinohara, Fujimoto, Laycock, Msallem, Ezuber and Newman]. A major opportunity is to extend crevice scaling laws to highly corrosion resistant alloys in order to resize crevices towards dimensions more accessible to interrogation tools. These approaches should find utility for study of localized corrosion in corrosion resistant alloys.

Corrosion in thin electrolyte layers deserves special attention. Formation of thin condensed layers is a routine occurrence in many engineering applications. For Yucca Mountain, the formation of condensed or deliquescent electrolyte layers on waste containers during cooling of the repository is of particular interest. Compared to the amount of electrochemical corrosion research carried out in bulk electrolytes, the amount done in thin electrolyte layers is relatively small; for selected examples refer to references below. The work that has been reported highlights the weaknesses of using electrochemical data generated under conditions of bulk inundation to understand corrosion in thin electrolyte layers. Many of the thin electrolyte layer approaches that have been demonstrated can be applied directly or with slight modification to the Yucca mountain corrosion problems.

In atmospheric corrosion studies there is a long history of using electrochemical approaches to measure time of wetness, atmospheric corrosivity, and corrosion rate. These measurements are made using so-called atmospheric corrosion rate monitors, or ACMs. Basic ACMs measure the galvanic current flow between interleaved or interdigitated dissimilar metals during atmospheric exposure [Mansfeld and Tsai, 1980]. Modified ACMs embed counter electrodes and metallic pseudoreference electrodes to enable three electrode measurements [Gonzalez, Otero and Cabanas, 1980]. The utility of non-contact Kelvin probe reference electrodes have also been demonstrated [Stratmann]. The use of such reference electrodes enables measurements in very thin electrolyte layers without complications arising from large solution resistances and remotely located reference electrodes.

In atmospheric corrosion studies, it is typically the case that the electrolyte layer thickness is largely uncharacterized. However, several different approaches have been used to limit the extent, or control electrolyte layer thickness in the 1 to 1000 micrometer range. These include the use of micropositioning to set the distance between working and counter electrodes with 10  $\mu\text{m}$  precision or better [Keddam, Hugot-Le-Goff, Takenouti, Thierry and Arevalo, 1992], the use of a partially submerged vertical rotating disk [Takehara, Saito and Yoshizawa, 1976], and direct microhydraulic control of solution layer thickness by precision syringe [Stratmann, Streckel, Kim and Crockett, 1990].

Condensation and evaporation of thin layers can be controlled by careful cycling of the substrate temperature (with the caveat that temperature cycling adds the complication of affecting electrochemical kinetics), or by controlling the prevailing relative humidity, which is usually accomplished in an enclosed chamber. Controlled condensation and evaporation combined with in situ electrochemical interrogation has enabled characterization of the electrochemical processes to be characterized under transient conditions [Stratmann and Muller, 1994]. Deliquescent layers can be formed by first inoculating a metallic surface with a soluble salt by applying and evaporating an inoculant solution, then exposing the surface to a humid gaseous environment [Fishman and Crowe, 1977].

Microelectrode approaches are enabling on several fronts. Micro “working” electrodes have been used successfully to sensitively characterize corrosion behavior under both aqueous and atmospheric conditions. A key advantage of a microelectrode is minimization of background current, which enables observation of very small metastable current transients [Riley, Wells and Williams]. Micro “reference” electrodes are available for measuring potential [Lu, Lu and Ives, 1992], pH [Vanhoud, Lewandowski and Little] and chloride ion concentration [Lu, Lu and Ives, 1992], but have not yet been broadly applied to characterizing local environment chemistry. Microelectrochemical cells enable small areas in complex microstructures such as particles and grain boundaries to be targeted and characterized using conventional electrochemical methods [Suter and Bohni, 1998]. Such approaches may be particularly illuminating in establishing corrosion mechanisms in weldments where there are a variety of microstructural and compositional changes over small distances.

The ultimate in small electrodes and small length scale electrochemical characterization is found in the imaging techniques derived from scanning tunneling microscopy (STM) [Ryan, Newman and Thompson, 1994] and

atomic force microscopy (AFM) [Li and Meier, 1998]. AFM has been combined with scanning Kelvin probe force imaging [Schmutz and Frankel, 1998] and with scanning electrochemical microscopy [Macpherson and Unwin, 2000] and applied to corrosion characterization.

A particularly daunting prospect from the experimental perspective is thorough characterization of the effect of environmental variables on corrosion behavior. Combinatorial chemistry approaches, which have been developed and adopted by the pharmaceutical, specialty chemicals and coatings industries, can be exploited by the corrosion community to characterize the influence of environment. New segmented working electrodes and multiplexed potentiostats approaches enable significant parallelization of experiments [Lunt, Brusamarello and Scully, 2000; Tan, 2003]. This enables test matrices to be completed in rapid fashion. It is also easy to imagine how combinatorial chemistry approaches might be used to explore and develop corrosion resistant alloys [Schmutz and Frankel, 1998] especially in cases where strong thresholds are suspected to exist upon incremental change in alloy composition.

Finally, while characterization of the structure and chemistry of passive films has mainly been the purview of surface analysis, photoelectrochemical [Cho, Kwon and Macdonald, 2002] and electrochemical impedance [Juttner, 1990] approaches for assessing defect states have also proven their utility.

## Surface science approaches

A broad range of surface analytical techniques have been applied to the study of surface films ranging from 2 nm to a few micrometers in thickness [Graham, 1992]. These techniques include Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), Mossbauer spectroscopy, X-ray absorption near edge spectroscopy (XANES), secondary ion mass spectrometry (SIMS) and electron energy-loss spectroscopy (EELS), among others. Such techniques have contributed greatly to our current understanding of corrosion and oxidation at the atomic scale. Nonetheless, many of the fundamental processes associated with passive film formation, dissolution and breakdown are not sufficiently characterized so that they can be modeled accurately. There has been a significant development in chemical imaging across the field of spectroscopy. Of particular note is the development of small area imaging XPS which provides mapping by speciation and not just by element type as is the case with SIMS, AES and EDAX. Since speciation is a major component to developing models of composition and structure of surface films, imaging-XPS is poised to play a major role in surface characterization.

New developments in synchrotron small area XPS offers great potential for ultra-high resolution chemical mapping and secondary electron imaging. At least two general strategies are available. The first strategy is to bring to bear new or improved instrumental techniques that yield structural and chemical information at very high resolution. For example, focused ion beam (FIB) tools have been available to researchers for some time. Recently, dual-beam FIBs, which integrate electron beam imaging and ion beam milling have become available. Focused ion beams can also be used to create high resolution AES and SIMS tools [Ferryman, Fulghum, Giannuzzi and Stevie, 2002]. Synchrotron radiation-based methods provide unique capabilities. Depth profiling thin layers with high resolution by glow discharge optical emission spectroscopy has good dynamic range and can profile layers from 10 nm to tens of micrometers in thickness [Shimizu, Habazaki, Skeldon, and Thompson, 2002]. High resolution XPS allows for high spatial resolution XPS analyses [Kiskinoya, 2000]. XPS in combination with site-specific molecular probes have proven fruitful for characterizing the site-specific acid/base character in passive films [Ma, Berthier and Marcus, 2002]. New approaches to surface analysis such as Laser-induced plasma spectrometry allow for excellent near surface chemical characterization [Vadillo and Laserna, 2004]. Newly developed atom probe approaches allow determination of chemistry and structure with atomic or near atomic resolution [Gribb and Kelly, 2004].

The second, perhaps more traditional strategy is to use combinations of techniques to develop comprehensive structure-chemistry determinations. Scanning tunneling microscopy (STM) and XPS approaches have proven to be a powerful combination when applied to passivated metal surfaces in this regard [Maurice, Yang and Marcus, 1996]. STM approaches are suitable for characterizing the evolution of thin passive films both in situ and ex situ [Maurice, Klein and Marcus, 2002]. XPS in conjunction with Raman Spectroscopy, Nuclear microanalysis for study of passive films is just one example of additional methods. There are myriad combinations of tools capable of resolving structure and chemistry of thin interfacial films [Thierry, Persson and Leygraf, 1988].

The use of high intensity synchrotron light sources X-rays methods is well established for the in situ study of passive films, localized dissolution, and dissolution products [Davenport and Gordon, 1992; MacBreen, 2002; Strehblow, 1998]. X-ray methods may be divided into scattering and absorption spectroscopy (XAS). Scattering techniques have been used to determine the structure of passive films. For example the structure of the passive film on a single crystal of iron was found to be a spinel oxide but one that differed from the structure of any known bulk oxide. The same structure was formed in air [Toney, Davenport, Oblonsky, Ryan and Vitus, 1997]. Similar diffraction experiments on copper found a cuprite formed electrochemically and also during air exposure [Chu, Robinson and Gewirth, 1999]. The reduction of the oxides can also be followed during electrochemical control.

Electrochemically induced changes on metal surfaces have also been studied using XAS. The x-ray absorption near edge (XANES) enables the oxidation and reduction of specific elements in alloys or of pure metals to be determined from the position and shape of the absorption edge around the binding energy of specific electron shells. Dissolution leads to a decrease in height of the edge best seen well above the binding energy. An excellent example of the use of XANES is the analysis of the behavior of the elements in stainless steels. It has been shown that the air formed films on stainless steels behave significantly differently on anodic polarization than the oxide films formed after cathodic reduction [Davenport, Sasone, Bardwell, Aldykiewicz, Taube and Vitus, 1994; Bardwell, Sproule, MacDougal, Graham, Davenport and Isaacs, 1992]. The air formed film preferentially forms an Fe oxide outer layer [Betz, Wehner, Toth and Joshi, 1974] that inhibits transpassive Cr oxidation to chromate. Detailed studies of the behavior of Fe oxide films have been carried out [Virtanen, Schmuki and Isaacs, 2002] and after cathodic reduction and concomitant dissolution of the Fe oxide, a Cr oxide-rich passive film forms which is susceptible to transpassive dissolution and loss of Cr. With Ni-containing stainless steels Ni dissolves slowly both during the cathodic dissolution of Fe and at the loss of Cr at the transpassive potential. A major advantage of XANES is that the changes at the surface can be monitored without requiring removal of the sample from solution or exposing to high vacuum [Oblonsky, Ryan and Isaacs, 1988].

X-ray fluorescence microprobe techniques have been used to study salt layers and the concentrated solutions during localized corrosion of stainless steels in artificial pits [Isaacs, Cho, Rivers and Sutton, 1995; Isaacs and Haung, 1996]. The composition of salt films on the stainless steel was found to be predominantly ferrous chloride, highly depleted in chromium and to a lesser degree in Ni. The adjacent saturated solution had a 5 Molar metal concentration. Mo was not found to follow the Cr having a depleted concentrate in the salt film and remained soluble in the pit solution. In the concentrated solution, XANES and extended x-ray absorption fine structure (EXAFS) have been used to study the coordination states of the metal ions in solution and it was found that the Mo behaved differently in chloride and bromide solutions [Kimura, Kaneko and Ohta, 2002].

## **Metallurgical Approaches**

In microstructurally and compositionally complex alloys, there are three broad metallurgical factors that affect localized corrosion. These are compositional variations in solid solution phases including localized solute depletion; microstructural heterogeneity associated with second phase particles, inclusions, and grain boundaries, and segregation of low-level impurity elements to internal and external surfaces. Engineering alloys always exhibit some measure of metallurgical instability—especially over very long periods of time, and how the microstructure changes with time and temperature must be understood in order to fully characterize susceptibility to localized corrosion. In the case of corrosion resistant alloys with compositions approaching that of Alloy 22, some of the basic relationships between alloy composition and corrosion behavior have not yet been characterized in detail.

Many alloys, including Alloy 22, are solid solutions over broad compositional ranges. To characterize the effects of alloying elements on corrosion behavior, high-throughput combinatorial chemistry approaches appear to be well suited. Such experiments involve deposition of compositionally graded alloys and interrogation of corrosion properties along the composition gradient using micro-electrochemical cells. Alternatively, compositionally graded materials can be deposited onto segmented working electrode arrays and interrogated using methods described earlier.

Engineering alloys contain dispersions of small particles that form during solidification, thermomechanical processing, or joining. These particles can be intentionally formed as in the case of strengthening precipitates, or be the unavoidable by product of impurity elements, which accumulate in discrete particles. In any case, when these

particles are of a sufficient size and chemistry they can alter the course of localized corrosion. In many important alloys, like stainless steels and high strength Al alloys, particles dominate localized corrosion behavior. Understanding the electrochemical behavior of such particles is of paramount importance. In many mature alloy systems the particle phases that form are known. Sometimes there are variations in the possible particle chemistries that depend on bulk alloy chemistry and processing. When uncertainty exists, electron microscopy, x-ray microchemical determinations and electron diffraction approaches can be used to unequivocally determine particle identity. Once identified, such phases can be prepared in bulk form for isolated characterization by conventional electrochemical methods. Preparation methods that have been employed include casting [Buchhei, Boger, Carroll, Leard, Paglia and Searles, 2001] and thin film deposition of compositional analogs [Ramgopal, Gouma and Frankel, 2002]. In both approaches, care must be taken to ensure that the chemistry and structure of the analogs are achieved to insure that the data collected are relevant.

Microfabrication methods like photolithography enable artificial microstructures to be made. Chemistry, structure and morphology can be tailored to mimic microstructural heterogeneity and surface oxide films. Ingot metallurgy and thin film deposition can be used to fabricate intermetallic compounds, solution depleted layers and solid solutions in bulk form for study by conventional electrochemical techniques. Such approaches have been very useful in developing and testing localized corrosion mechanisms.

Impurity elements can segregate to grain boundaries and to the surface of engineering alloys given sufficient time and temperature. This can lead to embrittlement or an increase in electrochemical reactivity of grain boundaries. Segregation of impurities to alloy surfaces can lead to a decrease in corrosion resistance. In high performance engineering alloys, the concentrations of impurity elements are very small. Even when segregated and concentrated at interfaces, the amount of impurity may be at or below the detection limit of the most sensitive surface analysis techniques. One recent advance in electron microscopy instrumentation, namely focused ion beam tools, aid in the analysis of boundaries and surfaces because they make it possible to make thin foils and cross sections that target specific locations in the microstructure [Lozano-Perez, Huang, Langford and Titchmarsh, 2001].

Other electron microscopy techniques continue to evolve in order to allow sensitive investigation of materials properties at decreasing length scales. Recently, a statistical software package (AXSIA) has been developed in order to form spectral images or elemental maps representing phases present on 10 nm length scales. These images are formed by collecting a series of x-ray spectra from a region of the sample using a scanning transmission electron microscope. The full spectrum from each beam position is stored in a database. An algorithm then looks for correlations at each beam position between spectral peaks, greatly enhancing the signal to noise ratio for trace elements and allowing their spatial distribution to be mapped. Such images have shown the presence of Cl distributed within an aluminum oxide layer that was 400 nm away from a pitted region. Such a technique can be applied in order to assess the influence of impurity segregation or solute depletion on corrosion.

## References for Methods and Tools

Bardwell, J.A., G.I. Sproule, B. MacDougall, M.J. Graham, A.J. Davenport and H.S. Isaacs, *Journal of the Electrochemical Society*, 139, 371, (1992).

Betz, G., G.K. Wehner, L. Toth and A. Joshi, *Journal of Applied Physics*, 45, 5312, (1974).

Buchhei, R.G., R.K. Boger, M.C. Carroll, R.M. Leard, C. Paglia and J.L. Searles, *JOM-Journal of the Minerals Metals & Materials Society*, 53, (2001).

Cho, E.A., H. Kwon and D.D. Macdonald, *Electrochimica Acta*, 47, 1661-1668, (2002).

Chu, Y.S., I.K. Robinson and A. Gewirth, *J. Chem. Phys.*, 110, 5952, (1999).

- Cox, A., S.B. Lyon, *Corrosion Science*, 36, 1167-1176, (1994).
- Cox, A. and S.B. Lyon, *Corrosion Science*, 36, 1177-1192, (1994).
- Davenport, A. and J.G. Gordon, Eds., *X-ray Methods in Corrosion and Interfacial Chemistry*, Vol. PV 92-1, Pennington NJ: The Electrochemical Society, 1992.
- Davenport, A.J., M. Sasone, J.A. Bardwell, A.J. Aldykiewicz, M. Taube and C.M. Vitus, *Journal of the Electrochemical Society*, 141, L6, (1994).
- Ferryman, A.C., J.E. Fulghum, L.A. Giannuzzi and F.A. Stevie, *Surface and Interface Analysis*, 33, 907-913 (2002).
- Fishman, S.G. and C.R. Crowe, *Corrosion Science*, 17, 27 – 37, (1977).
- Frankel, G.S., L. Stockert, F. Hunkler and H. Boehni, *Corrosion*, 43, 429-436, (1987).
- Gonzalez, J.A., E. Otero and C. Cabanas, *Br. Corrosion Journal*, 25, 125, (1990).
- Graham, M.J., *Pure and Applied Chemistry*, 64, 1641-1645, (1992).
- Gribb, A.A. and T.F. Kelly, *Advanced Materials and Processes*, 162, 31-34, (2004).
- Isaacs, H.S., J.-H. Cho, M.L. Rivers and S.R. Sutton, *Journal of the Electrochemical Society*, 142, 1111 (1995).
- Isaacs, H.S. and S.-M. Haung, *Journal of the Electrochemical Society*, 143, L277, (1996).
- Juttner, K., *Electrochimica Acta*, 35, 1501, (1990).
- Keddam, M., A. Hugot-Le-Goff, H. Takenouti, D. Thierry and M.C. Arevalo, *Corrosion Science*, 33, 1243-1252, (1992).
- Kimura, M., M. Kaneko and N. Ohta, *ISIJ Int.*, 42, 1399, (2002).
- Kiskinova, M., *Surface Review and Letters*, 7, 447-453, (2000).
- Laycock, N.J., M.H. Moayed and R.C. Newman, *Journal of the Electrochemical Society*, 145, 2622-2628, (1998).
- Laycock, N.J., J. Stewart and R.C. Newman, *Corrosion Science*, 39, 1791-1809, (1997).
- Leng, A. and M. Stratmann, *Corrosion Science*, 34, 1657, (1993).
- Li, J. and D.J. Meier, *Journal of Electroanalytical Chemistry*, 454, 53-58, (1998).
- Lozano-Perez, S., Y. Huang, R. Langford and J.M. Titchmarsh, *Electron Microscopy and Analysis 2001 Institute of Physics Conference Series*, 168, 191-194, (2001).

Lu, J.L., Y.C. Lu and M.B. Ives, *Journal of Electroanalytical Chemistry*, 326, 51-68, (1992).

Lunt, T.T., V. Brusamarello and J.R. Scully, *Electrochemical and Solid State Letters*, 3, 271-274, (2000).

Ma, H., Y. Berthier and P. Marcus, *Corrosion Science*, 44, 171-178, (2002).

MacBreen, J., Ed., *Electrochimica Acta*, 47, (2002).

Macpherson, J.V. and P.R. Unwin, *Analytical Chemistry*, 72, 276-285, (2000).

Mansfeld, F. and S. Tsai, *Corrosion Science*, 20, 853 – 872, (1980).

Maurice, V., L.H. Klein and P. Marcus, *Surface and Interface Analysis*, 34, 39-143, (2002).

Maurice, V., W.P. Yang and P. Marcus, *Journal of the Electrochemical Society*, 143, 1182-1200, (1996).

Noh, J.S., N.J. Laycock, W. Gao and D.B. Wells, *Corrosion Science*, 42, 2069-2084, (2000).

Oblonsky, L.J., M.P. Ryan and H.S. Isaacs, *Journal of the Electrochemical Society*, 145, 1922, (1988).

Pistorius, P.C. and G.T. Burstein, *Corrosion Science*, 36, 525-538, (1994).

Pride, S.T., J.R. Scully and J.L. Hudson, *Journal of the Electrochemical Society*, 141, 3028-3040, (1994).

Ramgopal, T., P.I. Gouma and G.S. Frankel, *Corrosion*, 58, 687-697, (2002).

Riley, A.M., D.B. Wells and D.E. Williams, *Corrosion Science*, 32, 1307-1313.

Ryan, M.P., R.C. Newman and G.E. Thompson, *Philosophical Magazine B*, 70, 241-251, (1994).

Schmutz, P. and G.S. Frankel, *Journal of the Electrochemical Society*, 145, 2295-2306, (1998).

Scully, J.R., D.E. Peebles, A.D. Romig, D.R. Frear and C.R. Hills, *Metallurgical Transactions A*, 23, 2641-2655, (1992).

Shimizu, K., H. Habazaki, P. Skeldon and G.E. Thompson, *Spectrochimica Acta B-Atomic Spectroscopy*, 58, 1573-1583, (2003).

Shinohara, T., S. Fujimoto, N.J. Laycock, A. Msallem, H. Ezuber and R.C. Newman, *Journal of the Electrochemical Society*, 144, 3791-3796.

Steinsmo, U. and H.S. Isaacs, 35, 83-88, (1993).

Steinsmo, U. and H.S. Isaacs, 140, 643-653, (1993).

- Stratmann, M. and J. Muller, *Corrosion Science*, 36, 327-359, (1994).
- Stratmann, M. and H. Streckel, *Berichte Der Bunsen-Gesellschaft-Physical Chemistry Chemical Physics*, 92, 1244-1250, (1988).
- Stratmann, M. and H. Streckel, *Corrosion Science*, 30, 681-696, (1990).
- Stratmann, M. and H. Streckel, *Corrosion Science*, 30, 697-714, (1990).
- Stratmann, M., H. Streckel, K.T. Kim and S. Crockett, *Corrosion Science*, 30, 715-734, (1990).
- Strehblow, H.H., Ed., *Synchrotron Rad. News*, 11, (1998).
- Suter, T. and H. Bohni, *Electrochimica Acta*, 43, 2843-2849, (1998).
- Takehara, Z., A. Saito and S. Yoshizawa, *Corrosion Science*, 16, 91-101, (1976).
- Tan, Y.J., *Fluctuation and Noise Letters*, 3, L419-L432, (2003).
- Thierry, D., D. Persson and C. Leygraf, *Journal of the Electrochemical Society*, 135, 305-310, (1988).
- Toney, M.F., A.J. Davenport, L.J. Oblonsky, M.P. Ryan and C.M. Vitus, *Phys. Rev. Let.*, 79, 4282, (1997).
- Vadillo, J.M. and J.J. Laserna, *Spectrochimica Acta B-Atomic Spectroscopy*, 59, 147-161, (2004).
- Vanhoud, P., Z. Lewandowski and B. Little, *Biotechnology and Bioengineering*, 40, 601-608.
- Virtanen, S., P. Schmuki and H.S. Isaacs, *Electrochimica Acta*, 47, 3117, (2002).
- Williams, D.E., C. Westcott and M. Fleischmann, *Journal of the Electrochemical Society*, 132, 1796-1804, (1985).
- Williams, D.E., C. Westcott and M. Fleischmann, *Journal of the Electrochemical Society*, 132, 1804-1811, (1985).

## **ACKNOWLEDGEMENTS**

The workshop was co-sponsored by the Office of Basic Energy Sciences and Office of Civilian Radioactive Waste Management of the U.S. Department of Energy, and their support is gratefully acknowledged. We are grateful to Ms. Christie Ashton of the Division of Materials Science and Engineering in BES for her efficient and effective support of with workshop logistics.

Assistance was provided through the Center for Electrochemical Science and Engineering at University of Virginia and the Yeager Center for Electrochemical Science at Case Western Reserve University.

## **APPENDIX**

Appendix A-Corrosion Workshop Participants

## **Appendix A-Corrosion Workshop Participants**

Joe H. Payer (**Co-Chairman**); Case Western Reserve University; [Joe.Payer@case.edu](mailto:Joe.Payer@case.edu)  
John R. Scully (**Co-Chairman**); University of Virginia; [jrs8d@j.mail.virginia.edu](mailto:jrs8d@j.mail.virginia.edu)

John Beavers; CC Technologies; [jbeavers@cctlabs.com](mailto:jbeavers@cctlabs.com)  
Jeff Braithwaite; Sandia National Laboratories; [jwbrait@sandia.gov](mailto:jwbrait@sandia.gov)  
Rudy Buchheit; Ohio State University; [buchheit@mse.eng.ohio-state.edu](mailto:buchheit@mse.eng.ohio-state.edu)  
Clive Clayton; State University of New York; [CClayton@notes.cc.sunysb.edu](mailto:CClayton@notes.cc.sunysb.edu)  
Thomas M. Devine, Jr.; University of California; [devine@socrates.berkeley.edu](mailto:devine@socrates.berkeley.edu)  
Steve Dexter; University of Delaware; [dexter@udel.edu](mailto:dexter@udel.edu)  
Joe Farmer; Lawrence Livermore National Lab.; [farmer4@llnl.gov](mailto:farmer4@llnl.gov)  
Greg Gdowski; Lawrence Livermore National Lab.; [gdowski1@llnl.gov](mailto:gdowski1@llnl.gov)  
Andrew Gewirth; University of Illinois; [agewirth@uiuc.edu](mailto:agewirth@uiuc.edu)  
Woods Halley; University of Minnesota; [woods@jwhp.spa.umn.edu](mailto:woods@jwhp.spa.umn.edu)  
Hugh Isaacs; Brookhaven National Laboratory; [Isaacs@bnl.gov](mailto:Isaacs@bnl.gov)  
Russ Jones; Pacific Northwest National Lab.; [rh.jones@pnl.gov](mailto:rh.jones@pnl.gov)  
Larry Kaufman; Massachusetts Inst. of Tech.; [larrykaufman@rcn.com](mailto:larrykaufman@rcn.com)  
Digby Macdonald; Pennsylvania State University; [ddm2@psu.edu](mailto:ddm2@psu.edu)  
Nancy Missert; Sandia National Laboratories; [namisse@sandia.gov](mailto:namisse@sandia.gov)  
Roger Newman; UMIST; [roger.newman@umist.ac.uk](mailto:roger.newman@umist.ac.uk)  
Chris Orme; Lawrence Livermore National Lab.; [orme1@llnl.gov](mailto:orme1@llnl.gov)  
Peter Scott; Framatome ANP; [peter.scott@framatome-anp.com](mailto:peter.scott@framatome-anp.com)  
David Shoosmith; University of Western Ontario; [dwshoesm@uwo.ca](mailto:dwshoesm@uwo.ca)  
David J. Wesolowski; Oak Ridge National Laboratory; [wesolowskid@ornl.gov](mailto:wesolowskid@ornl.gov)  
Frank Wong; Lawrence Livermore National Lab.; [wong71@llnl.gov](mailto:wong71@llnl.gov)

## **Contributors**

Jerry Frankel; Ohio State University; [frnakel10@osu.edu](mailto:frnakel10@osu.edu)  
Rob Kelly; University of Virginia; [rgkelly@virginia.edu](mailto:rgkelly@virginia.edu)

## **Observers**

Robert Budnitz; DOE\_OCRWM; [Robert.Budnitz@rw.doe.gov](mailto:Robert.Budnitz@rw.doe.gov)  
Tof Carim; Office of Basic Energy Sciences  
Yok Chen; Office of Basic Energy Sciences  
Tim Fitzsimmons; Office of Basic Energy Sciences  
Robert Gottschall; DOE\_BES; [Robert.gottschall@science.doe.gov](mailto:Robert.gottschall@science.doe.gov)  
Thomas Kiess; DOE\_OCRWM; [Thomas.kiess@rw.doe.gov](mailto:Thomas.kiess@rw.doe.gov)  
Nick Woodward; Office of Basic Energy Sciences  
Jane Zhu; Office of Basic Energy Sciences