



**FINAL REPORT
WASTE PACKAGE MATERIALS PERFORMANCE
PEER REVIEW PANEL**

FEBRUARY 28, 2002

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**Peer Review of the
Waste Package Material Performance
Final Report
February 28, 2002**

Prepared by:

Signature on file

John A. Beavers

Feb 2002

Date

Prepared by:

Signature on file

Thomas M. Devine, Jr.

Feb 2002

Date

Prepared by:

Signature on file

Gerald S. Frankel

Feb 2002

Date

Prepared by:

Signature on file

Russell H. Jones

Feb 2002

Date

Prepared by:

Signature on file

Robert G. Kelly

Feb 2002

Date

Prepared by:

Signature on file

Ronald M. Latanision

Feb 2002

Date

Prepared by:

Signature on file

Joe H. Payer, Chairman of Peer Panel

Feb 2002

Date

PREFACE

The members of the Waste Package Materials Performance Peer Review Panel greatly appreciate the assistance of the Department of Energy staff and contractors responsible for evaluating the performance of waste package materials proposed for a repository at Yucca Mountain, Nevada. Despite heavy work schedules, they have responded willingly to requests for both information and meetings to assist the Panel in its review. Panel members also thank the Subject Matter Experts who have provided advice and information and prepared helpful background reports to assist the Panel in its deliberations. In addition, the staff of the U.S. Nuclear Regulatory Commission and their Center for Nuclear Waste Regulatory Analyses, members and staff of the U.S. Nuclear Waste Technical Review Board, and staff of the State of Nevada Agency for Nuclear Projects and its contractors have provided valuable assistance. The information and points-of-view they have provided have helped the Panel understand the range of technical issues involved in evaluating waste package materials and the work being done to resolve those issues.

EXECUTIVE SUMMARY

At the request of the U.S. Department of Energy, Bechtel SAIC Company, LLC, formed the Waste Package Materials Performance Peer Review Panel (the Panel) to review the technical basis for evaluating the long-term performance of waste package materials in a proposed repository at Yucca Mountain, Nevada. The Panel was formed in March 2001; this Executive Summary accompanies their Final Report of February 28, 2002. In that report, the Panel identifies important issues for assessing the performance of waste package materials, evaluates the technical basis available for understanding these issues, and comments on approaches and plans to resolve unsettled issues. The report presents the Panel's findings, conclusions, and recommendations. Substantial technical information is included to provide background and perspective for the Panel's work.

Although the focus of this peer review was the assessment of the technical basis for evaluating the long-term performance of materials exposed to the conditions of the proposed repository, the Panel's findings are relevant to a broad range of important matters, including overall performance assessment, site recommendation, license application, and repository design and operation. These, however, were beyond the scope of the Panel. All are multi-faceted and require both technical and non-technical considerations to be taken into account in any decisions. Panel comments regarding these matters should be understood to have the qualifier "... from the perspective of long-term materials performance."

Throughout the peer review, the Panel interacted with Department of Energy staff and contractors responsible for evaluating the performance of waste package materials. Subject Matter Experts prepared helpful background reports to assist the Panel in its deliberations. The staff of the U.S. Nuclear Regulatory Commission and their Center for Nuclear Waste Regulatory Analyses, members and staff of the U.S. Nuclear Waste Technical Review Board, and staff of the State of Nevada Agency for Nuclear Projects and its contractors, and others provided valuable assistance. Their assistance is gratefully acknowledged.

The Panel concludes that the current waste package design is likely to meet the performance criteria for the repository, if some technical issues are favorably resolved. Although the technical basis supporting the suitability of Alloy 22 for the outer barrier of the waste package is substantial and growing, there will always be uncertainty in the evaluation of the long-term performance of materials in the repository. This uncertainty is primarily because of the extremely long life required for the waste packages. The Panel concludes that the confidence regarding the long-term performance of Alloy 22 can be substantially increased through further experiments and analyses, and the Panel recommends that this work be undertaken.

Technical Findings

The effective control of corrosion of waste package materials is essential to the satisfactory long-term performance of a Yucca Mountain repository and the Panel concludes that the Project staff is taking a sound approach to analyzing corrosion related issues. The need to strengthen the technical basis for assessing waste package performance is clearly recognized by the Project staff. While extensive experimental and analytical work to support performance assessments has been completed, a large amount of necessary work remains in Project plans and has yet to be completed. Only a modest portion of the work on fabrication issues is complete.

Although the nominal waters at Yucca Mountain are fairly benign and not corrosive, water composition can change at the metal surface. The range of environments that could exist on these surfaces depends on the composition of waters that can enter the drifts and changes to the

environment that can occur on hot metal surfaces and in crevices. Three conditions describe the surfaces of metal that will be subject to corrosion at Yucca Mountain: accumulated dust and particulate on the metal, deposits and scale on the metal, and tight areas of contact (crevices) between metals; moisture must be present for corrosion to occur under any of these conditions.

The proposed waste package material, nickel-base Alloy 22, has excellent corrosion resistance over a wide range of aqueous solution compositions and temperature. However, corrosion related failures are possible and three potential corrosion failure modes have been identified and are being evaluated by the Project staff: long-term uniform corrosion of passive metals, localized corrosion, and stress corrosion cracking. The Panel has identified several technical issues related to these failure modes that have the potential to require a change in the waste package material or design. Many of these issues are associated with the determination of the realistic boundaries for the environmental conditions and the corrosion behavior of the waste package within these boundaries. Included in the determination of the realistic environmental boundaries are the effects of temperature, radiation, pH, oxidizing potential, ionic species, and microbiological activity. The surface condition and metallurgy of the alloy, which are, in turn, affected by design and fabrication procedures and the composition of the alloy within the specification range of Alloy 22 will affect resistance of the waste package to failure by these corrosion modes. Of particular importance is the long-term metallurgical stability of the alloy under repository conditions.

The Panel does not recommend the use of titanium Grade 7 for construction of the drip shield if it is found to be susceptible to stress corrosion cracking under realistic repository conditions. Stress corrosion cracking of this alloy has been observed in laboratory tests performed by the Project. The benefits of this design are severely diminished if these tests are deemed to have been conducted under realistic repository conditions.

There is considerable interest in the effect of operating temperature on the long-term performance of the repository. In the high temperature operating mode, the waste package surface temperature is limited to no more than 180°C and in the low temperature operating mode, to no more than 85°C. From a materials standpoint, major incentives for operation at lower temperatures are reduced corrosion rates, a lower likelihood of localized corrosion or detrimental metallurgical aging processes, and less opportunity for evaporative condensation. On the other hand, lower temperature operation would expose wet waste package surfaces to greater radiolysis effects because they become wet sooner. With lower temperature operation, there also would be increased costs and risks associated with longer ventilation periods and a larger repository area would be required for a given amount of spent fuel. As with most design/operation decisions, there are tradeoffs associated with lowering the temperature, and there may be diminishing returns for further temperature reductions.

Organizational-Managerial Issues

The Panel notes a worrisome gap between the design/fabrication effort and the materials/corrosion effort. The former needs to recognize and control the effects of fabrication processes on metallurgical structure and residual stresses, and the latter needs to express findings in useable guidelines to direct design and fabrication decisions. The materials/corrosion work to date has focused on supporting performance assessment. The Panel concludes that it is time to balance this effort with work to support design and fabrication of the waste packages. This is not a recommendation to terminate the science program, but rather to redirect and balance the science effort to support design and manufacture/fabrication for long-term performance.

The Panel is concerned that adequate resources might not be allocated to complete the work necessary for evaluating the long-term performance of waste package materials. The Panel's perception is that a substantial effort is required to accomplish the needed work to support design and fabrication of durable waste packages. The Panel strongly recommends that adequate resources be provided to substantially build confidence in the long-term performance of waste packages. This area is particularly amenable to progress through experiments and modeling.

The Panel has identified two areas that especially require further focus and integration of Project efforts: determination of the realistic range of aqueous environments on waste package surfaces and design and fabrication of waste packages for corrosion resistance. For the former, the Panel recommends the direct, collaborative participation of the Project's technical experts in corrosion, materials science, geochemistry, and hydrology in work on these conditions. For the latter, the Panel recommends closer integration between the Project's design and fabrication engineers and the corrosion and materials experts working on performance assessment.

Increased involvement of technical experts from academia and industry in conceptual work, experimental method development, and analytical procedures could enhance the substance and level of confidence in the technical basis to support evaluation of the long-term performance of materials. A more effective means to engage a broader base of the corrosion science and engineering community in work relevant to the long-term performance of materials at Yucca Mountain would have significant benefits.

The Panel recommends the establishment of an External Advisory Board to help determine and maintain focus and direction in the execution of the research agenda of the staff. An Advisory Board should include both academics and industrial experts with credentials in areas important to the Project and should meet with the staff on a regular basis. Moreover, while the Project staff does include investigators who have important assets and skills, there is no visible senior, visionary leader with a deep materials science and engineering background and management credentials.

1. INTRODUCTION

At the request of the U.S. Department of Energy, Bechtel SAIC Company, LLC, formed the Waste Package Materials Performance Peer Review Panel (the Panel). The Panel's charge is to conduct a consensus peer review of the current technical basis and the planned experimental and modeling program for the prediction of the long-term performance of waste package materials being considered for use in a proposed repository at Yucca Mountain, Nevada.

1.1 ORGANIZATION OF THE PEER REVIEW

The Panel consists of a Chairman and six members who are technical experts in the materials science and engineering disciplines needed for the comprehensive peer review. A list of Panel members and brief biographies are attached (Appendices A and B).

During its review, the Panel called on the expertise of a group of Subject Matter Experts, engaged to provide technical advice to Panel members in the areas of corrosion, materials science, and geochemistry. These experts were given a general description of the proposed repository; however for the most part, they were not called upon to review the application, operating conditions or Project information in detail. The Subject Matter Experts provided advice to Panel members by participating in meetings, responding to questions, and preparing papers (see Compilation of Special Topics Reports, to be issued in March, 2002). The Panel retains full responsibility for assimilating any of the experts' work in the Panel's reports and recommendations.

This is the Panel's final report; the Panel issued an interim report on September 4, 2001. During their review, members of the Panel attended Project meetings, technical exchanges, and workshops. They met with and received technical information from Project personnel and others. Some exchanges worthy of special note include:

- Waste Package Materials Performance Peer Review Kickoff Meeting, Las Vegas, Nevada, May 23, 2001
- International Workshop on Long-Term Extrapolation of Passive Behavior, conducted by the U.S. Nuclear Waste Technical Review Board, Arlington, Virginia, July 19-20, 2001
- Panel Sub-Group Meeting on Localized Corrosion, conducted by the Panel, Arlington, Virginia, July 21, 2001
- State of Nevada and Nuclear Regulatory Commission Presentations to the Panel, conducted by the Panel, Cleveland, Ohio, July 24, 2001
- Panel Sub-Group on Waste Package Fabrication, conducted by the Panel, Livermore, California, August 10, 2001.
- Panel Sub-Group Meeting on Stress Corrosion Cracking Defensive Strategies, arranged by BSC with relevant Project staff, Las Vegas, Nevada, November 12, 2001

The Panel wishes to acknowledge the cooperative and open discussions and interactions that were experienced throughout this review period.

1.2 OBJECTIVES OF THE REVIEW

The overall objectives of the review, as stated in the Peer Review Plan, Revision 1, June 6, 2001, were to:

- Review the current basis for predicting long-term corrosion performance of Alloy 22 waste package and titanium Grade 7 drip shield materials and the on-going and planned experimental and modeling program to increase confidence in long-term performance projections.
- Assess the adequacy of the experimental and modeling program and recommend any augmentations of existing and planned tasks or additional new tasks that would significantly strengthen the program.
- Prepare an Interim and a Final Peer Review Report laying out the Panel's assessment of the current and planned program adequacy to assist the Department of Energy in prioritizing future work plans.

These overall objectives were broken down into sub-elements, each with an associated set of questions that constitute the focus of the peer review (Appendix C).

1.3 CONTENT OF THE FINAL REPORT

This Final Report presents the overall findings, conclusions, and recommendations of the Panel. It is a comprehensive report and builds upon the material and recommendations from the Interim Report. In addition to an Executive Summary and brief Introduction, the Final Report contains:

Overview

Section 2 provides the Panel's overall findings, presents technical issues that need to be resolved, and summarizes the Panel's main findings for specific topics. Section 3 presents a summary of the Panel's review and findings for specific degradation modes and factors that can contribute to the degradation of materials

Detailed sections: Section 4 through Section 10 [4, 5, 6, 7, 8, 9, 10] contain reports in each of the main areas of the Panel's review. These sections provide information to support the findings and recommendations summarized in Sections 2 and 3.

Contributing Factors: Section 11 presents summaries drawn from Special Topic Reports prepared for the Panel. The Panel used these reports as background and input to the review. Any views and comments expressed in the summaries and full reports do not necessarily reflect the opinion and findings of the Panel. Further, opinions expressed in the reports are not necessarily those of the Panel or reflected in the Panel's report and recommendations.

A "Compilation of Special Topic Reports", prepared for the Waste Package Materials Performance Peer Review will be released in March 2002.

2. MAIN FINDINGS

2.1 PERSPECTIVE

The U.S. Department of Energy is analyzing a site at Yucca Mountain, Nevada, for development as a geologic repository for the disposal of high-level radioactive waste and spent nuclear fuel. The containment strategy for the disposal site is twofold: first, complete isolation of the waste

until the first, full-thickness penetration of the waste package and, second, subsequent retardation of the egress of radionuclides from the penetrated waste package.

Although the waste packages, in all likelihood, will not be immersed in water because the repository is well above the water table, water does permeate the mountain from the ground surface down to the water table. Consequently, the waste packages will be exposed to air with high relative humidity. There is also a possibility that water droplets will fall onto the waste packages where water seeps into the emplacement drifts. The surrounding rock will increase in temperature from heat given off by the spent nuclear fuel, while the repository will remain at ambient, atmospheric pressure. Under these conditions, corrosion is the most significant potential degradation mode for waste package materials, although other potential degradation modes must also be considered.

Nickel-base Alloy 22 and titanium Grade 7, the principal alloys of interest, have excellent corrosion resistance over a wide range of aqueous solution compositions and temperatures. Two major considerations are the fabrication processes for the manufacture of waste packages and the time-temperature conditions of the repository. Fabrication processes, particularly welding, can have a major impact on corrosion resistance and performance. Temperature has major effects on the composition of the environment and the behavior of materials.

The Panel reviewed the approach, analysis, and methods used by the Yucca Mountain Project (the Project) and the current technical basis and the planned experimental and modeling program to support the evaluation of the long-term performance of waste package materials. The Panel's task was to assess the level of confidence in the Project findings, to identify any deficiencies, and to make recommendations to strengthen the technical basis and reduce uncertainties.

The Panel is composed of scientists and engineers with expertise in materials performance and environmental effects on materials. Their framework for assessment followed the traditional methodology for materials selection and determination of expected performance: (a) identification of the performance requirements and environmental conditions for the waste packages, (b) consideration of alternative materials suitable for the conditions, (c) identification of potential degradation modes for the materials, and (d) assessment of the technical basis for determining resistance to the degradation modes.

2.2 OVERALL FINDINGS

The Panel concludes, based on the body of technical information currently available, that Alloy 22 is a suitable material of construction for the outer barrier of a waste package: nevertheless, significant technical issues remain unsettled. Although the technical basis supporting the suitability of Alloy 22 is substantial and growing, there will always be uncertainty in the evaluation of the long-term performance of materials in the repository. This is primarily because of the extremely long life required for the waste packages. The Panel concludes that the confidence regarding the long-term performance of Alloy 22 can be substantially increased through further experiments and analyses, and the Panel recommends that this work be undertaken.

The Panel concludes that titanium Grade 7 might not be a suitable material of construction for the drip shield. Stress corrosion cracking of titanium Grade 7 has been observed in laboratory tests. If these tests are deemed to have occurred under realistic conditions for the drip shield over waste packages in the repository, then the benefits of titanium are severely diminished. The

Panel does not recommend the use of titanium for drip shields, if it is found to be susceptible to stress corrosion cracking under realistic repository conditions.

The Panel has identified technical issues that have the potential to require a change in the waste package material or design and suggests approaches to the resolution of these issues. We believe that further comprehensive analysis and testing can resolve these issues. The issues are presented in Section 2.7.

The effective control of corrosion of waste package materials is essential to the satisfactory long-term performance of a Yucca Mountain repository. The proposed waste package material, nickel-base Alloy 22, has excellent corrosion resistance over a wide range of aqueous solution compositions and temperature. The Panel concludes that the Project staff is taking a sound approach to analyzing corrosion related issues.

Although the nominal waters at Yucca Mountain are fairly benign and not corrosive, water composition can change at the metal surface. The range of environments that could exist on these surfaces depends on the composition of waters that can enter the drifts and changes to the environment that can occur on hot metal surfaces and in crevices. Three conditions describe the surfaces of metal that will be subject to corrosion at Yucca Mountain: accumulated dust and particulate on the metal, deposits and scale on the metal, and tight areas of contact (crevices) between metals; moisture must be present for corrosion to occur under any of these conditions. The Panel recommends that a strong technical basis be developed for materials performance under each of these conditions. To help accomplish this, the Panel recommends the formation of a task group of Project technical experts in corrosion, materials science, geochemistry, and hydrology to work together to determine the range of the composition of the environments that could contact waste package surfaces and changes that could occur in the environment on hot metal surfaces and in crevices. The task group should have the authority and responsibility to direct the work.

Corrosion and mechanical behavior of waste packages must be considered in the selection of design and fabrication methods. The Panel notes a worrisome gap between the design/fabrication effort and the materials/corrosion effort. The former needs to recognize and control the effects of fabrication processes on metallurgical structure and residual stresses, and the latter needs to express findings in useable guidelines to direct design and fabrication decisions. The materials/corrosion work to date has focused on supporting performance assessment. The Panel concludes that it is time to balance this effort with work to support design and fabrication of the waste packages. In particular, work is required on weld and weld repair processes.

In summary, the Panel concludes that the current waste package design is likely to meet the performance criteria for the repository, if some technical issues are favorably resolved. Overview findings on three important corrosion modes are presented below. In addition, comments are made regarding two important issues: (a) the effects of higher-temperature versus lower-temperature operating mode on the expected long-term performance of waste packages and (b) the likelihood of long-term uniform corrosion rates remaining very small for hundreds and thousands of years.

2.3 CORROSION DEGRADATION MODES

Three corrosion failure modes have been identified and are being evaluated by the Project staff: general corrosion of passive metals, localized corrosion, and stress corrosion cracking. The Panel

concludes that there is a substantial and growing technical basis to support the evaluation of the long-term performance of waste package materials in each of these areas.

Uniform Corrosion. Failure of the waste package by uniform corrosion is unlikely. The long-term corrosion behavior is determined by the structure and composition of the passive film on Alloy 22. The passive film is influenced by thermal treatments during waste package fabrication, dry exposure periods in the repository, and finally the exposure to aqueous environments when the surfaces become wet. Work is underway to better understand the structure and composition of the passive film under these conditions and to relate that to the long-term corrosion behavior. The Panel concludes that if the environmental conditions do not cause film-breakdown and localized corrosion or if the underlying metal does not undergo detrimental metallurgical changes to destabilize the film, then it is highly likely that the passive film will remain stable and uniform corrosion rates will remain very low. Two phenomena that could jeopardize the desirable long-term behavior are worthy of study: (a) surface segregation of sulfur and (b) transpassive corrosion. Surface segregation of sulfur can occur as a result of thermal treatments (equilibrium segregation) and as a result of uniform corrosion (anodic segregation). Reducing the bulk sulfur concentration of the alloy can minimize both thermal segregation and anodic segregation of sulfur. Transpassive corrosion might be caused by radiolysis of water sitting on the surface of the waste package (a process that the Project states is unlikely to produce transpassive potentials) and/or by a combination of all of the following: low pH, Fe+3 (from corrosion of steel structures), some amount of radiolysis of the water, and an inhomogeneous alloy microstructure (i.e., grain boundary segregated phosphorus, precipitates rich in chromium and molybdenum).

Localized Corrosion. Nickel-base Alloy 22 and titanium Grade 7 are extremely resistant to localized corrosion; they have exhibited no evidence of pitting or crevice corrosion after four-year exposures to environments similar to those that may form on waste packages in a Yucca Mountain repository at temperatures up to 85 C. Nevertheless, these alloys are susceptible to crevice corrosion under extreme conditions of environment and potential. The framework used by the Project for the evaluation of resistance to crevice corrosion is appropriate. The Panel recommends a more rigorous approach for determination of the critical potentials. The critical potential should be the repassivation of an intentionally creviced electrode following significant crevice corrosion. The corrosion potential should be modeled and measured under a range of exposure conditions, taking into account the initial surface condition and the effects of high temperature exposure to air. Furthermore, the Panel recommends that the Project perform experiments under conditions beyond those thought to be relevant to Yucca Mountain in order to examine the margins of corrosion resistance.

Stress Corrosion Cracking. The mitigation method, experimental approach, and modeling efforts for stress corrosion cracking are consistent with the state-of-the-art, and appropriate work generally is underway to verify the models. Research to date shows that nickel base Alloy 22 is highly resistant to stress corrosion cracking in the environments expected in the repository. Modeling is an essential component of the stress corrosion cracking program, because the laboratory test techniques have inadequate sensitivity to crack growth for the prediction of acceptable long term performance of the waste package. The Panel recommends additional work to address some deficiencies in the current program including improving tests for establishing sensitivity to crack initiation and propagation, replacing the threshold stress component of the slip dissolution model with the threshold stress intensity factor model, and developing constants specific to Alloy 22 for the film rupture/slip dissolution model. The Panel recommends that

alternative models for stress corrosion cracking be considered by the Project. Alternative models can provide validation and support for the Project approach. Alternative models also may be required, if the current models are found to be deficient.

The Panel recommends that the effectiveness of heat treatment for stress mitigation be thoroughly evaluated by finite-element thermal and stress analysis and by residual stress measurements on prototype containers. The Panel further recommends that the stress corrosion cracking behavior of Alloy 22 be evaluated with different stages of aging and in environments containing trace impurities, such as lead, that may influence cracking behavior.

2.4 HIGHER OR LOWER TEMPERATURE OPERATING MODES

There is considerable interest in the effect of operating temperature on the long-term performance of the repository. In the high temperature operating mode, the waste package surface temperature is limited to no more than 180°C and in the low temperature operating mode, to no more than 85°C. The maximum temperature and time-temperature behavior within the drifts can be controlled by operational parameters: distribution by waste package type, spacing between packages, and the amount and duration of ventilation prior to closure. From a materials standpoint, major incentives for operation at lower temperatures are reduced corrosion rates, a lower likelihood of localized corrosion or detrimental metallurgical aging processes, and less opportunity for evaporative condensation.

On the other hand, lower temperature operation would expose wet waste package surfaces to higher radiation fields the accompanying radiolysis effects because they become wet sooner. The potential effects of radiolysis on the environment and corrosion behavior need to be determined. Other disincentives for operation at lower temperature are the increased costs and risks associated with longer ventilation periods and a larger repository area required for a given amount of spent fuel. As with most design/operation decisions, there are tradeoffs associated with lowering the temperature and there may be diminishing returns for further temperature reductions.

Major benefit was gained in increased confidence and certainty of the hydrological-geological analysis and modeling when the Project discarded the very hot repository case, the base case for the Total System Performance Assessment conducted for the Viability Assessment. In the very hot case, the boiling/dry-out zones from adjacent drifts overlapped and the dry-out zone extended tens of meters into the rock near the repository. In both of the lower temperature cases currently under consideration, no dry-out zone overlap occurs, greatly reducing the volume of rock and water affected by temperature. In addition to the hydrological-geological benefits, the change from consideration of the very hot case also increased confidence in the control of damage to the waste package materials from corrosion and long-term metallurgical aging processes.

The Panel concludes that the benefits of moving from the high temperature operating mode, as currently defined, to the low temperature operating mode, are not clearly greater and might be offset by the radiolysis effects, in addition to the burdens of long-term ventilation and increased area for the repository. Work is required for testing and analysis at the higher operating temperatures before final conclusions can be drawn (see Technical Issues to be Resolved below).

2.5 LONG-TERM UNIFORM CORROSION OF PASSIVE METAL

Based on studies published in the open literature and on the results of investigations by the Project, the Panel has concluded that the waste package of Alloy 22 is unlikely to fail by uniform corrosion in the repository at Yucca Mountain. Nevertheless, important work remains to be done to confirm and enhance the resistance of Alloy 22 to uniform corrosion. Alloy 22 depends completely on its protective surface films for resistance to uniform corrosion. Research is needed (1) to characterize the oxide films formed on Alloy 22 during high temperature heat treatments; (2) to characterize the changes that occur to the air-formed oxide films on Alloy 22 during exposure to the range of aqueous solutions relevant to Yucca Mountain.

Although failure of the waste packages by uniform corrosion is not likely, there are two possible causes of significant uniform corrosion of Alloy 22 that cannot be ruled out at this time: (1) transpassive corrosion and (2) corrosion caused by surface segregation of sulfur. In section 7, the Panel recommends specific experiments to alleviate concerns regarding uniform corrosion induced by transpassivity and surface segregation of sulfur. The outcomes of the experiments on surface segregation might indicate the need to reduce the bulk sulfur concentration of Alloy 22 to a value considerably less than the current specified maximum value and to limit the temperature of stress relief annealing of the waste package canisters to less than 1100°C.

2.6 ALLOY SPECIFICATION AND COMPARISON

The Panel regards Alloy 22 as a representative member of a family of highly corrosion resistant nickel-chromium-molybdenum alloys. Today's commercial alloys arise from a steady evolution in alloy development. It is unlikely that the evolution is complete. Due to either technical or commercial incentives, modifications within or around the chemical composition specified for Alloy 22 will emerge. The chemical composition of heats of commercially available Alloy 22 can vary within the specified range for each element. The Panel recommends that the Project staff determine the effects of alloy composition within the specified ranges of Alloy 22. It is possible that a more restrictive chemical composition specification for given elements would reduce uncertainty and increase confidence with respect to the stability of the alloy and the corrosion behavior of waste packages.

Conversely, there will be a strong economic incentive to use less expensive alloys. This should be evaluated most carefully. The Panel recommends that the Project not designate metals less corrosion resistant than Alloy 22 type metals, in view of confidence and uncertainties. Clearly, 304, 316, 825 and others would fail under much more benign conditions than would Alloy 22. It is prudent to use the most corrosion resistant alloy available unless strong, credible evidence is found that a less resistant alloy will work.

The Panel recommends that a back-up alloy be included in certain of the tests performed on Alloy 22 to address the risks associated with the possibility that, further into the Project, Alloy 22 is found to be inadequate. In addition, the Project should include a comparison alloy, such as 316L stainless steel, Alloy 825, Alloy 600 or Alloy 690, in a greater number of tests than is presently the case. This would provide a means for quantitatively comparing the performance of Alloy 22.

2.7 TECHNICAL ISSUES TO BE RESOLVED

The Panel has identified the following technical issues that have the potential to require a change in the waste package material or design. As noted above, the Panel concludes that the current

waste package design is likely to meet the desired performance criteria in the repository, if these issues are resolved favorably. The Panel believes that further comprehensive analysis and testing, such as those we suggest below, can resolve the issues in a timely fashion.

The need to strengthen the technical basis for assessing waste package performance is clearly recognized by the Project staff. While extensive experimental and analytical work to support performance assessments has been completed, a large amount of necessary work remains in Project plans and has yet to be completed. Only a modest portion of the work on fabrication issues is complete.

The Panel is concerned that adequate resources might not be allocated to complete the work necessary for evaluating the long-term performance of waste package materials. The Panel's perception is that a substantial effort is required to accomplish the needed work to support design and fabrication of durable waste packages. The Panel strongly recommends that adequate resources be provided to substantially build confidence in the long-term performance of waste packages. This area is particularly amenable to progress through experiments and modeling.

Design and fabrication procedures: Metallurgical structure, residual stresses, and metal surface condition are all affected by fabrication procedures and, in turn, these conditions can greatly affect corrosion behavior. The Panel recommends a coordinated analysis and testing program between the design/fabrication effort and the materials/corrosion effort. The inclusion of realistic mock-ups and prototypes, in addition to laboratory specimens is expensive, but necessary.

Develop and validate weld procedures: The closure weld and its postweld processing are critical to long-term performance of waste packages. The two primary issues regarding long-term integrity of the welds in the Alloy 22 corrosion barrier are the level and nature of residual stresses associated with the closure welds and the stability of the weld metal microstructure. The production and testing of full-scale mockups is required, and a weld repair procedure must be developed and validated.

Realistic boundaries for environmental conditions: The determination of the realistic range of aqueous environments on metal surfaces is well underway. The Panel recommends that the Project complete a comprehensive experimental and analytical modeling program to establish the boundaries for three environmental conditions: moist dust, mineral scale and deposits, and crevices. The determination of environment should include temperature, oxidizing potential, pH, and composition of ionic species. Work on microbiologically influenced corrosion needs to refocus on the consequences of this corrosion-related process within the realistic boundaries.

Corrosion behavior within the range of realistic environmental conditions: Project staff should determine the performance boundaries of Alloy 22 in each of the identified corrosion modes: uniform corrosion, localized corrosion, and stress corrosion cracking. The testing should go beyond the range of realistic conditions in order to determine the margins of safety.

Radiolysis from gamma radiation: There is no evidence to suggest that radiation damage to the waste package canister material will alter its mechanical properties; therefore, radiation damage studies of alloy 22 are not warranted. In addition, there is no evidence that radiation damage of the passive film will alter its protective properties. However, the production of H₂O₂ and other products by radiolysis from gamma rays can result in a positive shift in the open circuit potential and possible degradation of passivity. The Panel recommends experiments and analysis of radiolysis effects at gamma radiation fluxes that will exist when condensed water is present on waste packages.

Proper measure of crevice corrosion susceptibility: The critical potential for localized corrosion of Alloy 22 should be determined by a repassivation potential procedure for intentionally creviced samples that undergo crevice corrosion.

Corrosion potential over long periods: Values for the corrosion potential are used in models of corrosion modes. The corrosion potential should be measured over long periods of time in a range of environments with varying chloride concentration, oxyanion concentration, pH, temperature, and radiation. Initial surface conditions must be considered. Theoretical approaches for predicting the corrosion potential over long periods of time and the influences of the various environmental parameters should supplement the experimental work.

Long-term metallurgical stability: Cr-Mo depletion and Long Range Ordering. Long term exposure of Alloy 22 to higher temperatures than those expected for the repository can lead to the degradation of corrosion resistance by Cr-Mo depletion and degradation of mechanical properties by long range ordering. The Panel recommends that Project staff determine whether chromium and molybdenum depletion occurs adjacent to the grain boundaries, and if so the time and temperature relationship for this depletion and its impact on corrosion and stress corrosion cracking. The Panel recommends that long range ordering be given equal importance to that for precipitation because of the implications of ordering for stress corrosion cracking and the potential effects of deformation adjacent to the induction heated and quenched zone accelerating the ordering kinetics.

Effects of sulfur and phosphorus: Sulfur and phosphorus are minor constituents in Alloy 22, and when enriched to high concentrations at grain boundaries and surfaces, they can have detrimental effects on corrosion and stress corrosion cracking resistance. The Panel recommends that Project staff: 1) measure the effects of sulfur on passive film stability in relevant repository environments; 2) model and/or measure the rate of sulfur accumulation on the surface as a function of corrosion rate, if sulfur affects the passive film stability; and 3) evaluate the potential for grain boundary impurity segregation as a function of time and temperature in the bulk and weld metal and in the heat affected zone of welds.

Effectiveness of tensile stress reduction for mitigating stress corrosion cracking: A principal component of the Project's stress corrosion cracking control strategy is to reduce the tensile stresses on waste package surfaces. Experience from large-diameter rolls in paper making machines demonstrates that this is not easily accomplished. There is insufficient experimental data and analytical modeling to support the position that there will be no significant tensile stresses on the waste packages. Experimental and modeling work to support this effort needs to consider the time-temperature constraints during processing to avoid detrimental metallurgical structures on cooling.

Stress corrosion crack growth and consequence: Because of the repository's long time frame, the stress corrosion crack growth rates of interest are less than the current experimental detection limits. The Panel recommends further work to demonstrate sufficiently slow crack growth through calibration and validation of stress corrosion cracking models. Stress corrosion cracks cover only a small fraction of a metal surface; they provide a tight, tortuous path through a metal thickness. The Panel recommends an analysis of the likely location, distribution, and geometry of stress corrosion cracks. This will provide useful input to the determination of water ingress through the waste package wall and the eventual egress of radionuclides from the waste package in the event that stress corrosion cracking does occur.

Hydrogen embrittlement of Alloy 22: The nickel-chromium-molybdenum family of alloys is known to be susceptible to hydrogen embrittlement. The degree of susceptibility is a function of

alloy composition, cold working, and thermal history among other variables. Hydrogen can result as a by-product of corrosion processes. The Project has discounted hydrogen effects in Alloy 22 based on plans to use the alloy in an annealed condition and the known resistance of other nickel-chromium-molybdenum alloys in the annealed condition. The Panel recommends experimental work on Alloy 22 to support this position. While the fabrication strategy is designed to eliminate tensile stresses from the outer surface of the waste packages, industrial experience has shown this to be difficult to achieve completely. It is prudent to determine the affects of tensile stresses that can result from fabrication processes such as quenching and welding.

2.8 ORGANIZATIONAL-MANAGERIAL ISSUES

Five fundamental elements make up the waste package design and performance portion of the overall Project: design, engineering, analysis, modeling, and testing. These five fundamental elements are organizationally separated in the current structure. The Panel considers that better integration of these elements is essential. The Panel has identified two areas that especially require further focus and integration of Project efforts: determination of the realistic range of aqueous environments on waste package surfaces and design and fabrication of waste packages for corrosion resistance. For the former, the Panel recommends the direct, collaborative participation of technical experts in corrosion, materials science, geochemistry, and hydrology in work on these conditions. For the latter, the Panel recommends closer integration between the design and fabrication engineers and the corrosion and materials experts working on performance assessment.

Increased involvement of technical experts from academia and industry in conceptual work, experimental method development, and analytical procedures could enhance the substance and level of confidence in the technical basis to support evaluation of the long-term performance of materials. Unfortunately, current management and administrative policies and procedures tend to limit broader involvement. A more effective means to engage a broader base of the corrosion science and engineering community in work relevant to the long-term performance of materials at Yucca Mountain would have significant benefits.

The Panel recommends the establishment of an External Advisory Board. Such a Board would be helpful in determining and maintaining focus and direction in the execution of the research agenda of the staff. As mentioned above, the five fundamental elements related to the design and performance of the waste package are organizationally separated at present. An Advisory Board should include both academics and industrial experts with credentials in areas important to the Project and should meet with the staff on a regular basis, perhaps twice a year on-site with interim phone conference updates. We note, moreover, that while the Project staff does include investigators who have important assets and skills, there is no visible senior, visionary leader with a deep materials science and engineering background and management credentials.

The Panel recommends that a back-up alloy and comparison alloy be included in the experiments and analysis. A back-up alloy should be included in certain of the tests performed on Alloy 22 to address the risks associated with the possibility that, further into the Project, Alloy 22 is found to be inadequate. In addition, a comparison alloy, such as, 316L stainless steel, Alloy 825, Alloy 600 or Alloy 690, should be included in a greater number of tests than is presently the case. Results obtained for the comparison alloys will provide a means for quantitatively describing the

performance of Alloy 22. This recommendation also appears in the technical sections above; the Panel considers this to be both an organizational and a technical issue.

3. SUMMARY OF DEGRADATION MODES AND CONTRIBUTING FACTORS

3.1 INTRODUCTION

In the current design, the repository includes waste packages constructed of an outer barrier made of nickel-chromium-molybdenum Alloy 22 surrounding an inner container of Type 316 nuclear-grade stainless steel. When the repository is closed, the waste packages will be covered by a titanium Grade 7 (titanium-palladium) alloy drip shield. Under anticipated repository conditions, corrosion is expected to be the most significant degradation mode for the Alloy 22 and titanium Grade 7 alloy surfaces that will be exposed to the repository environment. Hence, the rate of corrosion will be a critical factor in determining the service life of the waste packages. Alloy 22 and titanium Grade 7 are among the most corrosion resistant engineering materials that are available today. Nevertheless, like all engineering materials, these alloys are subject to environmental degradation under certain circumstances. The likelihood that a given type of corrosion phenomenon will occur is dependent upon a complex interplay among the metallurgy of the alloy, the repository environment, and the stress distribution of the waste package while in service. The identification of potential degradation modes and the evolution of corresponding control strategies are, therefore, crucial to the long-term stability of the waste package. Failure of the containment due to corrosion would ultimately allow release of radionuclides to the environment.

The Panel's views on potential degradation modes and descriptions of factors that are likely to affect anticipated corrosion phenomena are summarized in the following sections.

3.2 REPOSITORY CONDITIONS: OVERVIEW OF TIME, TEMPERATURE, ENVIRONMENT

A particularly challenging aspect of the analysis of the durability of the waste packages in the Yucca Mountain Repository is the extraordinarily long time period for performance. During an operational phase of 50 years, emplacement of waste packages will be carried out. This will be followed by a monitoring phase to 300 years. After which, the repository will be closed beginning the closure phase. In the analysis of potential degradation modes for the waste packages, it is important not only to consider the conditions that could initiate a particular form of damage, but also to consider the time period over which those conditions persist.

Of particular importance are the temperature of the waste package surfaces and the chemical composition of wet environments in contact with the waste packages over time. The conditions in the repository will be determined by a combination of natural and man-made factors. The waste material gives off heat and radiation, which both decrease with time. Thermal effects diminish over several thousands of years, while radiation effects diminish after a few hundred years. At the repository level, waste packages will be isolated beneath 300 meters of rock and will be a couple hundred meters above the water table. At this level, the waste packages will sit in air on support pallets. Although the ambient air will be saturated with water equivalent to 100% relative humidity, it is highly unlikely that the waste packages will be fully immersed in water. Nonetheless, moisture will condense and seepage from the rock can drip onto metal

surfaces. While the amounts of moisture will be small, there would be sufficient water for corrosion. Hence, corrosion resistant metals are required.

Operational factors affect the time-temperature behavior in the repository and in the surrounding rock. These factors include the waste package loading, spacing of waste packages within the repository and duration and level of ventilation prior to closure. Two operational modes are now under consideration. In the higher-temperature operating mode, the waste package surface temperature could reach 180°C, the surrounding rock would be heated above boiling, and the rock would be dried out near the drifts. In the low-temperature operating mode, the waste package surface would be maintained below 85°C, the surrounding rock would not be heated above boiling, and there would be a minimal dry-out zone in the rock.

In addition to the challenges, there are several favorable aspects of the long-term storage. The waste packages will be exposed to one, long and slow, temperature cycle. There will be no moving parts. This favors good materials performance. The static exposure will not subject the waste packages to potentially detrimental cyclic loads. The low heat fluxes and extremely slow heating and cooling will not expose the waste packages to large thermal gradients or rapid thermal expansion and contraction. In a higher temperature operating mode, the waste packages would be exposed to dry conditions for long times (several hundred years) before the surfaces are wetted.

It is broadly accepted that dry waste packages will not undergo significant corrosion damage. When the metal surfaces are wet, there is a potential for corrosion damage. Great emphasis has rightfully been placed upon the determination of times-of-wetness and the corresponding temperature and chemistry of the wet environments. The topics covered in this overview include:

- Time-Temperature-Relative Humidity
- Presence of Moisture
- Composition of Waters and Corrosive Environments
- Atmospheric Conditions
- Mechanical Loads and Stresses on Waste Packages
- Damage Processes and Waste Package Penetrations

3.3 COMPOSITION OF AQUEOUS ENVIRONMENTS

In the view of the Panel, the most critical issues concerning the environment on the waste package involve the determination of the nature of the plausible extremes of environments. Temperature, composition of the environment, and the presence of microbes all can contribute to or affect these plausible extremes. 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. The Project staff should base such a determination upon known physical and chemical processes, inherent variability throughout the repository, and uncertainties in quantitative determination of the coupled processes that affect the environment. The Project should also make a similar determination of the performance bounds of waste package and drip shield materials. A comparison of the corrosion performance bounds to the environment bounds would allow the Project to estimate the likelihood that the waste package or drip shield would be exposed to environmental conditions under which corrosion failure would be likely to occur.

The Project staff's approach to determining the corrosion performance of proposed materials has focused on the use of concentrated simulated waters based on analyses of J-13 well water. The concentration levels in the test solutions have ranged up to 1,000 times the concentration of J-13. Project staff has also studied acidified solutions. In addition, some corrosion work has been performed in single salt solutions with concentrations up to 5 M. The majority of the work has been performed at temperatures below the boiling point of pure water at the elevation of Yucca Mountain (96°C). These solutions do not represent relevant, plausible extreme environments, particularly at the temperatures being used in the Long-Term Corrosion Test Facility. Concentrated aqueous solutions can exist in the liquid phase at temperatures well above the boiling point of water.

The Panel recommends that Project staff:

- Expand the current work on understanding the effects of the interactions between seepage waters and hot (greater than 100°C) metal surfaces on both the solution composition and the corrosion of engineered materials. The goal is to provide information on both the nature of the deposits that form and the type and rate of corrosion underneath the deposits. Experiments at high temperatures should have higher priority than lower temperature (less than 100°C) studies. The Panel notes that Project staff has recently begun experimental work in this area and we support and encourage this new direction.
- Continue to focus on developing a technical basis for environmental extremes that are realistic for each of the three surface scenarios (moist dust, scale, and crevices). These analyses must also include a delineation of the inherent uncertainties, such as the relative importance of transient vs. steady state environments.
- Improve coupling between thermal-hydro-chemical, engineered barrier system, and environment calculations and the experimental results. Data needed for the environment on the waste packages must drive the nature of the computational and experimentation thermal hydrology work in the unsaturated zone.
- Shift the focus in the study of microbiologically influenced corrosion. It is unlikely that the Project will be able to demonstrate unambiguously that microbes are not viable under expected repository conditions. Instead, the Project should characterize the possible metabolites and the effects of these on the engineered materials, including any steel components used in the repository.

3.4 METALLURGICAL STABILITY

There are three processes that can affect the metallurgical stability of Alloy 22. These are: 1) precipitation of intermetallic phases, 2) ordering of the nickel and solute atoms to have specific locations on the crystal lattice, and 3) enrichment of impurity atoms such as sulfur and phosphorus at crystal boundaries and free surfaces. The presence of intermetallic phases and grain boundary segregation can alter the corrosion and mechanical performance of Alloy 22, lattice ordering can promote hydrogen-induced cracking, and surface enrichment of sulfur can degrade passivity. Each of these processes is thermally activated and can be described by the appropriate kinetic equations to predict reaction rates as a function of temperature and time. While these metallurgical processes occur very slowly at proposed repository conditions, it must be demonstrated that either they will not occur during the life of the repository or, if they do occur, that they will not significantly affect the canister performance. Welding and stress

mitigation process can both produce grain boundary precipitation that serves to initiate the process for further growth at repository conditions.

The Project is focusing on developing the necessary models to predict the precipitation and ordering in Alloy 22 as a function of repository relevant times and temperatures. The Project is making experimental measurements of precipitation using materials aged for extended periods (up to 40,000 hours at 260, 343, and 427°C) at Haynes Alloys. These materials have been shared with the Project and they serve as an excellent source of aged material. The extent of precipitation is being measured primarily by scanning electron microscopy and some by transmission electron microscopy analysis, with an emphasis on grain boundary precipitation. Phase identification is being done by transmission electron microscopy for P, μ , σ , carbide and Ni₂(Cr, Mo). The kinetics of ordering reactions in Alloy 22 is being treated by the Project in a manner very similar to that of precipitation. The sluggishness of these kinetics is a significant hindrance to obtaining sufficient data for a high confidence extrapolation to 10,000 years. Very small ordered domains have been observed by transmission electron microscopy, but the volume fraction was difficult to measure. Therefore, the Project has used some bounding arguments to establish the extrapolation to 10,000 years. The results show that long-range ordering will form in 10,000 years at 270° to 300°C. The Project has chosen not to evaluate either grain boundary or surface segregation effects. While the kinetics of thermally activated segregation will be very slow at repository temperatures, the potential effects of segregation, should it occur, are significant. Also, surface enrichment during anodic dissolution does not require much corrosion and is, again, potentially very significant should impurities such as sulfur degrade the passive film.

The Panel recommends that Project staff:

- Determine whether chromium and molybdenum depletion occurs adjacent to the grain boundaries and, if so, determine the time and temperature relationship for this depletion and the impact of this depletion on corrosion and stress corrosion cracking.
- Give long-range ordering importance equal to that given to precipitation because of the implications of ordering for stress corrosion cracking, hydrogen embrittlement, and the potential effects of deformation adjacent to the induction-heated and quenched zone accelerating the ordering kinetics.
- Measure the effects of sulfur and phosphorus on passive film stability in relevant repository environments; model and/or measure the rate of sulfur and phosphorus accumulation on the surface as a function of corrosion rate, if sulfur and phosphorus affect the passive film stability; and evaluate the potential for grain boundary impurity segregation as a function of time and temperature and in the heat affected zone.

3.5 LONG TERM UNIFORM CORROSION

Experimental measurements of the uniform corrosion of Alloy 22 performed by the Project, as well as empirical studies of the uniform corrosion of nickel-chromium binary alloys and nickel-chromium-iron/molybdenum ternary alloys conducted by other researchers, strongly suggest that waste packages will not fail in the repository at Yucca Mountain as a result of the uniform corrosion of Alloy 22.

The resistance of Alloy 22 to uniform corrosion is the result of the highly protective nature of the films that form on the surface of Alloy 22. The oxide films formed on Alloy 22 in air and the

passive films formed in aqueous solutions are multi layered. The most important component of the multi-layered films is the inner barrier layer, which resembles Cr_2O_3 . The precise composition and structure of the entire film, and that of the inner layer is a function of the chemistry of the solution, in particular the pH of the solution, and the composition of the alloy.

The ability to predict the long-term, uniform corrosion behavior of Alloy 22 requires (1) complete knowledge of the structure and composition of Alloy 22's passive films and air-formed oxide films, and (2) complete understanding of the environmental and metallurgical factors that dictate the films' compositions and structures. The most important environmental factors are temperature, solution pH, and corrosion potential. The most important metallurgical factors are the bulk chromium and sulfur concentrations of Alloy 22.

The Project has begun to characterize the high temperature oxide films and the passive films that form on Alloy 22. Results to date are consistent with published results for films on nickel-chromium binary alloys and nickel-chromium-iron/molybdenum ternary alloys.

Collectively, the measurements of the uniform corrosion rate of Alloy 22 by changes in weight of test coupons in the Long Term Corrosion Test Facility, and by electrochemical techniques of samples immersed in a variety of electrolytes indicate the uniform corrosion rate of Alloy 22 in the passive state is extremely low and would result in losses in thickness of only several mm in 10,000 years of continuous exposure to environments that might contact the waste package in the repository.

The Project has demonstrated that large increases (≈ 500 mV) occur in the corrosion potential of Alloy 22 in acidic, aqueous solutions at 90°C . Based on increases in oxidation rate of Alloy 22 in short time (≈ 10 hr.) potentiostatic tests at high potentials, there was initial concern that high corrosion potentials would be accompanied by higher rates of uniform corrosion. Tests that are underway by the Project have shown that the ennoblement of the corrosion potential of Alloy 22 is, in fact, associated with very low rates of corrosion.

The ability of Alloy 22 to resist uniform corrosion depends on the stability of its passive film. Changes in the passive film might be caused by changes in the environment and/or changes in the alloy. Analyses by the Panel identified two possible processes that could lead to high rates of uniform corrosion of Alloy 22 in the repository at Yucca Mountain are (1) increases in corrosion potential caused by a combination of radiolysis of the water and the formation of oxidizing species, such as Fe^{+3} , by the corrosion of steel structures proximate to the waste packages and (2) surface segregation of sulfur by either thermal treatments or anodic segregation.

The most important recommendations by the Panel regarding the uniform corrosion of Alloy 22 are related to (1) characterization of the passive films and air-formed oxide films of Alloy 22; (2) determination of the critical bulk sulfur concentration of Alloy 22 below which surface segregation of sulfur by either thermal treatments or anodic segregation will not occur; (3) determination of the risk that a combination of high oxidizing potentials (caused by radiolysis of the water and Fe^{+3} from corrosion of nearby steel components), high temperatures and adverse metallurgical processes (such as surface segregation of sulfur and the formation of chromium-rich second phases) would simultaneously exist and cause high rates of uniform corrosion of Alloy 22.

Finally, efforts to model the passive film and uniform corrosion rate of Alloy 22 should continue. The teaching of the history of engineering is that margins tend to get used up to enhance the ratio of performance to cost. In the context of the use of Alloy 22 for waste packages, the tendency will be to fully exploit the corrosion resistance of Alloy 22 by decreasing the wall thickness of the waste container. Modeling the uniform corrosion behavior of Alloy 22 will help to define the

needed thickness plus safety margin required of the waste containers. In addition, models can help to explore the different corrosion rates that will result from the myriad of combinations of temperature, solution composition and corrosion potential over long periods of time.

The Panel recommends that the Project staff:

- Surface segregation of sulfur and transpassivity are the two most likely factors that would cause significant rates of uniform corrosion of Alloy 22. Therefore, changes in the structure and composition of the passive film as a function of surface segregation of sulfur and as a consequence of highly oxidizing potentials should be investigated.
- The Panel recommends that two causes of surface segregation of sulfur be investigated: equilibrium segregation due to high temperature heat treatments and anodic segregation resulting from uniform corrosion of Alloy 22. The Panel recommends the determination of critical bulk sulfur concentrations below which heat treatments and anodic segregation do not cause significant increases in the uniform corrosion rate of Alloy 22.
- Determination of the likelihood of radiolysis of the water causing transpassive dissolution of fully homogenized Alloy 22. This should be done for the range of solution compositions relevant to the repository at Yucca Mountain and in particular, the full range of solution pH should be investigated.
- The Panel recommends that changes in structure/composition of the high temperature oxide films as a result of immersion in the various solutions relevant to the repository at Yucca Mountain be investigated. Changes in the films need to be investigated at a range of potentials and temperatures. Such experiments have been proposed by the Project and some work is already underway.
- The Panel recommends testing the uniform corrosion rate of coupons in the Long Term Corrosion Test Facility at temperatures higher than the present maximum of 90 °C. Higher test temperatures are warranted (1) by the increase in oxidation rate of Alloy 22 with increasing temperature, which was observed in short duration electrochemical tests, and (2) by the knowledge that salts with deliquescence points of $\approx 25\%$ RH, might contact the surface of the waste package. The presence of salts with low deliquescence points would place the waste package in contact with an aqueous phase at temperatures as high as $\approx 160^\circ\text{C}$, albeit for a relatively short period of time.
- The Panel recommends testing the uniform corrosion rate of Alloy 22 at high passive potentials for long periods of time. Short time electrochemical tests indicate the uniform corrosion rate of Alloy 22 increases with applied passive potential. High corrosion potentials might be established on waste canisters of Alloy 22 as a result of the combined effects of Fe^{+3} corrosion products from steel structures in the vicinity of the waste package and radiolysis of the water on the surface of the waste package.

Determination of the combinations of radiolysis of water, composition of the water, in particular, solution pH and concentration of Fe^{+3} , and metallurgical factors, including surface segregation of sulfur, grain boundary segregation of phosphorus, and precipitates of chromium rich and molybdenum rich phases, that might interact synergistically to initiate transpassive dissolution at relatively low potentials. Results in the literature for Ni-Cr alloys suggest that such factors might initiate transpassivity locally, resulting in the formation of oxidizing corrosion products (e.g., Cr(VI) species) that lead to high rates of uniform dissolution of the alloy.

3.6 LOCALIZED CORROSION

Alloy 22 and titanium Grade 7 are extremely resistant to localized corrosion; they have exhibited no evidence of pitting or crevice corrosion after four-year exposures in the environments predicted to form on the waste package. However, these alloys are susceptible to crevice corrosion under extreme conditions of environment and potential. The Project is using the ΔE criterion for localized corrosion susceptibility, which is based on the difference between a critical potential, E_{CRIT} , and the corrosion or open circuit potential, E_{OC} . This approach assumes that localized corrosion will not occur if ΔE is positive, that is, if the E_{OC} is less than E_{CRIT} . If properly applied, this is an appropriate, viable, and conservative approach to prediction of long-term susceptibility to localized corrosion. This approach requires accurate knowledge of both E_{CRIT} and E_{OC} as a function of all the important environmental conditions (chloride, heavy metal, and inhibiting ion concentration, temperature, pH) and, in the case of E_{OC} , time.

Even though the ΔE criterion is valid and useful for the prediction of localized corrosion, the Project's approach for determination of the values of E_{CRIT} and E_{OC} , from which ΔE is calculated, is not appropriate. The Project has determined ΔE values from potentiodynamic polarization curves measured on uncreviced, freshly-prepared samples in a few different predicted waste package environments. Neither Alloy 22 nor titanium Grade 7 regularly exhibits localized corrosion under these conditions, but Alloy 22 does corrode transpassively at high potentials. Because ΔE is positive and large for all tested environments, Project staff predicts that localized corrosion will never occur. However, because the critical potentials measured are associated with the onset of transpassivity and not localized corrosion, it is inappropriate to use these data for the prediction of localized corrosion. Project staff has not explored other environments from which extrapolations could be made, including more aggressive environments. The Panel recommends that the Project follow an approach for determination of ΔE that is similar to that taken by other organizations, such as the Center for Nuclear Waste Regulatory Analysis. E_{CRIT} should be determined in aggressive environments that cause localized corrosion. A conservative value of E_{CRIT} should be used, such as $E_{R,CREV}$, the repassivation potential for crevice corrosion after considerable crevice growth.

Another major problem with the model developed by the Project is the use of E_{OC} values determined in potentiodynamic polarization curves. Such values are not representative of realistic waste package surfaces, which will be affected by the whole fabrication procedure, emplacement, and some period of exposure to hot air. The open circuit potential value is expected to vary with time as a result of continued improvement in passivity and changes in the environment. The Panel recommends that realistic and relevant E_{OC} values be measured and modeled, so that predictions can be made of how the open circuit potential will vary over long periods of time.

Temperature is a critical factor in localized corrosion with higher temperatures being more likely to cause localized corrosion. The Panel recommends that $E_{R,CREV}$ and E_{OC} values used for ΔE be determined at higher temperatures and, most particularly, at all temperatures to which the waste packages might be exposed in the presence of an aqueous layer.

The Panel further recommends that the Project staff:

- Undertake studies of localized corrosion propagation and arrest to supplement work on initiation because these factors will control the accumulated extent of damage from localized corrosion should it occur. Experiments in aggressive environments provide the

opportunity to study growth and arrest behavior. Since there is a chance that the waste package surface will be exposed only to a moist dust environment rather than to dripping or full immersion, the possible influence of such an exterior environment on limiting localized corrosion growth should be studied.

- Examine the effects of metal surface condition on localized corrosion. The metal surface condition can have a large influence on the localized corrosion behavior. In general, the susceptibility to localized corrosion increases as the roughness of the surface finish increases. On the other hand, protective surface films can reduce the likelihood for localized corrosion.
- Address the influence of structural changes on the susceptibility to localized corrosion. The structure of Alloy 22 might change during long-term aging at moderate temperatures; it will certainly change locally as a result of the multipass weld required to seal the canister. The Panel recommends that experiments for determination of $E_{R,CREV}$ described above be performed on welded samples.
- Investigate environments containing possible oxidizing agents, such as peroxide or ferrous/ferric. The possible effects of radiolysis should be reevaluated for the current waste package design and expected condition of spent fuel.
- Examine localized corrosion behavior for the most relevant conditions that can result in wet environments in contact with metal surfaces: moist dust surface associated with humid air exposure or scale and deposits formed by evaporated drips. Full immersion of metal surfaces is a highly unlikely condition in the repository. It is unlikely that the thin aqueous layer on a waste package will be able to support the cathodic reactions needed to maintain localized corrosion to the same extent as possible in bulk solutions. This has not been addressed by anyone in the field of localized corrosion. The Panel recommends that the Project complete analysis of the initiation, propagation, and arrest of crevice corrosion and pitting under the conditions listed above.

3.7 STRESS CORROSION CRACKING

Stress corrosion cracking is a corrosion damage mode during which slow crack growth in a metal or metal alloy is caused by the conjoint action of a tensile stress and a cracking environment. Stress corrosion cracking may compromise the integrity of the waste package. Project staff is addressing this integrity threat in the design of the waste package and in the research program. The Project plans to mitigate stress corrosion cracking of the waste package through the use of the highly stress corrosion cracking resistant Alloy 22 and by control of residual tensile stresses. Research to date shows that nickel base Alloy 22 is highly resistant to stress corrosion cracking in the environments expected in the repository. Residual tensile stresses introduced during fabrication will be relieved by a stress anneal of the entire canister prior to filling and final closure. In the vicinity of the final closure welds, beneficial residual compressive stresses will be introduced into the outer surfaces of the waste package by laser peening or local induction annealing treatments.

The mitigation method, experimental approach, and modeling efforts for stress corrosion cracking are consistent with the state of the art and appropriate research work generally is underway to verify the models. However, the Panel has identified a few deficiencies with the current program.

The Project staff has proposed two stress corrosion cracking models: an initiation model based on a threshold stress intensity factor and a propagation model based on film rupture/slip dissolution. Sensitivity of the crack growth measurement techniques is a critical issue for experiments designed to verify both of the models. In the current experimental procedures used by the Project staff, the sensitivity to crack growth has not been established and appears to be inadequate. The Panel recommends that the maximum sensitivity to crack growth in the threshold stress intensity factor and crack propagation tests be established and improved. If necessary, a combination of accelerated testing, longer exposure periods, and fractography could be used.

In the film rupture/slip dissolution model, crack propagation is assumed to occur above a threshold stress. The threshold stress criterion used in the model is not conservative. Threshold stresses for the initiation of cracking on surfaces containing defects are generally much lower than those of smooth surfaces on which the threshold values used in the model are based. The Panel recommends that the threshold stress component of the slip dissolution model be replaced with the threshold stress intensity factor model for the welded portions of the waste package which will contain preexisting flaws.

The calculations of the constants in the film rupture/slip dissolution model for Alloy 22 are based on relationships developed for 304 stainless steel in 288°C water. It is likely that these constants are not applicable because of differences in the deformation behavior between 304 stainless steel and Alloy 22. The Panel recommends that Project staff develop constants specific to Alloy 22 for the film rupture/slip dissolution model.

The Panel further recommends that alternative models for stress corrosion cracking be considered by the Project. Alternative models can provide validation and support for the Project approach. Alternative models also may be required if the current models are found to be deficient.

The Project plans to reduce residual tensile stresses in the waste package to mitigate the initiation of stress corrosion cracking by means of a stress anneal and water quench of the entire Alloy 22 waste canister, followed by an induction anneal or laser peening of the final closure welds. Based on experience with suction roll shells in the pulp and paper industry, the quenching process after solution annealing could produce unacceptably high tensile residual stresses. On the other hand, slow cooling could lead to the initiation and growth of deleterious grain boundary precipitates. The Panel recommends that the issue of heat treatment for stress mitigation and alloy stability be thoroughly evaluated.

Two approaches can be employed to minimize tensile residual stresses induced by cooling after solution annealing. The first is to cool the fabricated containers slowly. This approach may require the use of an alternative nickel base alloy (to Alloy 22) that is not susceptible to sensitization during the slow cooling process. The second is to carefully design and control the quenching process so that minimal levels of tensile residual stress are produced at or near free surfaces during the quenching operation. The selected approach should be verified by finite-element thermal and stress analysis and by experimental measurements on prototype containers.

The Project's future corrosion test plans include the evaluation of the resistance to stress corrosion cracking of aged and welded-and-aged microstructures in simulated repository environments in the long-term corrosion test facility. The specimens will be aged to produce grain boundary precipitation, but currently there are no plans to evaluate the different stages of aging. The early stages may be more deleterious than later stages. For example, the potential for chromium and molybdenum depletion near the precipitates may be greater early in the aging

process. This depletion may be healed later in the process. The Panel recommends that the effects of early stages of ordering, grain boundary segregation, and impurity segregation on stress corrosion cracking be evaluated. These processes may be dependent on the composition of the alloy, so the Project staff should evaluate the role of heat-to-heat variation on stress corrosion cracking behavior for the different stages of aging.

Minor constituents in the repository environment may influence cracking behavior. In a study of secondary-side intergranular stress corrosion cracking in Alloy 600 tubing from one-through and recirculating steam generators, lead was found in the leading edges of cracks in several instances including three where lead contamination in the aqueous environment was not reported. The Panel recommends that the issue of the effects of minor constituents, such as lead, in the repository environment on stress corrosion cracking be evaluated in the testing program.

3.8 HYDROGEN EFFECTS

The nickel-chromium-molybdenum family of alloys has a well-known history of hydrogen embrittlement susceptibility. The degree of susceptibility is a function of alloy composition, cold working, and thermal history among other variables. Hydrogen is potentially available during repository operation as a product of the cathodic partial reaction in a general corrosion process or, perhaps more likely, in a localized corrosion cell associated with crevice geometries or microbial activity. It appears that the Project has discounted hydrogen effects in this nickel-based alloy since the structural requirements for the waste package outer barrier at the Yucca Mountain site are such that Alloy 22 could be used in the annealed condition which, given the history of other nickel-chromium-molybdenum alloys, is likely to be resistant to hydrogen embrittlement. There is, however, no known research on the hydrogen susceptibility of Alloy 22 that would support that position. While the fabrication strategy is designed to eliminate tensile stresses from the outer surface of the waste packages, industrial experience has shown this to be difficult to achieve completely. It is prudent to determine the affects of tensile stresses that can result from fabrication processes such as quenching and welding.

The Panel recommends that experimental work be undertaken to explore the hydrogen embrittlement susceptibility of cold worked and cold worked and aged Alloy 22 in repository environments to simulate service conditions associated with residual stresses derived from welding and fabrication.

3.9 FABRICATION OF WASTE PACKAGES

Design and fabrication details can have a great effect upon corrosion and mechanical behavior of waste packages. The Panel notes a gap between the design/fabrication effort and the materials/corrosion effort on the Project. The former needs to recognize and control the effects of fabrication processes on metallurgical structure and residual stresses, and the latter needs to express findings in useable guidelines to direct design and fabrication decisions. For example, thermal treatments need to be selected with awareness of their effects upon metallurgical structure. Waste packages can be fabricated to meet the relevant specification regarding mechanical performance but have a detrimental microstructure for corrosion performance. The condition of the metal surface, i.e. surface roughness, residual stresses, oxide films and surface contaminants, can adversely affect corrosion performance.

The materials performance and corrosion work to date has focused primarily on supporting performance assessment. The Panel concludes that it is time to balance this effort with work to support design and fabrication of the waste packages. In particular, work is required on weld and weld repair processes. This is not a recommendation to end the science program, but rather to redirect and balance the science effort to support design and manufacture/fabrication for long-term performance. Many of the same scientist/engineers and experimental/modeling procedures are appropriate to address the important issues with regard to fabrication of durable waste packages.

Fabrication processes affect the surface condition, metallurgical condition, and stress patterns of the waste packages. Welds are a primary area of concern. The effects of other fabrication processes, such as solution annealing, assembling of dual cans, and induction heating are also important. Tight areas of contact (crevices) between metals are potential trouble spots for corrosion.

The Panel recommends that the Project staff:

- Undertake a weld procedures development and validation program. The closure weld and its postweld processing are critical to long-term performance of waste packages. The two primary issues regarding long-term integrity of the welds in the Alloy 22 corrosion barrier are the level and nature of residual stresses associated with the closure welds and the stability of the weld metal microstructure. The production and testing of full-scale mockups is required and a weld repair procedure must be developed and validated.
- Carry out a weld filler metal qualification program. The ERNiCrMo-10 filler metal has been used in the early development studies because it is the matching composition to the Alloy 22 base metal. It is likely that better long-term performance can be achieved by the use of an alternate filler metal. The effect of postweld annealing on the weld microstructure is not clear, nor is the long-term stability of the weld metal relative to long range ordering.
- Evaluate alternate welding processes for the closure weld. While the GTAW process is reliable and dependable, it is slow and results in high levels of residual stress. Electron beam welding is attractive because it eliminates the need for a weld joint and can be conducted in a single pass, thus reducing the weld time significantly. A "single shot" process such as friction welding is also very attractive from both a metallurgical, residual stress, and productivity standpoint. Because friction welding is a solid-state process, many of the concerns regarding long term metallurgical stability resulting from segregation during weld solidification are minimized. There may also be other "hybrid" processes that are applicable.
- Determine the composition effects within the chemical specification for Alloy 22. Composition specifications for Alloy 22 are relatively broad, and the microstructure and properties of Alloy 22 are likely to be sensitive to chemistry and processing history within the specified composition. The goal is to narrow the chemistry ranges so that detrimental phases are kept to a minimum while maintaining satisfactory mechanical properties and corrosion resistance. A set of vacuum melted ingots weighing on the order of 50 pounds could be hot rolled to plate stock, and thus provide a substantial supply of test material. The effects of thermal exposures could then be determined, along with spot checks of the mechanical properties and corrosion behavior. In addition, autogenous GTA weld beads could be made on test coupons and examined before and after thermal

exposures to provide information on how to optimize the filler metal chemistry. It would also be useful to make several heats of weld wire with modified compositions to check the weldability.

3.10 RADIATION EFFECTS

The waste canister and surrounding environment will be subjected to a flux of neutrons and gamma rays from the stored radioactive waste. These fluxes can cause the following damage: 1) neutrons will produce atomic displacement damage in the metal, 2) neutrons will produce atomic displacement damage and gamma rays will cause electron-hole pairs in the passive film and 3) gamma rays will cause radiolysis of the surrounding environment. The peak neutron flux has been calculated to be about 5×10^4 n/cm²-s. The total neutron fluence, taking the most conservative estimate with no nuclear decay of the waste, will be 1.5×10^{16} n/cm² in 10,000 years. The peak gamma flux is about 1000 rad/hr at the time of emplacement (DOE Report-Dose calculation); decreases to approximately 10 rad/hr after 200 years; and decreases to approximately 0.1 rad/hr after 400 years. Radiolysis from gamma radiation is only a factor in the environment on the waste package surfaces when the waste packages are wet.

There is no evidence to suggest that radiation damage to the waste package canister will alter its mechanical properties; therefore, radiation damage studies of alloy 22 are not warranted. Also, there is no evidence that radiation damage of the passive film will alter its protective properties; although, this is based on studies by Saito et al. (1997) of Type 304 SS at 280°C. There are differences in the passive film formed on the iron based Type 304 SS at 280°C and the lower temperature (less than 170°C) film formed on the nickel based Alloy 22.

Results suggest that the production of H₂O₂ by radiolysis is the primary cause of a shift in the open circuit potential, but that this effect has not been sufficiently studied for Alloy 22 at gamma fluxes that will exist when condensed water is present.

The Project staff has calculated nitrogen oxide, nitrogen acids and ammonia production during the period when the waste package is exposed only to moist air. Also, little consideration has been given to the effect of radiolysis in condensed water and its effect on the corrosion behavior of Alloy 22. Glass et al. (1986) have measured the effect of radiolysis of J-13 well water on the corrosion behavior of Type 304 and Type 316 SS and found a 150 to 250 mV shift in the open circuit potential. Gamma radiation effects have not been conducted on alloy 22 although an approximation of these effects have been conducted by measuring the open circuit potential as a function of H₂O₂ concentration in both simulated acidified water and simulated concentrated water. These measurements were made at 25°C and a shift in the open circuit potential of about 225 mV was noted for simulated acidified water and about 300 mV for simulated concentrated water at an H₂O₂ concentration of 72 ppm. The critical issue is the actual concentration of H₂O₂ expected in the repository environment, at the time that liquid water is formed, and the corresponding shift in the open circuit potential.

The panel recommends that the Project complete the following analysis: 1) perform a calculation of the H₂O₂ concentration expected in the repository water, 2) measure the open circuit potential at the repository relevant H₂O₂ concentration, 3) directly measure the shift in the open circuit potential of alloy 22 in the presence of gamma irradiation, 4) assess the stability of the open circuit potential as a function of time for Alloy 22 exposed to gamma irradiation. Radiolysis measurements should be conducted using repository relevant waters in an autoclave system that allows continuous measurement of the open circuit potential to be made up to 170°C. High

temperature measurements are desirable because of the need to measure film stability and because this stability is temperature dependent. It would be desirable to measure the current-voltage response of the material in the gamma flux but this is of a lesser priority than measuring the stability of the open circuit potential as a function of time. It would also be desirable to measure the film chemistry following long-term exposure to the ionizing gamma irradiation field, but this is a lower priority because of the complexity of measuring film chemistry when samples are transported through air. Available gamma sources generally produce at least a factor of 100 times higher flux than that expected in the repository. Therefore, tasks numbered 1 and 2 are needed to provide specific data on open circuit potential shifts at repository relevant conditions. The current-voltage curves should be determined as a function of H₂O₂ concentration at repository relevant temperatures.

3.11 ENNOBLEMENT

During the past year, Project personnel have made open circuit potential measurements on Alloy 22 samples exposed in the Long Term Corrosion Test Facility at Lawrence Livermore National Labs for as long as four years. The open circuit potentials were considerably higher than those found for fresh samples immersed in fresh solution. Details of these observations can be found in recent Project reports. The corrosion potential of aged Alloy 22 samples in the old solution from the Long Term Corrosion Test Facility was found to be over 500 mV higher than that of new samples in new solution. Measurements on new samples in the old solution and on aged samples in new solution indicated that the ennoblement was caused partly by enhanced passivity and partly from an increase in the oxidation potential of the solution.

Despite the increase in corrosion potential observed in the samples exposed in the Long Term Corrosion Test Facility, no evidence of localized corrosion has been found on any of the samples. These observations underscore the resistance of Alloy 22 to localized corrosion. Furthermore, potentiodynamic polarization experiments have shown that the open circuit potential remained well below the potentials associated with transpassivity.

It is clear that ΔE determined from a potentiodynamic polarization curve on a fresh sample in fresh solution is not representative of the situation that can develop with time. The surface will change as a result of the improved passivity and the oxidizing power of the solution may increase.

The Panel recommends that the electrochemical measurements on samples exposed in the Long Term Corrosion Test Facility continue, as should measurements on fresh samples in old solution and on aged samples in fresh solution. These experiments will provide improved understanding of the ennoblement process.

4. REPOSITORY CONDITIONS AND POTENTIAL DEGRADATION MODES

4.1 REPOSITORY CONDITIONS: OVERVIEW OF TIME, TEMPERATURE, ENVIRONMENT

A particularly challenging aspect of the analysis of waste packages in the Yucca Mountain Repository is the extraordinarily long time period required for performance. During an operational phase of 50 years, emplacement of waste packages will be carried out. This will be followed by a monitoring phase to 300 years. At that time, the repository will be closed

beginning the closure phase. The Panel's main objective was to assess the technical basis for the determination of waste package performance over 10,000 years. In order to do this, it was necessary to consider the time-temperature-environment conditions in the repository over this long time. In the analysis of potential degradation modes for the waste packages, it is important not only to consider the conditions that could initiate a particular form of damage, but also to consider the time period over which those conditions persist.

The exposure conditions for waste packages in the repository are subject to the initial repository configuration and natural processes over time. Change over time can be affected by engineered processes, such as waste package loadings and distribution of waste packages in the repository and by natural processes, such as the amount of precipitation on the mountain. Of particular importance are the temperature of waste package surfaces and the chemical composition of wet environments in contact with the waste packages.

The waste material gives off heat and radiation at rates that decrease with time. Thermal effects diminish over several thousands of years, while radiation effects diminish over a few hundred years. At the repository level, the waste packages will be isolated beneath 300 meters of rock and are a few hundred meters above the water table. At this level, the waste packages will sit in air on support pallets. The ambient air will be saturated with water equivalent to 100% relative humidity. Although it is highly unlikely that the waste packages will be fully immersed in water, however, moisture will condense and seepage from the rock could drip onto metal surfaces. While the amounts of moisture will be small, there would be sufficient water for corrosion, and corrosion resistant metals are required.

Operational factors in the repository affect the time-temperature behavior of the waste packages and the surrounding rock. These factors include the waste package loading, spacing between waste packages, and the duration and level of ventilation prior to closure. Two operational modes are now under consideration. In the higher-temperature operating mode, the waste package surface temperature could reach 180°C, the surrounding rock would be heated above boiling, and the rock would be dried out near the drifts. In the lower-temperature operating mode, the waste package surface would be maintained below 85°C, the surrounding rock is not heated above boiling, and there would be a minimal dry-out zone in the rock.

There are several favorable aspects of the long-term storage. The waste packages will be exposed to one, long and slow, temperature cycle. There will be no moving parts. This favors good materials performance. The static exposure will not subject the waste packages to potentially detrimental, cyclic loads. The low heat fluxes and extremely slow heating and cooling will not expose the waste packages to large thermal gradients or rapid thermal expansion and contraction. In a higher temperature operating mode, the waste packages would be exposed to dry conditions for long times (several hundred years) before the surfaces are wetted.

It is broadly accepted that dry waste packages will not undergo significant corrosion damage. When the metal surfaces are wet, there is a potential for corrosion damage. Great emphasis has rightfully been placed upon the determination of times-of-wetness and the corresponding temperature and chemistry of the wet environments. These results are summarized below, and more details on the chemistry of wet environments are presented in a separate section of this report. Other aspects of interest, e.g. the mechanical loads and stresses on waste packages and the form and distribution of penetrations in waste packages, are also presented here.

4.1.1 Time-Temperature-Relative Humidity

The duration and level of ventilation prior to closure will have a significant effect upon the time-temperature response of the rock near the repository. With ventilation for 50 years, the mountain-scale thermal-hydrological model predicts completely dry drifts with temperatures rising above boiling after 500 years and cooling back to near boiling after 1000 years. The dry zone would extend approximately 10 meters into the rock surrounding each drift, and the drifts would be spaced so the dry zones from adjacent drifts would not overlap. With 300 years of ventilation, temperatures would not reach 85°C in the rock, with highest temperature being reached after 500 years. These data are for a thermal loading of 1.35 kW/m. Lower thermal loadings would result in lower temperatures and smaller dry zones.

Drift-scale, analytical models for a range of thermal loadings have determined the waste package temperature and relative humidity in the air surrounding the packages. There is good agreement between the Project results and those from the Center for Nuclear Waste Regulatory Analysis. A similar description of the behavior emerges for the time-temperature-relative humidity conditions.

During the emplacement and ventilation period, the waste package temperature and relative humidity in the drifts will be low as heat and moisture are removed from the repository. On closure, the temperature will rise to a peak temperature within 10-20 years, and the relative humidity will be further reduced. This will be followed by a long period over which the waste packages cool and the relative humidity increases.

For 50 years of ventilation prior to closure, a peak temperature of waste packages of 160 to 180 °C would be reached after approximately 15 years. At the time of the peak temperature, the relative humidity in the drifts would be less than 20% and the packages would be dry. The packages would likely remain dry for hundreds of years. The following summary statements were determined by taking data for temperature-relative humidity behavior from a Project presentation (YMBlink_08/02/01.ppt). On cooling, the following is a set of matching temperature-relative humidity values:

Waste Package Temp, °C	Relative Humidity, %	Condition
100	55-90	Wet
110	45-60	Wet
120	35-45	(Dry)
130	30-35	Dry
140	25	Dry
150	20	Dry

Correspondingly, 200 years after emplacement, the temperature would be 120-140 °C and relative humidity would be about 40%, and after 500 years, the temperature would be 110-120 °C and relative humidity is less than 60%. After 900 years, the temperature would be 100°C with a relative humidity of 80% and condensation of moisture would be present. The relative humidity level at which sufficient moisture forms to support corrosion processes varies with local chemistry, but it is likely that 20% is dry, 80% is wet and sufficient moisture forms around 60%.

For 300 years of ventilation prior to closure, the peak waste package temperature would not exceed 75 to 85 °C. The relative humidity would decrease on closure as temperature increases, but because the rock temperatures never exceed boiling and there would be no dry zone created. For this case, the packages would be dry for 300 years if the ventilation removes sufficient moisture. After closure at 300 years, there may be a dry period but the relative humidity would be high enough for moisture to form on waste package surfaces.

Over very long times as the repository returns to ambient, the conditions during the operation phase are not significant. The following set of waste package temperatures and time were determined by taking data from a Project presentation (YMBlink_08/02/01.ppt).

Waste Package Temp, °C	Higher Temp Conditions	Lower Temp Conditions
120 C	500 years	N.A.
100 C	1000 years	N.A.
80 C	3000 years	At closure to 1000 years
60 C	10,000 years	5000 years
40 C	25,000 years	25,000 years
Ambient (~25 C)	100,000 years	100,000 years

A conclusion from this data set is that it is crucial to get the first several hundred to one thousand years correct i.e. have high confidence that the waste packages are durable for this time period. During this period, the gamma radiation levels have dropped dramatically and temperature has decreased. As the exposure time increases, the conditions become more benign, the likelihood of localized corrosion and stress corrosion cracking decrease, and the uniform corrosion rates decrease.

4.1.2 Presence of Moisture

Yucca Mountain is located in a desert climate; however, there is water that moves from the ground surface through the rock and past the repository level to the water table below. The waste packages sit on support pallets in air at the repository and in a zone of unsaturated rock a couple of hundred meters above the water table. Full immersion of metal surfaces is a highly unlikely condition in the repository due to the low infiltration rates of water and the sufficiently high rate of transport away from the drifts. The two forms of water of interest are the water that can seep from the rock and drip onto waste packages and the water that can condense from the air onto the waste packages.

Condensation: At sufficiently high temperatures and low relative humidity, no aqueous phase will be present on the waste package or drip shield surfaces. As the waste packages cool and relative humidity rises, moisture will condense on the surface. For pure water on a clean surface, the critical relative humidity for the formation of several monolayers of water is approximately 70%. Deliquesce and capillary forces can lead to the formation of moisture at lower relative humidity.

Deliquescence is important for the proposed repository because soluble salts are expected to be present on the metallic surfaces. These salts can arise from airborne dust and scales from seepage water evaporation, and they can result in the formation of an aqueous environment at relative humidity less than 70%. In the proposed repository, the most likely scenario is that there will be a mixture of salts on the metallic surfaces.

Capillary condensation represents another mechanism by which an aqueous environment can exist at relative humidity less than saturation. As the radius of a pore decreases, the free energy of the liquid water decreases, allowing it to form at a lower relative humidity. The practical importance of capillary condensation in terms of the corrosion of waste packages is two-fold: fine porosity in deposits will act as reservoirs for water and areas of near-intimate contact between surfaces will condense water and hold it.

Seepage and Dripping Water: The amount of water that can seep into the drifts is not large. The expected seepage rate into drifts over the first couple of thousand years is 0.1 m³/yr (YMBlink_09/10-12/01.ppt). The amount of seepage into drifts and drips onto waste packages will vary both spatially throughout the repository and temporally for a given area of drip shield or waste package. Factors could focus seepage water from a larger area onto a smaller region, but these same factors would divert that water from other areas. The volume and patterns of dripping are likely to change with time. Many drifts may never see any seepage water. While these amounts of moisture are small, the waste packages will not remain dry, and the chemical composition of the environments that can form on the drip shield and/or waste packages must be considered.

When the rock fractures are unsaturated, the capillary forces are quite high and rapid flow or dripping of water from the rock is unlikely. If the rock is saturated, capillary forces become quite small and water can flow more rapidly through fractures. Portions of the water moving across the repository front will remain in the rock and flow around the drifts.

Three conditions describe the surfaces of metal that will be subject to corrosion at Yucca Mountain:

- **Condensation leading to moist dust:** The moist dust condition is the most likely condition for the vast majority of waste package and drip shield surfaces. These are areas where no drips fall upon the surface. In the moist dust condition, the metal surface is not contacted by dripping waters; the formation of an aqueous environment on the surface is controlled by surface temperature, relative humidity in the air around package, and the composition of dust and deposits on the surface.
- **Dripping seepage water forming mineral scale and deposits:** Mineral scale and deposits will form on surfaces where drips fall onto the waste package or drip shield. In the wet scale/deposit condition, dripping water from the rock contacts the alloy directly. Drips can fall onto the upper surface of drip shield and could fall onto waste packages where the drip shield is not effective. It is expected that in these areas, a mineral scale will accumulate due to evaporation of the water on the hot surfaces.
- **Crevice areas at metal-to-metal contact surfaces:** Crevices are formed at designed structural contact areas (e.g., where the waste package rests upon a support pallet). Depending upon the design and fabrication details, crevices may also be present at other (unintended) areas on waste packages and drip shields. Drips or condensation can wet the crevices formed at areas of metal-to-metal contact. Crevices must be considered as a different environmental condition because reaction at the metal surfaces can result in the

formation of products. Limitations in the transport of products out of crevices results in changes in the local crevice environment. Crevice environments are typically more aggressive than the corresponding environment outside the crevice.

4.1.3 Composition of Waters and Corrosive Environments

Chemical species and water compositions: Before considering any chemical interactions with the waste package and drip shield materials, the aqueous environments can be bounded as saturated brines dominated by Na-CO₃-HCO₃-NO₃, Na-Ca-Mg-Cl-NO₃, or Na-Mg-SO₄-Cl-NO₃. The main conclusion of relevance from this analytical treatment is that the solutions on the waste package will evolve into either an alkaline solution (pH ca. 11-12) containing high concentrations of sulfate, carbonate, nitrate, and chloride, or a near-neutral solution (pH ca. 6) containing high concentrations of chloride and nitrate with or without sulfate. For localized corrosion, the high chloride solutions would be considered the most aggressive, with higher ratios of chloride concentration to the sum of the concentrations of other anions being more deleterious. As the temperature of the metal 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.

Low melting point metals such as mercury and lead are known to exacerbate corrosion in a wide range of materials. In addition, some species containing elements such as arsenic can be potent accelerators of hydrogen uptake into metals, leading to increased risk of hydrogen cracking. These types of species can have effects at low levels (ppm). Other species such as bromine have been introduced during the excavation process as LiBr, which has been used for dust reduction and tracer studies. In addition to their presence at Yucca Mountain or their introduction during excavation or ventilation, the amount of the elements present, their chemical form, and the extent to which they can access the surfaces of the waste package and drip shield need to be considered.

Mixed ionic solutions: Mitigating some of the corrosion effects of having an aqueous environment at lower relative humidity (and thus higher temperatures) due to the presence of mixed salts is the fact that most anions tend to inhibit the localized corrosion of metals in the presence of chloride. Thus, although the salt with the lowest deliquescent point will initially dominate the ionic content of the solution, the solution will be comprised of a *mixture of all of the salts present on the surface*, even those with high deliquescent points. As the relative humidity continues to increase, the fluid will contain increasing proportions of the salts with high deliquescent points. The specifics of the composition evolution will depend on the composition of the soluble species on the surface. The Center for Nuclear Waste Regulatory Analysis staff has done analyses to show that a mixture of NaCl, NaNO₃, and KNO₃ can have a deliquescence point as low as 30%.

pH of Environment: Based on geochemistry, the lowest pH of the incoming water would be near-neutral (pH 6), and the highest pH would be near 10 or 11. Several species in the expected seepage water and rock have buffering effects on the pH. In addition to the carbon dioxide system, the silica present in the rocks will tend to keep the pH below about 10. The pH of solution at any site on a waste package will be a complex function of temperature, time, position in the repository, and seepage water composition. Nonetheless it is highly unlikely that a water of initial pH of less than 6 or more than 10 will drip onto the waste package.

It is highly unlikely that a low pH 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 (fixed at 0.89 atm). The acid gases (*e.g.*, HCl, HNO₃) would need to be maintained at pressures well above those attainable in the mountain in order to maintain the pH of the solutions at low values. Interactions between the waste package and the environment can affect the pH. If the cathodic and anodic reactions of the corrosion couple are separated physically by substantial distances as in crevice corrosion, the hydrolysis of the metal ions formed from the dissolution will act to lower the local pH at the anode within the crevice. The presence of rock dust, along with the natural waters, will provide a sink for hydrogen ions that will impede lowering of the pH below 6. At the cathodic areas, increases in pH may occur, as the natural waters and groundwater are not strongly buffered in that direction. However the presence of silica in the rock and rock dust will tend to buffer the pH below 10.

Oxidizing potential: A thermodynamic argument can be made that places the upper bound for the open circuit potential of the waste package and drip shield as the reversible potential for dissolved oxygen gas reduction (for pH below 7). No other reducible species expected in the repository has higher reversible potentials. Although dissolved oxygen gas has the most positive reversible potential, the kinetics are quite sluggish on almost all materials, and materials with oxide films tend to have slow kinetics. Therefore, the thermodynamic boundary of the water line as the highest oxidizing potential for the waste package and the drip shield is likely extremely conservative. Nonetheless any argument for a lower bound on the oxidizing potential of the waste package and drip shield must involve kinetic arguments based upon the electrochemistry of the materials involved.

Dust and scale deposits: During the operation phase and prior to closure, rock dust and material entrained in the ventilation air can deposit on the waste package surfaces. Fine particulate dust (< 2.5 μm diameter) deposit on all surfaces independent of gravity, but controlled by convection and thermophoretic effects. Coarse particles (diameter 2.5 to 15 μm) are likely to dominate the dust in the repository and tend to settle on horizontal surfaces. It is likely that at least the top 1/3 of the waste package and drip shield will be covered with a dust layer of significant thickness. The dust layer will consist of fine and coarse particulate from the excavation and emplacement processes, entrained material from the ventilation system, and other matter carried in on the waste package themselves from production.

As the temperature decreases and relative humidity increases, a moist dust condition will develop. When and where seepage occurs, waters can drip onto metal surfaces. The incoming waters contain dissolved salts, and evaporation of water from the metal surface can lead to the formation of mineral scales and deposits. For the Alloy 22 waste package, the aqueous environments originating from the seepage are relevant at locations where the drip shield is not functioning as designed, whereas the condensation of water from gas can apply to areas of waste package surface even if the drip shield is fully functional. If condensation of water is the only source, then the aqueous environment will be determined by the hydration of the dust and other matter on the waste package. If seepage is an additional source of water, then any dissolved salts in the seepage water contribute to the environment on the metal surface.

Radiation: The waste package and surrounding environment will be subjected to a flux of neutrons and gamma rays from the stored radioactive waste. The peak neutron flux has been calculated to be about 5×10^4 n/cm²-s. The neutron dose decreases by a factor of 200 after about 150 years. The total neutron fluence, taking the most conservative estimate with no nuclear decay of the waste, will be 1.5×10^{16} n/cm² in 10,000 yrs. The peak gamma flux is about 1000

rad/hr. This gamma flux decreases by a factor of 100 (10 rad/hr) after about 200 years and another factor of 100 (0.01 rad/hr) after about 400 years.

Radiolysis in the aqueous environment can cause of a positive shift in the potential of the metal surface through production of H_2O_2 and other radiolysis products. This effect has not been sufficiently studied for Alloy 22 at gamma fluxes that will exist when condensed water is present. This effect is likely to be limited to the first couple of hundred years and will only be a factor when surfaces are wet.

Radiation fluxes can damage metal and passive films by (a) neutrons produce atomic displacement damage in the metal and the passive film, and (b) gamma rays cause electron-hole pairs in the passive film. There is no evidence to suggest that radiation damage to the waste package canister material will alter its mechanical properties; therefore, radiation damage studies of Alloy 22 are not warranted. Also, there is no evidence that radiation damage of the passive film will alter its protective properties.

Microbiologically Influenced Corrosion: Microbes are known to be present at Yucca Mountain, and they will undoubtedly be carried in during excavation as well as any ventilation period. The by-products of microbes can increase general corrosion as well as localized corrosion of metallic materials. In addition, the physical presence of microbial colonies and the structures they build can lead to crevice corrosion. In order for microbes to have an effect, several criteria must be met: (a) the microbes must be present, (b) they must be viable (*i.e.*, have conditions under which they can reproduce), (c) their metabolism must either produce species that are deleterious to the material of interest or use species that are beneficial or required for corrosion protection, and (d) the effects of the metabolism must reach the material surface.

In the case of Yucca Mountain, the relevant criteria to consider are (b) and (c); it is accepted that microbes could well be present or be introduced, and conservatism dictates that it be assumed that their effects reach the material surfaces. Criterion (b) can be used to bound the times during which microbes could be active in the repository. To do so, it seems reasonable to consider the range of environmental conditions over which microbes are known to exist. Based upon the hardiest microbes known, the environment must provide condensed water, a food source, a sufficiently low temperature (< 120 C), and a pH between 0 and 11. Microbes are known to thrive in sulfuric acid concentrations as high as 10%, and salt concentrations of several moles per liter. Microbes are able to survive in natural oxidizing environments, but they themselves be oxidized at potentials achieved with oxidants such as peroxide. A fruitful direction of research on microbially induced corrosion is to investigate the effects of microbial by-products on the corrosion of Alloy 22 and titanium Grade 7 under the range of plausible conditions of the environment.

4.1.4 Atmospheric conditions

Atmospheric pressure in repository is fixed at 0.89 atm. Yucca Mountain "breathes"; the fractures through the rock layers are sufficiently interconnected that a pressure gradient cannot be maintained within the mountain. From the perspective of the environment, this condition has several ramifications: (a) there is a continual supply of oxygen from ingress of air, maintaining the gaseous environment inside the drift as oxidizing, and (b) the partial pressure of volatile gases (such as HCl, HNO_3 , H_2S) is limited to the atmospheric pressure at Yucca Mountain. The later limits the acidity due to the dissolved acidic gases.

It is important to investigate the possibility of pressure differences developing in local regions such as under or within mineral scales on the waste package. These scales and deposits can form from evaporative drying of waters. If such locally elevated pressures are possible, this condition might lead to the elevation of the local acid gas partial pressure that would, in turn, allow lower pH values to occur than would be the case in the nominal atmosphere.

4.1.5 Mechanical loads and stresses on Waste Packages

The waste packages are exposed to one, long and slow, temperature cycle. There are no moving parts. The loaded waste packages are heavy, however the inner and outer canisters are thick-walled so applied loads are relatively small. The inner canister is designed to be the primary structural component of the waste package. Low mechanical loads and static conditions favor good materials performance. The static exposure does not submit the waste packages to potentially detrimental, cyclic loads. The low heat fluxes and extremely slow heating and cooling do not expose the waste packages to large thermal gradients or rapid thermal expansion and contraction. In a higher temperature operating mode, the waste packages are exposed to dry conditions for long times (several hundred years) before the surfaces are wetted.

The primary source of stresses in the waste packages will be residual stresses from the fabrication and sealing processes. Cold working and forming of the canister body and lids result in residual stresses in the metal, and welding results in high residual stresses in the weld metal and heat-affected zone of welds. Stress relief thermal treatments, induction heating and laser peening are planned to mitigate tensile stresses. Experience has shown that while stress mitigation can be quite effective, it is difficult to completely eliminate residual tensile stresses. Rock fall onto waste packages or drip shields will result in local, residual stresses on the structures.

4.1.6 Damage Processes and Waste Package Penetrations

Stress corrosion cracking or hydrogen embrittlement would result in the growth of cracks in the metal and could lead to crack-like penetrations. Stress corrosion cracks result from a combination of environmental interactions and tensile stresses at the metal surface. The Cyclic loads or periodic loading and unloading exacerbate damage by the environmental cracking mechanisms. Through-the-wall penetrations of the waste package can occur by environmental cracking if detrimental environmental conditions and tensile stresses persist for the entire wall thickness. Any penetrations would be narrow, tight cracks through the metal. Transport of moisture in or radionuclides out through these cracks would be by a tortuous path. In order to determine the extent of retardation of radionuclide transport through these penetrations, analytical modeling is required.

The most vulnerable locations for cracking are the along the welds, and the final closure weld is the most vulnerable of all. It is highly unlikely that any cracking damage would lead to a waste package cracking apart or opening up. Rather, damage by cracking would be a single penetration or an array of separate penetrations. A full thickness penetration in the body of the waste packages is unlikely because there is no sustained tensile stress through the wall. Based on industrial experience, full penetrations at welds are observed when stress corrosion cracking occurs, but the cracks are constrained to isolated areas and not continuous along the entire length of welds. An additional mechanical load, for example internal pressure of a vessel or a pipeline,

is required for rupture to occur. The waste packages do not have this additional load, so penetrations but not rupture would be expected.

In the analysis of potential degradation modes to waste packages, it is important not only consider the conditions that could initiate a particular form of damage, but also to consider the likelihood that the conditions would persist and allow the damage to continue. While some cases are autocatalytic and propagation continues, there are other cases where propagation slows or stops. Uniform corrosion rates typically slow with time. Localized corrosion processes often exhibit a critical temperature below which the process stops and no further damage occurs.

Penetrations from crevice corrosion would be localized patches of damage beneath the crevice former. If the damage persisted and the crevice remained tight, this could lead to full penetration in the local area. Uniform corrosion (the slowest process) will eventually lead to patchy penetrations of the waste packages. While this damage is referred to as uniform, there are areas where penetrations are deeper. These would likely be along the upper surface of the waste package where deposits and moisture could collect. The form, size and distribution of potential penetrations are important in the determination of the degree of containment and retardation of release of radionuclides from a damaged waste package.

4.2 POTENTIAL DEGRADATION MODES

In the present design, the repository includes waste packages constructed of an outer barrier made of nickel-chromium-molybdenum Alloy 22, which will surround an inner container of Type 316 nuclear grade stainless steel. Additionally, the waste packages will be enclosed by a titanium Grade 7 (titanium-palladium) alloy drip shield. Under anticipated repository conditions, corrosion is expected to be the most significant potential degradation mode for the Alloy 22 and titanium Grade 7 alloy surfaces that will be exposed to the repository environment. Corrosion resistance will in turn determine the service life of the waste packages.

Alloy 22 and titanium Grade 7 are among the most corrosion resistant engineering materials that are available today. Nevertheless, all engineering materials are subject to environmental degradation under certain circumstances. The likelihood that a given mode of corrosion will occur is dependent upon a complex interplay among the metallurgy of the materials of construction, the chemistry of the repository environment, and the mechanical state of the waste package while in service. The identification of potential degradation modes and the evolution of corresponding control strategies are, therefore, critical to the long term stability of the waste package. Failure of the containment due to corrosion within the first 10,000 years of operation would allow release of radionuclides to the environment with attendant risk to the public safety and, correspondingly, diminished repository integrity.

The chemical stability of the materials of construction of any engineering system is a function of the service environment in which the system is called upon to perform. Corrosion resistance is, in turn, intimately associated with the microstructure of the materials of construction. In short, the structure-property-performance relationships that are at the core of materials science and engineering are clearly at work in determining corrosion resistance.

The Project staff has identified the following degradation modes for analysis: uniform corrosion of passive metals, localized corrosion, and stress corrosion cracking. The Project staff has concluded, based on research and analysis to date, that these corrosion modes are most significant. The Panel believes, however, that some modes have not been fully studied. The Panel has identified three long-term metallurgical phenomena of interest: (a) phase

transformations and precipitation, (b) long-range ordering of solute atoms, and (c) solid-state segregation of impurity atoms. These processes can potentially influence both corrosion and the mechanical behavior of waste package materials of construction as the packages age. The Panel believes that the Project has not fully evaluated these phenomena in research to date. Additionally, mechanical failure and hydrogen embrittlement are potential modes of failure for the waste package. Pre-existing sub-critical flaws will be present in the waste package, for instance, as a result of welding, and these flaws can lead to mechanical failure if the fracture toughness of the metal degrades as a result of aging phenomena. Similarly, corrosion reactions can generate hydrogen, which might in turn cause hydrogen embrittlement of the aged alloy. Other factors that can influence the degradation modes are radiation effects, microbiological activity, and fabrication artifacts. These factors can influence long-term performance by either affecting the environment in contact with the waste packages or by affecting the waste package materials of construction.

5. COMPOSITION OF AQUEOUS ENVIRONMENTS

5.1 INTRODUCTION

In the view of the Panel, the most critical issues concerning the environment on the waste packages involve the determination of the nature of the plausible extremes of environments. The temperature, composition of the environment, and the effects of microbes can all contribute to or affect these plausible extremes. A technically defensible approach to the problem of determining the waste package environment is to define the physical/chemical bounds of environments that can be expected based upon known physical and chemical processes, inherent variability throughout the repository, and uncertainties in quantitative determination of the coupled processes that affect the environment. A similar determination of the performance bounds of the waste package and drip shield materials would then allow a comparison to determine the likelihood that the waste package or drip shield would be exposed to environmental conditions under which failure would be likely to occur. Comparison of the bounds of expected environments with the limiting environments for safe operation of waste package and drip shield materials would provide the critical conditions for the engineered barrier. The probability of failure could be determined from the likelihood for formation of various environments and the likelihood of failure in those environments.

This section describes the extent to which bounds on the environment can be set, given the current state of scientific knowledge about the relevant physical processes. Important parameters and processes to be considered include: combinations of temperature, relative humidity, and pressure; the source, composition, pH, and buffering capacity of waters that may come in contact with the engineered structures; the chemical and physical characteristics of the rock, dust, and entrained matter from the air; cathodic reactions in the waste package environment; and the possible effects of microbes. An underlying issue is the relative importance of transient vs. steady state environments.

5.1.1 Physical Description of the Aqueous Environments on Metal Surfaces.

Sound analyses of the corrosion of any structure require an understanding of the realistic range of aqueous environments that can contact the structure's surfaces and the possible surface

conditions of the materials of construction. The effects of such environments on structural integrity can then be established by combining these knowledge bases. The purpose of this section is to review the likely and plausible aqueous environments and surface conditions that might occur on the drip shield and waste package in the proposed repository. The compositions of the natural waters in Yucca Mountain and the materials of construction, the deposition of particles onto the surfaces, and the scenarios for water ingress will control the nature of the environment that develops.

Compositions of Natural Waters in Yucca Mountain. For the purposes of this Panel report, "waters" refers to the aqueous solutions moving through Yucca Mountain before any interaction with waste package or drip shield materials, that is, the waters that may seep into the drift and drip onto the metal surfaces. "Aqueous environment" refers to the wet condition on the metal surface. An aqueous environment is a combination of the aqueous solution, any solid particulates present, and soluble gases.

The natural waters moving through Yucca Mountain vary substantially in composition and are the subject of ongoing work by the Project. Based on Project analyses to date, the compositions of the waters in the vicinity of the repository can be grouped into two distinct types: sodium-carbonate waters and calcium-chloride/sulfate waters¹ (Rosenberg, 2001). Both are near neutral in pH under ambient conditions. The former type includes the perched waters in Yucca Mountain and has been often represented by J-13 well water. This solution composition (see Table 1) was used in performance assessment as a proxy for seepage water. The latter type includes waters from the unsaturated zone of Yucca Mountain, that is, the pore waters within rocks in hydrostratigraphic units surrounding the repository. Examples of analyses of pore waters are included in Table 1. Although the relative amounts of dissolved ionic species in the natural waters will vary, an ensemble of anions is likely to be present in all aqueous environments within Yucca Mountain. This conclusion has important implications for the initiation and propagation of localized corrosion (Section 8).

Although all of the naturally occurring waters in Yucca Mountain are dilute, the radioactive decay of the waste will heat the surrounding environment and subsequently concentrate ionic species, as some of the water evaporates, leaving behind the same amount of salts in a smaller amount of water. The spatial and thermal extent of the heating depends on many variables including the range of temperature of operating mode selected. Nonetheless, significant evaporative concentration is expected to occur in all scenarios considered to date.

This evaporative concentration will alter the chemical composition. A technically defensible framework for understanding these changes is the concept of chemical divides (Garrels, 1967, Eugster, 1978). As a natural water is evaporated, the evolution of its composition is controlled by a sequence of precipitation events determined by the differences in solubility of the various minerals relevant for the ionic species and the initial species concentrations present. This approach has two major implications for the waste package environment: it provides a means to classify disparate natural water compositions into a limited number of chemically simple types, and it allows the initial chemical composition of a natural water to be used to determine, in the main, the major stages of its evaporative evolution.

In most natural waters the first chemical divide occurs when the solubility of CaCO_3 is reached. Precipitation of calcite will then occur. The result of the divide is determined by the initial relative concentrations of calcium and carbonate (as shown in Figure 1). If the calcium content of the solution is greater than the initial carbonate concentration, the solution evolves along one path, whereas if the carbonate content of the solution is greater than the initial calcium

concentration, then the solution composition evolves along a different path. For the range of Yucca Mountain natural waters analyzed to date, this chemical divides approach predicts that there are three possible types of end-point solutions. The perched waters (as represented by J-13 water) will evolve toward alkaline brine with the major ions being sodium (Na^+), carbonate (CO_3^{2-}), and bicarbonate (HCO_3^-). This type of solution is referred to as an $\text{Na-CO}_3\text{-HCO}_3$ brine. On the other hand, the unsaturated zone waters will evolve towards an $\text{Na-CO}_3\text{-HCO}_3$ brine, a near-neutral, Na-Ca-Mg-Cl brine, or a near-neutral $\text{Na-Mg-SO}_4\text{-Cl}$ brine (Rosenberg, 2001).

Thus, based upon these accepted principles of geochemistry, the range of Yucca Mountain waters *entering the drift* can be grouped into one of three brines, based upon the dominant ions present: an $\text{Na-CO}_3\text{-HCO}_3$ brine, a near-neutral, Na-Ca-Mg-Cl brine, or a near-neutral $\text{Na-Mg-SO}_4\text{-Cl}$ brine. Note the nitrate (NO_3), a significant ion present in Yucca Mountain waters is not included in this illustration. The chemical divide approach provides a means to bound the concentrations of the major components. Although spatial and temporal variation in the exact concentrations of the species in the seepage waters are expected, all are constrained by the physical chemistry so that their major components described by one of these three brines. From a corrosion testing perspective, these three brines can be used as the bases to investigate the effects of minor species that influence corrosion behavior (*e.g.*, F^- , Pb^{2+}) with the confidence that the effects of the matrix waters will also be taken into account.

It is also important to note that in addition to the dominant ions, other important ions will be present and carried along unaffected by the chemical divides. For example, nitrate is present in the natural waters and will be carried along in both divides as the solubility of nitrate salts is much higher than the salts mentioned above. These other ions, such as nitrate, can have inhibiting or accelerating effects on the corrosion processes. Their contributions can also be assessed by using these three major brines as the base solutions.

Materials of Construction. As the waters from the rock seep into the drift, they will interact with the materials of construction of the engineered barrier system. The engineered barrier system consists of four types of structures: the ground control system, the drip shield, the waste package, and other supporting structures. The ground control system is designed to provide a robust support system for the drift wall with minimal maintenance requirements. Its role is to maintain stable underground openings during the operations, monitoring, and closure phases. It consists of circular steel sets with steel wire fabric that will be placed in approximately 70% of the drifts. Fully grouted rock bolts will be used as needed (in approximately 30% of the drifts). The drip shield consists of a titanium Grade 7 shield with titanium Grade 24 structural members connected to feet of Alloy 22. The drip shield is designed to minimize direct dripping and rockfall onto the waste package. The drip shield will be emplaced just prior to final closure after a 30 to 300 year monitoring phase. The other engineering structures inside the drift include the invert and pallet, as well as the crane rails. The invert and the crane rails will be made of steel whereas the pallet will be made of Alloy 22 with Type 316L SS connecting tubes. The outer barrier of the waste package in the current design is cylinder of Alloy 22 surrounding a cylinder of Type 316NG SS.

The compositions of these structures are important because the environment on the waste packages can be altered by interactions between these materials and the seepage waters described above.

Scenarios for Aqueous Environment Development. The Panel has concluded that three conditions describe the metal surfaces that will be subject to corrosion in the proposed repository:

- a. condensation of water leading to formation of moist dust on the metal surface,
- b. dripping seepage water forming mineral scale and deposits on the metal surface, and
- c. crevice areas.

Full immersion of metal surfaces is a highly unlikely condition in the repository due to the expected low net infiltration rates (on the order of 5 to 20 mm/y) and the sufficiently high rate of transport away from the drift. The variations in the net infiltration rates do have impact on the expected spatial and temporal variations in environment within the repository.

Condensation leading to moist dust. The moist dust condition is the most likely condition for the vast majority of waste package. In the moist dust condition, the metal surface is not contacted by dripping waters; the formation of an aqueous environment on the surface is controlled by surface temperature, relative humidity in the space around package, and the composition of dust and deposits on the surface. The dust layer will consist of fine and coarse particulates from the excavation and emplacement processes, entrained material from the ventilation system, and other matter carried in on the waste package from production. At sufficiently high temperatures (and corresponding low relative humidity), the waste package surface will be dry. As the temperature decreases and the relative humidity increases, an aqueous solution will form; its composition is determined by soluble species in the particulates, soluble gases from the air, and reactions among the solution, particulates, and alloy. The important properties of the moist dust layer that will affect corrosion behavior are the size and thickness of the dust layer, the amount and distribution of moisture in the layer, the composition of the dust, the physical structure of the dust (i.e., porosity), and the electrical and ionic conductivity of the layer.

Dripping seepage water forming mineral scale and deposits. Mineral scale and deposits will form on surfaces where drips fall onto the waste package or drip shield. In the wet scale/deposit condition, dripping water from the rock contacts the alloy directly. Drips can fall onto the upper surface of the drip shield and could fall onto waste packages where the drip shield is not effective. It is expected that in these areas, a mineral scale will accumulate due to near complete evaporation of the water on the hot surfaces. The seepage water composition, the soluble species in the previously deposited particulates, the soluble gases from the air, and reactions among water, particulates, and metallic surfaces control the solution composition for the wet scale/deposit condition. The changes in water chemistry at scale and deposits on metallic surfaces will be determined by composition of the dripping water, thermal effects, and any interactions of the solution with the metal surface. The corrosion effects of the scales formed may range from highly protective to corrosion inducing, depending upon their nature.

Crevice areas. Crevices are formed at designed structural contact areas (e.g., where the waste package rests upon a support pallet). Depending upon the design and fabrication details, crevices may also be present at other (unintended) areas on waste packages and drip shields. Mineral scale deposits could also form occluded regions. Drips or condensation can wet the crevices. The aqueous environment within these crevices is controlled by the composition of the incoming water, transport of chemical species from the surface and within the crevice, and reactions within the crevice. The products of any corrosion processes within the crevice can significantly affect the crevice solution composition.

5.1.2 Net Infiltration Rate: Availability of Seepage Waters

The net infiltration rate of water into the drifts will have important effects on both condensation and dripping, although the relative contributions of condensation and dripping to the aqueous environment will vary both spatially throughout the repository and temporally for a given area of drip shield or waste package. The net infiltration rate (the rate at which water can be expected to reach the drift from the rock above) at Yucca Mountain is low, but not negligible. Although work continues, the estimates of the average net infiltration to the drift range from 2 to 7 mm/y for current climatic conditions, with increases up to from 4.7 to 20 mm/y under certain climatic change scenarios [epri report]. Flow modeling by the Project has indicated that spatial variations of infiltration rate may be significant with some areas showing fluxes six times higher than the average input flux due to focused flow via fractures (Civilian Radioactive Waste Management System Management and Operating Contractor, 2001). Capillarity effects on flow due to the presence of the drifts may act to divert some of the infiltration away from the drip shield and waste package, thereby decreasing the access of the seepage waters to the waste package. Even in the absence of capillarity effects, the amount of water impinging on the engineered structures is expected to be small relative to the amount needed to completely immerse the waste package. Nonetheless, the drifts are not expected to be completely dry throughout the 10,000 year time period of interest, so scenarios by which an electrolyte can form on the drip shield and/or waste package must be considered.

5.1.3 Relevance of Environment Development Scenarios to Engineered Components

Both condensation and dripping are relevant for the titanium Grade 7 drip shield. During any dry period after its installation, rock dust and material entrained in the ventilation system will collect on the surfaces of the drip shield. Fine particulates (less than 2.5 μm diameter) deposit on all surfaces independent of gravity, but controlled by convection and thermophoretic effects (Seinfeld and Pandis, 1998). Coarse particles (diameter 2.5 to 15 μm) are likely to dominate the dust in the repository and tend to settle on horizontal surfaces. Nonetheless, it is likely that a portion of the waste package and drip shield will be covered with a dust layer of significant thickness. Surface charge on the dust would also lead to electrostatic interactions between the particulates and the metal surface. As the temperature decreases, the moist dust condition can develop as described above. Once seepage occurs, the drip shield is designed to divert the drips from the waste package. During this time, the areas of the drip shield that are subject to drips will form mineral scales and deposits.

For the Alloy 22 waste package, the aqueous environments originating from the seepage are relevant at locations where the drip shield is not functioning as designed, whereas the condensation of water from gas can apply to areas of waste package surface even if the drip shield is fully functional. If condensation of water is the only source, then the waste package environment will be determined by the hydration of the dust and other matter on the waste package.

Due to their location, the ground control structures will be exposed to seepage water well before the drip shield or waste package. The steel sets and rock bolts will likely see the most seepage water as they will not be substantially protected by capillarity effects on flow. In fact, any capillarity effects will lead to seepage water running down the walls of the drift, likely along the steel sets. Note that these structures are expected to last up to 300 years during the monitoring

phase. Although outside the scope of this Panel review, the Panel recommends that some corrosion studies be carried out on these materials to determine the corrosion rates that can be expected. In addition, these studies would provide important information concerning the release and transport of ferrous ion by the steel structures. The ferrous ions will quickly be converted to ferric ion by the oxidizing environment within the drift. The extent to which these ferric ions are then transported from the steel sets or rock bolts to the drip shield or waste package by the seepage water could be important. The availability of the ferric ion as an oxidizing species on the drip shield and waste package may impact the likelihood of localized corrosion of these materials. Under the near-neutral or alkaline pH conditions expected in the concentrated brines, the ferric ion will precipitate and not be an effective oxidizer. Under acidic conditions within active localized corrosion sites, however, the ferric ion would not only serve to accelerate the corrosion, but also to provide a source of protons to maintain a low pH. Finally, the steel provides a substrate on which certain microbes may colonize, as discussed in more detail below in Section 5.3.

5.2 CRUCIAL TECHNICAL ISSUES FOR THE WASTE PACKAGE ENVIRONMENT

5.2.1 Determination of Extremes of Environments

The concept of determining the practical extremes of an environment as a step in the assessment of the corrosion performance of a proposed structure is consistent with current scientific and engineering practice. The application of this concept to an environment as complicated as that of the environment on the waste packages for the proposed repository is a daunting task involving substantial assumptions. The assumptions include:

- the absence of relevant, important, but unknown, chemical or physical processes;
- proper consideration of transient vs. steady state effects;
- accuracy of computational models as abstractions of real physical phenomena;

Despite the assumptions and limitations inherent in this approach, it provides a logical, technically defensible framework for providing input into the estimation of the corrosion performance of the engineered structures within the proposed repository.

Temperature, Relative Humidity, and the Presence of an Aqueous Environment. The temperature of the waste package surface and the relative humidity of the gas adjacent to the material are two of the parameters that strongly influence the waste package environment. Together these two parameters exert considerable control on the existence of an aqueous solution on the waste package. At sufficiently high temperatures and low relative humidity, no aqueous phase will be present on the waste package or drip shield surfaces and aqueous corrosion will not occur. The temperature and relative humidity are linked. As the temperature in the drift rises, the relative humidity decreases; conversely, as the temperature decreases as the repository cools, the relative humidity increases. It is important to keep in mind this link between temperature and relative humidity as high temperatures and high relative humidity are generally mutually exclusive, as long as the drift environment remains in the unsaturated zone. For pure water on a clean surface, the critical relative humidity for the formation of a liquid aqueous phase capable of supporting corrosion reactions is approximately 70% (Leygraf and Graedel, 2000). For either thermal operating mode under consideration, such a relative humidity is not expected for close to

1,000 y. Two important effects make it likely that aqueous environments will form at some locations under lower relative humidity and therefore at higher temperature and earlier times: deliquescent salts and capillary condensation.

Deliquescence describes the tendency of a compound to form a saturated aqueous solution at relative humidity less than 100%. At relative humidity above 75%, pure NaCl will form a saturated solution in equilibrium with solid salt. Deliquescence is important for the proposed repository because the expected presence of sparingly soluble species on the metallic surfaces, such as the dust and scales from seepage water evaporation, will lead to the formation of an aqueous environment at relative humidity less than 70%. Different pure salts have different deliquescence points, ranging as low as 20% for KF to as just below 100% for K_2SO_4 .

In the proposed repository, the most likely scenario is that there will be a mixture of salts on the metallic surfaces. This condition complicates the determination of the deliquescence point, sometimes referred to as the critical relative humidity RH_{crit} (Brossia, *et al.*, 2001), due to interactions among the ions. For example, consider a mixture of $NaNO_3$ and NaCl and water. Although the individual pure salts each has an RH_{crit} well above 70%, a mixture of the two can have an RH_{crit} as low as 64%. The Center for Nuclear Waste Regulatory Analysis staff has done analyses to show that a mixture of NaCl, $NaNO_3$, and KNO_3 can have a deliquescence point as low as 30% (Brossia, *et al.*, 2001).

The practical importance of a low deliquescence point is that an aqueous environment can exist at higher temperatures (and therefore also at earlier times). For example, during the first hundred years after closure, the temperature of the waste package is expected to be between 120 and 160 C for the high-temperature operating mode with a corresponding relative humidity of between 18 and 38%. If only NaCl were present on a flat surface, then aqueous corrosion could not occur during this time period as no aqueous solution can be in equilibrium until the relative humidity reaches ca. 75% which is not predicted to occur until ca. 900 years after enclosure. At that point the temperature will be below 120°C. However, if a deliquescent mixture of salts were present that has a RH_{crit} of 20%, then an aqueous environment could be present through virtually the entire emplacement period, including the time at high temperature. As described in detail in the section on localized corrosion (Sect. 3.1.5), materials are more susceptible to localized attack at higher temperatures.

Mitigating some of the corrosion effects of having an aqueous environment at lower relative humidity (and thus higher temperatures) due to the presence of mixed salts is the fact that most anions tend to inhibit the localized corrosion of metals caused by the presence of chloride. Thus, although the salt with the lowest deliquescent point will dominate the ionic content of the solution, the solution will be comprised of *a mixture of all of the salts present on the surface*, even those with high deliquescent points. As the relative humidity continues to increase, the fluid will contain increasing proportions of the salts with higher deliquescent points. The specifics of the composition evolution will depend on the composition of the soluble species on the surface. Nonetheless it is highly unlikely that a pure chloride solution will ever be present on the engineered structures.

Capillary condensation represents another mechanism by which an aqueous environment can exist at relative humidity less than saturation. As the radius of a pore decreases, the free energy of the liquid water decreases, allowing it to form at a lower relative humidity. This effect is described quantitatively by the Kelvin equation (Gdowski, 2001). For example, at 25°C a pore with a radius of 1 nm will be filled with water when the relative humidity is at or above 35%. The effect of temperature is modest; the pore of radius 1 nm has a saturation relative humidity of

55% at 120°C. The practical importance of capillary condensation in terms of the environment is two-fold: fine porosity in deposits will act as reservoirs for water and areas of near-intimate contact (crevices) between surfaces will condense water and hold it.

Limitations to the Total Pressure. Limitations on the total gas pressure that can be achieved in the waste package environment must also be considered. Yucca Mountain "breathes"; the fractures through the rock layers are sufficiently interconnected that a pressure gradient cannot be maintained within the mountain. From the perspective of the environment, this condition has several ramifications: (a) there is an inexhaustible supply of oxygen from ingress of air, maintaining the gaseous environment inside the drift as oxidizing, and (b) the partial pressure of volatile gases (such as HCl, HNO₃, H₂S) is limited to the atmospheric pressure at Yucca Mountain. For example, at a temperature of 100°C, a partial pressure of HCl of 0.1 torr would be required to maintain a 0.6 M HCl solution (ca. pH 0.2) at equilibrium (Gdowski, 2001).. This pressure would need to be compatible not only with the amount of Cl⁻ available, but also the ability to replenish this HCl as the gas will escape from the mountain with time.

Amounts of Water and Ionic Species. The amount of water that impinges on the waste package is critically important in the concentrations of the solutions that develop. Using net infiltration models, the Project predicts 4.7 to 19 mm/y for the current climate and proposed glacial climate, respectively (Civilian Radioactive Waste Management System Management and Operating Contractor, 2001). Thus, one extreme for the average amount of water on a waste package can be found by assuming that all of the water from net infiltration impinges on the waste package, leading to an estimate of 5 L of seepage water per cm² of waste package over the 10,000 year time period of interest.

This calculation assumes uniform distribution of infiltration. Two factors that could focus seepage water from a larger area onto a much smaller region of the repository are fractures in the repository and local drip shield failures. Of course, these same factors would divert that water from other areas. In addition, capillary barrier effects of the emplacement drifts may divert water flow around the drift. Many drifts may never see any seepage water. This discussion highlights the challenges involved in developing accurate estimates of parameters at Yucca Mountain. Even a bounding approach requires inherent assumptions. Nonetheless, it does appear that a technically defensible rationale exists currently for assuming some limitation in the amount of available water.

To estimate the possible surface concentrations of ionic species that may develop on the waste package, further assumptions are necessary regarding species concentrations of the seepage water and the degree of retention of these species on the waste package.

Compositions of Natural Waters and Changes Due to Evaporative Concentration. Several natural waters may be relevant to the waste package environment as described above. The most important characteristics for determining plausible extremes of environments are the pH, the major ionic composition, the presence and concentrations of important minor species, and the relative importance of transient environments and steady state environments.

The pH of the solution on the waste package surface is a critical value in determining its corrosivity. Based on the geochemistry of the rock (Bethke, 1996), it seems highly likely that the lowest pH of the incoming water would be near neutral, and the highest plausible pH would be near 10 or 11. Several species in the expected seepage water and rock have buffering effects on the pH. In addition to the carbon dioxide system, the silica present in the rocks will tend to keep the pH below about 11. The exact pH of the solution on any single waste package will be a complex function of temperature, time, position in the repository, and seepage water

composition, as well as interactions between the waste package and the environment. Nonetheless it is highly unlikely that a water of initial pH of less than 6 or more than 11 will contact the waste package.

The major ionic composition of the aqueous environments on the waste package and drip shield due to the seepage water and evaporative concentration can be well bounded by the three brines described above. Before considering any chemical interactions with the waste package and drip shield materials, the aqueous environments can be bounded as saturated brines dominated by Na-CO₃-HCO₃-NO₃, Na-Ca-Mg-Cl-NO₃, or Na-Mg-SO₄-Cl-NO₃. For localized corrosion, the latter two types of brines would be considered the most aggressive, with higher ratios of chloride concentration to the sum of the concentrations of other anions being more deleterious.

Low melting point metals such as mercury and lead are known to exacerbate corrosion in a wide range of materials. In addition, some species containing elements such as arsenic can be potent accelerators of hydrogen uptake into metals, leading to increased risk of hydrogen cracking. Fluoride is known to increase the dissolution of passive Ti. Other species such as bromine have been introduced during the excavation process as LiBr that has been used for dust reduction and tracer studies. The extent to which the drip shield and waste package can be exposed to such species must be considered. In addition to their presence at Yucca Mountain or their introduction during excavation or ventilation, the amount of the elements present, their chemical form, and the extent to which they can access the surfaces of the waste package and drip shield need to be considered.

In general, the trace elements listed above are associated with volcanic gases and ash, and may largely arise from these sources at Yucca Mountain. Mercury concentrations in natural waters are typically between 0.01 to 10 ppb (Ehrlich, 1996), and a current source worldwide is from atmospheric pollutant deposition. Reported ground water concentrations at Yucca Mountain are below 100 ppb, the detection limit of the method used for the analyses. Concentrations as low as 1×10^{-12} mol/L ($\sim 0.1 \times 10^{-9}$ g/L) can be measured using cold vapor atomic fluorescence spectroscopy, and clearly lower values within the range mentioned above are likely at Yucca Mountain. Dissolved lead can be derived from the burning of fossil fuels, but more likely originates from the tuff itself. Lead is found in the fracture-lining manganese-oxide minerals, for example (Carlos et al., 1993). Lead concentration is not reported for J-13 well water (Harrar et al., 1990) and is in the 1-100 ppb range for Yucca Mountain waters, with one evaporation pond at the Nevada Test Site containing ~ 1000 ppb lead. The likely sources of fluoride are the tuff and aerosols. Concentration is ~ 2 mg/L in J-13 well water (Harrar et al., 1990) and typically is not reported for other Yucca Mountain water analyses. Arsenic is found in general in ground waters where its concentration can range from 1 to 10 μ g/L, with higher concentrations being typical in the arid western parts of the United States (Welch et al., 2000). Arsenic may also substitute for tetrahedrally-coordinated silicon in silicate minerals, and might leach out in small amounts as these minerals dissolve at higher pHs. However, the most readily available form of arsenic may be associated with iron-oxide minerals in the fractures (Bowell, 1994; Welch et al., 2000).

These four trace elements could all come into contact with the waste package, although to variable extents. Likely mechanisms include deposition of infiltrating water onto the waste package, reaction of water with dust particles on the waste package surface, and deposition of heated water from the overlying rock during the thermal evolution of the repository. It is not clear how soluble these trace elements might remain in evaporating fluid as solid phases precipitate on the waste package. For example, the majority of the lead could be precipitated as

PbCO₃ or PbSO₄ solids. Arsenic or mercury, on the other hand, could remain as a relatively easily adsorbed and desorbed component of a moist dust coating. Mercury will complex dominantly with chloride and hydroxyl ions in most well-oxygenated surface and near surface waters, with mercury-chloride complexes dominant at low pH, and Hg(OH)₂⁰ dominant above pH ~ 6. In evaporating solutions, mercury may precipitate at the highest pHs as a mercury-oxide (HgO) if evaporation proceeds to near completion and chloride is reduced by precipitation of other phases (Martell and Smith, 1998).

Relative Importance of Transient vs. Steady State Aqueous Environments: Especially with regard to the environment on the waste packages, the concept of plausible environment extremes may be misleading as this might imply, to some, a specific steady state environment condition as being the most severe whereas repetitive transient environments may be more problematic. This issue is particularly acute for the scenarios in which dripping of seepage water occurs onto hot surfaces. The dynamics of the dripping and subsequent evaporation will interact to determine the form, size, and chemical composition of the deposits that form. If the dripping was highly localized, thick salt layers could build up to the side of the drip area. If the pattern were random over the surface and variable, washing of the thick salt layer would be more likely to occur, limiting development of a salt layer. Coupling would also occur among the dissolved oxygen concentration, the surface electrochemistry, the hydrodynamics, and heat transfer dynamics making the problem extremely challenging to any modeling effort. The Panel, therefore, recommends that the Project experimentally probe the relative effects of transient and steady state environments on the corrosion of the engineered barrier materials.

Effects of metal dissolution products and interactions with waste package. After an aqueous phase forms on the waste package and drip shield, interactions will occur between the waste package environment and these engineered structures. These interactions will involve both electrochemical reactions (metal dissolution, reduction of dissolved oxygen gas, water, other reducible species) and chemical reactions (hydrolysis of metal ions, precipitation of metal oxides and hydroxides). The effects of these interactions on the waste package and drip shield corrosion are considered in subsequent sections of this report. The effects of these interactions on the environment include changes in the local pH and changes in the amount of water (or other species) available.

If the cathodic and anodic reactions of the corrosion couple are separated physically by substantial distances, the hydrolysis of the metal ions formed from the dissolution will act to lower the local pH at the anode. This lowered pH can lead to increased dissolution that can be exacerbated by concentration of aggressive anions locally. This, in turn, can lead to increased hydrolysis, subsequent increased dissolution, and so forth. This "autocatalytic" scenario is a well-accepted principle in the initiation of localized corrosion as described in Section 8.

Such decreases in local pH can be bounded by the pH of a saturated solution of the metal salts represented in the alloy of interest. A saturated solution of CrCl₃ (to represent the most hydrolysable element in Alloy 22) has a pH close to 0 (Wang and Pourbaix, 1980; Mankowski and Szklarska-Smialowska, 1975). Active crevice sites in pure Ti at 150 C in 1M NaCl were found to have a pH of approximately 1 (Greiss, 1968). Note that the creation of local pH to these values will be slowed or possibly prevented by the buffering capacity of the environment. As discussed above, this capacity will be determined by the concentrations of those species that can exchange protons or hydroxyls and the kinetics of those exchange reactions. For example, the presence of rock dust, along with the natural waters, will provide a sink for hydrogen ions via cation exchange and/or mineral dissolution that will impede lowering of the pH below 6. In order

for a further drop in pH to occur, the production rate of acid from hydrolysis of metal ions must be sufficient to overcome the buffering ability of the volume of solution from which buffering ions can diffuse over the same time period.

At the cathodic areas, increases in pH may occur, as the natural waters and groundwater are not strongly buffered in that direction. However, the presence of silica in the rock and rock dust will tend to buffer the pH below 11. Exchange of protons with cations in the rocks or consumption of protons by dissolution of minerals will release additional cations to solutions, raising the ionic strength.

Cathodic reactions. In order for corrosion to occur, cathodic reactions that consume the electrons generated by the dissolution of metal must be able to occur on surfaces that are in both electrical and ionic contact with the anodic area. In the case of aqueous corrosion relevant to the environment on the waste packages, four types of cathodic reactions should be considered: (a) reduction of dissolved molecular oxygen, (b) ferric ion reduction (also known as iron-mediated oxygen reduction), (c) nitrate ion reduction, and (d) reduction of radiolytic peroxide. Assessment of the importance of each must consider both thermodynamics (as described by the redox potential of the reaction), and its kinetics (described by the exchange current density (i_0), the Tafel slope (b_c), and the diffusion limited current density (i_{dl})).

With regard to bounding the electrode potential of an interface, the open circuit potential of a material cannot exceed the redox potential of the most noble of possible cathodic reactions. The reversible potentials of the four reactions listed are as follows:

$$\text{Oxygen Reduction: } E_r = 1.23 - 0.059\text{pH} - 0.015\log p_{\text{O}_2}$$

$$\text{Ferric Ion Reduction: } E_r = 0.77 + 0.059\log [a_{\text{Fe}^{3+}}/a_{\text{Fe}^{2+}}]$$

$$\text{Nitrate Reduction}^2: E_r = 0.96 + 0.015\log ([a_{\text{NO}_3^-}]/p_{\text{NO}}) - 0.059\text{pH}$$

$$\text{Peroxide Reduction: } E_r = 0.72 + 0.059\log [a_{\text{H}_2\text{O}_2}] - 0.059\text{pH}$$

From this list, it can be seen that the highest redox potential belongs to that of dissolved oxygen gas. Thus, a thermodynamic argument can be made that places the upper extreme for the open circuit potential of the waste package and drip shield as the reversible potential for dissolved oxygen gas reduction (for pH below 7). No other reducible species expected in the repository has higher reversible potentials.

Although dissolved oxygen gas has the most positive reversible potential, the kinetics are quite sluggish on almost all materials: this is a barrier for those attempting to develop fuel cells, but an advantage from a corrosion perspective. Platinum is known as a metal with fast electrochemical kinetics for a wide range of reactions. The open circuit potential of platinum is often used as a practical measure of the oxidizing power of the solution as it is assumed that it is poised at the redox potential of the most rapid reduction reaction, that is, it is implicitly assumed that the oxidation kinetics of platinum are much slower than the exchange current density of the redox reaction. Although such measurements are often sufficiently accurate in some laboratory solutions, this complication makes interpretation of the platinum open circuit potential as the highest open circuit potential possible for other electrodes ambiguous. Hoare has concluded based on a kinetic argument that platinum in oxygenated acid would reach the reversible potential for dissolved oxygen gas reduction in approximately 500 y (Hoare, 1975). For the elevated temperature and high salt concentrations expected in the repository conditions, the time might be expected to be longer as both the dissolved oxygen gas concentration will be lower (due to reduced dissolved oxygen gas solubility in solution) and the material surfaces are expected to be less catalytic than platinum. Further complications arise in natural waters. Measured values of potential on platinum in natural waters are well below (ca. 300-400 mV over a pH range of 2 to

10) the water potential for dissolved oxygen reduction (Gdowski, 2001). The open circuit potential measured on platinum in natural waters represents a mixed potential of the dissolved oxygen gas reduction reaction and the slow oxidation of platinum to PtO as well as any oxidizable solution species (*e.g.*, organic molecules). This situation leads to slow, upward drift in the open circuit potential as the platinum surface is slowly converted to PtO and the oxidizable species are depleted (if possible). Considerations of these scenarios and the implications on the passive current density for the engineering alloys under consideration for the drip shield and waste package should be encouraged

Imposing the thermodynamic boundary of the reversible potential for dissolved oxygen reduction as the highest open circuit potential for the waste package and the drip shield is likely to be extremely conservative. Platinum is well known to be a superior catalyst for most electrochemical reactions. Materials with oxide films have substantially slower kinetics. Nonetheless any argument for a lower extreme on the open circuit potential of the waste package and drip shield must involve kinetic arguments based upon the electrochemistry of the materials involved. For example, an upper extreme for the open circuit potential of carbon steel undergoing active corrosion could be obtained by combining the appropriate electrode kinetics of steel dissolution with the diffusion limited current densities for the reduction reactions listed above under the plausible environment extremes.

Effects of Microbial Activity on the Environment. Microbes are known to be present at Yucca Mountain (Horn and Meike, 1995; Davis, et al., 1998; Horn, et al., 2002), and they will undoubtedly be carried in during excavation, as well as during any ventilation period. Effects of microbial metabolism on metallic corrosion, via byproducts, physical occlusion of surfaces by their domiciles, and so forth, have been observed and are well documented (Dexter, 1986). The by-products of microbes can increase the rate of general corrosion as well as localized corrosion of metallic materials. In addition, the physical presence of microbial colonies and the structures they build can lead to crevice corrosion.

In order for microbes to have an effect, several criteria must be met: (a) the microbes must be present, (b) they must be viable (*i.e.*, have conditions under which they can reproduce), (c) their metabolism must either produce species that are deleterious to the material of interest or use species that are beneficial or required for corrosion protection, and (d) the effects of the metabolism must reach the material surface. In the case of Yucca Mountain, the relevant criteria to consider are (b) and (c); it is accepted that microbes could well be present or be introduced, and conservatism dictates that it be assumed that their effects reach the material surfaces, as there is no plan at present to limit or prevent such access.

Criterion (b) can be used to bound the times during which microbes could be active in the repository. To do so, it seems reasonable to consider the range of environmental conditions over which microbes are known to exist. Based upon the most hardy microbes currently known, the environment must provide condensed water, a food source, a sufficiently low temperature (less than 150°C), and a pH between 0 and 11 (Horn and Meike, 1995). Microbes are known to thrive in sulfuric acid concentrations as high as 10%, and salt concentrations of several moles per liter. Microbes are able to survive in natural oxidizing environments, but can themselves be oxidized at potentials achieved with oxidants such as peroxide.

Although ionizing radiation can also prevent microbes from being viable, the high radiation fields that are expected cannot be depended upon to keep the waste package environment or drifts sterile. As demonstrated by experience in Unit 2 of Three Mile Island (Hofstetter and Ausmus, 1989; Booth, 1987; Green, 2002; Pinhero, 2002), even high radiation fields (50,000

Rad/h) in water are insufficient to eliminate all microbes as long as there are nutrients and water present.

For the high-temperature operating mode, the temperature and relative humidity required for viability bound the viability of microbes to times greater than approximately 20 years (assuming 150°C max viability temperature) after emplacement on some canisters (MacKinnon, 2001). For the low-temperature operating mode, microbes would be viable at all times based upon the temperature and likely presence of water. The high concentration of salts will tend to inhibit the growth of microbes until further increases in humidity lead to less concentrated solutions. Nonetheless the presence of microbes cannot be excluded from consideration over the majority of the time period of interest.

With respect to corrosion of the waste package and drip shield in the proposed repository, analysis is required of the possible effects of the microbes on the corrosion of Alloy 22 and titanium Grade 7, as well as on the steel sets and rock bolts. Steel is known to be susceptible to a range of microbes, with sulfate reducers being the most documented (Dexter, 1996; Stoecker, 2001). The main effects for steel are increases in uniform corrosion rate and the appearance of pitting corrosion. Titanium alloys and nickel-based alloys of the Alloy 22 family are known to be much more resistant to all forms of corrosion, including microbial effects. Nonetheless immunity from microbial effects cannot be assumed. The Panel recommends that the Project reorient the major direction of its research on microbiologically-influenced corrosion from viability studies to investigations of the effects of microbial by-products on the corrosion of Alloy 22 and titanium Grade 7 under the range of plausible conditions of the environment on the waste packages.

5.2.2 Appropriate Corrosion Testing Environments

Understanding the parameters that control the environment allows an informed selection of testing environments for corrosion studies of the drip shield and waste package. Four aspects of the environment should be considered: temperature, chemical composition, potential, and type of exposure.

Temperature is one of the most important parameters to consider in the selection of corrosion testing environments. As discussed elsewhere in this report, temperature affects the passive corrosion rate, as well as the likelihood and severity of localized corrosion. The temperature range of the waste package in the repository is from approximately 180° to 25°C over the time horizon of interest. The Panel recommends that a range of environment temperature be tested, with a focus on temperatures above 100°C.

A great deal of discussion has focused on the appropriate chemical composition of the test solution. One approach would be to perform tests in the most aggressive solution plausibly expected. A saturated solution of a pure chloride salt (CaCl₂, NaCl, or MgCl₂) can exist at elevated temperature (up to 160°C for CaCl₂ at sea level) with high concentrations of chloride (greater than 10 M). This approach ignores the near certainty of the presence of a mixed salt solution under all temperature and relative humidity conditions and would thus be very conservative.

A second approach to test solution development is to use compositions based upon the waters expected at Yucca Mountain. In order to consider the effects of evaporative concentration, concentrated solutions based on the major ionic species measured in the various natural waters found at Yucca Mountain could be used. The addition of trace elements known to have potent

effects on corrosion processes and found to be present at Yucca Mountain can also be included. Trace elements to consider include lead, mercury, fluoride, and arsenic. In addition, the chemical effects of microbial activity can be assessed by additions of expected by-products.

The electrode potential under actual service conditions is controlled by the principle of the conservation of charge as applied to electrochemical reactions. Due to time-dependent changes in the electrode kinetics and chemistry, attempting to precisely define the open circuit potential of the engineered materials in the proposed repository is a daunting challenge. Using electronic devices, the potential of an interface can be poised at pre-selected levels and the electrochemical activity monitored. Extremes on the open circuit potential have been discussed above, and thus data from potentiostatic holds from a well-selected range of applied potentials could be of great use in evaluating the corrosion performance bounds of the engineered materials.

It is unlikely that the waste package will be fully immersed in several cm of solution. It is more likely that at different times, thin aqueous films, alternate immersion, and dripping water characterize the exposure. Although full immersion is the simplest form of corrosion test environment, there can be substantial differences in material behavior relative to the other exposure types, with alternate immersion or dripping being more severe in some cases. Care must be taken to select relevant exposure parameters, although it must be recognized that control of other parameters such as potential are more difficult in the alternate immersion and dripping test scenarios.

5.2.3 Modeling of the Chemistry

Modeling of the chemical composition of the water in contact with the engineered materials is an important component of the assessment effort. Modeling of the chemistry can allow insights to be gained concerning both plausible extreme conditions and kinetics. Geochemical modeling is well developed. Several software packages are available that can predict speciation, precipitation, and equilibrium distributions for a given set of input reactions and parameters. Nonetheless, many challenges remain. The procedures for dealing with elevated temperatures, concentrated solutions, and reactions involving some important species are still under development. Not only do the data required for such codes not exist, but also there are substantial challenges in measuring those parameters (*e.g.*, activity coefficients).

The use of geochemical reaction models to predict the chemical composition of water in contact with the engineered materials is important to the assessment effort. Such modeling helps define plausible extremes of the chemical environment and gives insight to the processes that might affect the engineered barrier.

Geochemical modeling as a field is well developed (Bethke, 1996): there is a variety of well documented and tested software available and a community of scientists experienced in this type of analysis. Modeling software typically predicts species distribution in solution and how it changes over the course of a reaction process, the effects of precipitation and dissolution reactions as well as microbial metabolism, the progress of kinetically controlled reactions, and the effects of varying temperature.

The models are currently capable of generating useful predictions, but their accuracy can be improved in certain respects. Most notably, there is need to establish better methods for predicting the activity coefficients for species in very concentrated solutions at temperatures well above 25°C. An effort to this end is currently underway at Lawrence Livermore National Laboratory.

Modeling of transient environments is not nearly as well developed as the modeling of equilibria. The coupling of the thermohydraulics of dripping and the resulting chemistry the transient evolution of the environment represents a massive technical challenge. It would be of interest for the Project to apply some of its expertise used in the thermohydraulic-chemical modeling in the unsaturated zone to the issue on the waste package.

5.3 ASSESSMENT OF PROJECT APPROACH TO TECHNICAL ISSUES

5.3.1 Plausible Extremes of Environments

Test Environments Currently Used. The Project staff has focused most of its corrosion work on five solution compositions that are all based on analyses of J-13 well water. These test solutions vary in pH, ionic strength and composition as shown in Table 2. Also included are the acronyms for the solutions that are used elsewhere in this report.

The Project's approach to testing environment determination has focused on the use of concentrated simulated waters based on analyses of J-13 well water. Evaporative concentration effects have been simulated by uniformly increasing concentrations of the species in the J-13 well water. In addition, solutions with substantially lower and higher pH than J-13 have been studied. Some corrosion work supported by the Project has also been performed in single salt solutions (concentrations up to 5 M). The majority of the work has been performed at temperatures below the boiling point of pure water at the elevation of Yucca Mountain (96°C). All of the data from the Long-Term Corrosion Test Facility has been generated in the solutions described in Table 2.

The Panel does not believe that these test environments are the most appropriate for assessing the corrosion performance of the engineered components. There is no evidence that they represent plausible extremes of the environments on the waste package and drip shield, particularly with regard to temperature.

In order to better define plausible extremes of the environments that develop on waste package and drip shield surfaces, the Project has initiated a coordinated evaporative concentration and evaporative drip corrosion program in which simulated waters are being dripped onto hot (90°C) Alloy 22 specimens. Analyses will be performed on the scales that form and the effects of this type of exposure on corrosion of the Alloy 22, both plate and welded plate. The Panel strongly recommends expanding this program to the more elevated temperatures (up to 180°C) that are characteristic of the expected waste package surface temperatures in order to develop a better understanding of the scale and chemistry development that is likely to occur.

Temperature, relative humidity, pressure combinations on waste package. A detailed analysis of the modeling of the temperature and relative humidity of the waste package and drip shield are outside the scope of this Panel Report. The Project is using thermal-hydraulic-chemical modeling for a range of scales (mountain, near field, drift) as critical inputs to the environment. In this report, the outputs of those models are assumed accurate, and only the effects of those results on the environment are discussed.

The two operating modes currently being considered lead to two significantly different time-temperature-relative humidity profiles. In both operating modes the temperature of the waste package begins to increase at the end of the ventilation period. For the high-temperature operating mode, the temperature rises to approximately 180°C within the first 100 years, falling to 80°C in the 1,000 to 2,000 year time period. During that first 100 years, the relative humidity

remains below 20%, rising to greater than 50% within several hundred years. The low-temperature operating mode is designed to keep the drift wall temperature below the boiling point. This operating mode leads to a maximum waste package surface temperature of 90°C (approximately 100 years after the end of ventilation). The relative humidity of the drift reaches a minimum of 30% at the same time as the maximum temperature. The relative humidity then rises as the temperature decreases, reaching 60% seven hundred years after the end of ventilation. It should be noted that a range of waste package temperature and relative humidity will exist throughout the repository due to the effects of the type of waste and the location of the waste package within the repository footprint. Again, this fact reinforces the need to develop information on defensible extremes for parameters.

To this point the Project staff has assumed that the pressure inside the repository is limited by the atmospheric pressure at elevation throughout the life of the repository (Gdowski, 2001). This assumption is certainly valid during the emplacement period and any ventilation period for the bulk drift environment, *i.e.*, the mountain breathes. It is important to investigate the possibility of pressure differences developing in local regions such as under or within mineral scales on the waste package from evaporative drying of waters. If such locally elevated pressures are possible, this condition might lead to the elevation of the local acid gas partial pressure that would, in turn, allow lower pH values to occur than would be the case in the nominal atmosphere.

5.3.2 Defining the Plausible Bounds of the Environment

Amounts and Sources of Water: The Project's approach to the amount of water available is quite conservative. No limitation on corrosion due to this limitation is assumed. Although the thermal-hydraulic-chemical models indicate that much of the infiltration water will be diverted around the drifts due to the presence of capillary barrier forces, the uncertainty inherent in such calculations prevents removing corrosion from consideration.

There is a large, ongoing effort to characterize the relevant waters at Yucca Mountain. This includes work to determine the complete chemical composition of and species present in the waters--perched water, groundwater, and water from the pores of the unsaturated zone--and a considerable effort to assess the accuracy and precision of the data, especially of trace elements. Measurements of trace elements such as lead and mercury are not only challenging analytically, but are also prone to contamination (such as lead in well water from lubricants used in the drilling process).

The chemical divides concept (Garrels, 1967; Eugster, 1978) allows solutions to be grouped into a finite series of chemically similar systems 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 Project has used the chemical divides approach as a guide for evaluating the plausible extremes of the chemical composition of the aqueous solutions that develop on the waste package. The Project approach is described in detail elsewhere (Rosenberg, 2001). These experiments have used solutions representative of J-13 well water (to represent perched water and groundwater) as well as pore water from the unsaturated zone. The evaporation has been done at temperatures below boiling (75-85 C). The results of these experiments agreed with the predictions from the chemical divides principle. When evaporated, the J-13 water evolved into an alkaline Na-HCO₃-CO₃-NO₃ concentrated solution (a brine). The unsaturated zone pore water composition evolved into a near neutral (pH 5.5) Na-Mg-SO₄-Cl-NO₃ brine. The relative

amounts of sodium, magnesium, sulfate, and chloride are a strong function of the starting composition of the water before evaporation. The main conclusion of relevance from their analyses is that the solutions on the waste package will evolve into either an alkaline solution (pH ca. 11-12) containing high concentrations of sulfate, carbonate, nitrate, and chloride, or a near-neutral solution (pH ca. 6) containing high concentrations of chloride and nitrate with or without sulfate.

The implications from the Project staff's analyses are consistent with the current state of knowledge in the field, and include the following:

- i. 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 Yucca Mountain (96 C). According to the Project, the most extreme plausible case is the formation of a CaCl_2 solution at 140 C/35% RH.³
- ii. 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.
- iii. 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_3) would need to be maintained at pressures well above those attainable in the mountain in order to maintain the pH of the solutions at low values.

The Project staff has noted that it is aware of several caveats with respect to the analyses described above. These caveats include seven effects that have not been considered quantitatively to date, namely: (a) the effects of deposited dust or particulates, (b) the effects of an adherent, porous deposit or scale on the waste package, (c) metal-to-metal crevices, (d) interactions between the environment and the waste package, (e) radiation effects on the environment, (f) bounding on the types and amounts of trace elements, and the (g) effects of microbes.

Scenarios for Aqueous Environment Development: Condensation Forming Moist Dust: Although little analysis has been done on the subject, the Project's current thinking is that the moist dust condition is less aggressive than either the wet scale/deposit condition or the metal-to-metal crevice condition. This conclusion remains to be demonstrated. The quantitative analyses now underway on the chemistry, deposition rate, and corrosion effects on the chemistry of the environment of deposited dust or particulates (from, for example, excavation, and entrainment during the proposed ventilation period) need to be assessed. Any influence on the buffering capacity or buffering point of the environment should be investigated as well as the amount of dust expected and its chemical composition. The Panel recommends that the effective deliquescence point of these dusts be determined in order provide input to the TSPA with regard to temperature/RH combinations that result in aqueous environments.

Dripping Forming Porous Scales: The effects of the presence of an adherent, porous deposit or scale on the temperature of the waste package have not been rigorously evaluated to date. The Project staff has recognized that water chemistry will change at scale and deposits on metal

surfaces, but has produced limited experimental data and analysis. The Project is currently extending its evaporative concentration work to dripping studies in which relevant waters are dripped onto high temperature material surfaces. Some initial calculations on the effect of scales on the temperature of the waste package have indicated that such changes are small. The Panel recommends that the effects of this water/hot metal surface interaction on both the solution composition and the corrosion of engineered materials be evaluated for the relevant range of starting solution compositions. The goal is to provide information on both the nature of the deposits that form and the type and rate of corrosion underneath the deposits. This program should be expanded and have higher priority than the lower temperature studies.

Metal-to-Metal Crevices: The Project staff has recognized the changes in water chemistry associated with crevices, but only limited experimental data have been acquired and limited analyses performed to date. The Panel recommends that these studies be expanded to include the higher temperatures and plausible aqueous compositional extremes characterized elsewhere. In particular, studies of the pH changes that can occur within metal-metal crevices filled with YM wet rock dust would be of use. Polarization of such specimens to elevated potential at elevated temperature would allow a quantitative determination of the effective buffering ability of the rock dust. This buffering would act to prevent the formation of stable crevice corrosion.

Interactions between the environment and the waste package: To date the Project has not investigated the effects of metal dissolution products and interactions with waste package on the environment. Plans have been drafted to do so, and these should be encouraged. Both modeling and experimental work will be required to make a full assessment of these effects.

To date little work has been done by Project staff focused on identification or characterization of the cathodic reactions of relevance in the environment. The majority of the electrochemical characterization has focused on the anodic kinetics of Alloy 22 and titanium Grade 7 in a wide variety of testing solutions based on the natural waters at temperatures below boiling. The Panel recommends kinetic studies of the relevant reduction reactions in an effort to investigate the existence of a kinetic bound to the OCP of Alloy 22 and titanium Grade 7. These studies should be conducted in the solutions that represent plausible extremes of the aqueous environment including trace elements and the expected products of radiation (*e.g.*, nitrate, peroxide).

Radiation: It has been difficult to determine the expected radiation levels at the waste package surface due to changes in waste package design and the effects of different operating modes. Such information is required to determine the extent to which radiolysis will occur in the water near the waste package surface, leading to the formation of peroxide. The peroxide would tend to increase the potential of the waste package and, therefore, can be of importance in the corrosion processes on the waste package. The assessment must also consider the temperature stability of the peroxide as the highest radiation levels will occur during the times of highest temperature. According to current Project analyses, by the time there is condensed water present, the gamma flux has decayed by a factor of 100 or more to approximately 1-10 R/hr. Most tests to determine shifts in oxidizing potential have been measured at much higher fluxes, *e.g.*, 10^6 R/hr. However, the Project has looked at radiolysis of moist air that will be present during the first 300-500 yrs (Reed and Van Konynenburg). With the high nitrogen concentration present in the air, nitric acid is produced. Nitric acid is also strong oxidizer, but there's little water for the nitric acid to alter at these early times due to the high temperatures. What has not been considered is the situation in which the deposited dust and salts lower the effective deliquescence so that nitric acid is produced at a time when an aqueous environment is present. The Panel recommends that the influence of radiation on the environment be considered for such conditions.

Effects of Microbes: Preliminary studies of the effects of radiation on microbe viability have been performed, demonstrating that a total dose of 3 MRad will kill bacteria present that were grown from inoculation of J-13 water with Yucca Mountain rock. This dose level is that used for sterilizing surgical instruments, so the result is not surprising. The Project considers it a first step in the assessment of the effects of radiation on the microbes. It will need to be coupled with the radiation and thermal/humidity calculations to determine over what time periods the waste package surface is likely to be sterile because either the radiation field or temperature is too high, or there is an absence of condensed water. The Panel recommends a change in approach. Commercial experience at Three Mile Island and elsewhere has shown that sufficient microbes can survive high fields that given nutrients and water, the development of microbial colonies is possible. Relying on the radiation to sterilize the drift seems non-conservative. Instead, the temperature and water availability requirements of microbes should be established.

The effects of microbe metabolism on the corrosion of the waste package and drip shield are currently underway. Materials of interest have been exposed to synthetic groundwater solutions containing bacteria cultivated from Yucca Mountain tuff and sterilized controls. In addition, limited studies have been performed with bacteria thought to be potentially more aggressive (a strain of *Thiobacillus ferrooxidans* that is known to oxidize both reduced sulfur species and iron.

Several conclusions have been drawn by the Project from these studies: (a) growth of microbe colonies from Yucca Mountain rock in J-13 water is possible, (b) these microbes require condensed water, (c) the Yucca Mountain microbes appear to increase the passive current density of Alloy 22 by a factor of 2 (based on electrochemical measurements), (d) the *T. ferrooxidans* bacterium had no measurable effect on Alloy 22, but seemed to increase the passive dissolution of titanium Grade 7, and (e) a total dose of 3 Mrad is sufficient to sterilize the tuff.

The Panel recommends a focus on the influence of microbial by-products on localized corrosion. Rather than the use of a simple "rate enhancement factor" of two for uniform, passive dissolution, determination of the effects of microbes on the localized performance bounds of Alloy 22 should be the emphasis of the MIC studies. The question that needs to be answered is: Do the presence of microbes or their by-products tend to increase the likelihood of stable crevice corrosion? Studies of viability should focus on the needs for water and the conditions under which the proteins in the cell walls denature.

5.3.3 Validation of Modeling of Chemistry

To date, the validations of the modeling of the waste package environment chemistry have been primarily qualitative (*e.g.*, comparison of results of evaporation experiments with the predictions of the chemical divides principle). Some quantitative comparisons have been made between these experiments and the results of calculations of the in-drift chemical environment using their precipitate/salt model (Civilian Radioactive Waste Management System Management and Operating Contractor, 2001). For the limited data available at that time, the agreement was excellent.

Further comparisons and progress on predictions and measurements under elevated temperature should be encouraged. In addition, means to computationally address the possible effects of microbes on the chemical environment would be extremely useful.

5.4 CONCLUSIONS AND RECOMMENDATIONS

The Panel recommends that the Project undertake a comprehensive experimental and analytical modeling program for all three environmental conditions discussed above: moist dust, mineral scale and deposits, and crevice areas at metal-to-metal contact surfaces.

1. **Moist dust:** The Panel recommends that the effective deliquescence point of these dusts be determined in order provide input to the TSPA with regard to temperature/RH combinations that result in aqueous environments. Chemical and physical property studies of dust, particulates, and entrained matter have begun and are needed. In addition, measurement of likely dust and entrained material deposition rates are underway and need to be extended. The soluble ion content and effects on buffering capacity of these deposits are also needed to determine the extent to which they will affect the environment on the engineered materials. In addition, the Panel recommends that the influence of radiation on the environment be considered for the situation in which the deposited dust and salts lower the effective deliquescence so that nitric acid is produced at a time when an aqueous environment is present.
2. **Mineral scales and deposits:** The Panel strongly recommends expanding the dripping water program to the more elevated temperatures (up to 180 C) that are characteristic of the expected waste package surface temperatures in order to develop a better understanding of the scale and chemistry development that is likely to occur. Related work on steel should also be performed as the steel sets, and other steel structures are expected to last up to 300 years (*i.e.*, during the monitoring phase).
3. **Crevice areas:** Studies of the pH changes that can occur within metal-metal crevices filled with YM wet rock dust would be of broad use. Polarization of such specimens to elevated potential at elevated temperature would allow a quantitative determination of the effective buffering ability of the rock dust. This buffering would act to prevent the formation of stable crevice corrosion.

In addition, the Panel further recommends:

4. Studies and analyses to determine the plausible extremes of the waste package environment should continue with the following foci: (a) experimentally probe the relative effects of transient and steady state environments on the corrosion of the engineered barrier materials, (b) environments formed under higher temperature conditions in the presence of mixtures of salts.
5. The Panel recommends that the Project reorient the major direction of its research on MIC from viability studies to investigations of the effects of microbial by-products on the corrosion of Alloy 22 and titanium Grade 7 under the range of plausible conditions of the environment.
6. The Panel recommends the formation of a task group of technical experts in corrosion, materials science, geochemistry, and hydrology to work on both the experimental determination and analytical modeling of the environment. Integration across disciplines is vital in this area of inquiry.

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6. MATERIALS: METALLURGICAL STABILITY

6.1 SUMMARY OF ISSUES

There are three processes that can affect the metallurgical stability of Alloy 22. These are: 1) precipitation of intermetallic phases (Raghavan et al. 1982, Cieslak, et al., 1986), 2) ordering of the nickel and solute atoms to have specific locations on the crystal lattice (Raghavan et al., 1982, Tawancy, 1981, Hodge et al., 1993, Rebak and Koon, 1998), and 3) enrichment of impurity atoms such as sulfur and phosphorus at crystal boundaries and free surfaces. (Berkowitz and Kane, 1980, Briant, 1988). The presence of intermetallic phases and grain boundary segregation can alter the corrosion and mechanical performance of Alloy 22 (Heubner et al., 1989), lattice ordering can enhance hydrogen-induced cracking (Sridhar, et al., 1980) and surface enrichment of sulfur can degrade passivity. Each of these processes is thermally activated and can be described by the appropriate kinetic equations to predict reaction rates as a function of temperature and time. While these metallurgical processes are very slow at proposed repository conditions, it must be demonstrated they will not occur during the life of the repository or they will not significantly affect the canister performance.

Intergranular corrosion (IGC) and intergranular stress-corrosion (IGSCC) result when the grain boundary microchemistry differs from the surrounding alloy. Grain boundary microchemistry changes result from: 1) precipitation of an electrochemically active phase, 2) depletion of passive film forming elements adjacent to the grain boundary and 3) enrichment of impurities that either alter the passive film stability or are more electrochemically active than the surrounding material. Each of these processes can produce a microchemistry that renders the grain boundary more electrochemically active than the surrounding material such that preferred or localized corrosion

occurs along the grain boundaries. The corrosion penetration rates for IGC can then be substantially greater than the general corrosion rate of the alloy. Intergranular corrosion can occur in the absence of stress but usually requires more severe corrosion conditions than does IGSCC. However, the susceptibility of an alloy to IGSCC is often tested by a corrosion test for IGC. A grain boundary phase could contribute to IGC and IGSCC by being more electrochemically active than the surrounding material and also by establishing a galvanic couple with the matrix. Because the compounds that precipitate in an alloy have a different composition than the alloy, they will establish a galvanic couple with the surrounding material. Also, it is possible that the precipitate has a higher corrosion rate than the surrounding material such that the grain boundary becomes the preferred corrosion path. Depletion of passive film forming elements adjacent to the grain boundaries, such as chromium in sensitized austenitic stainless steels (Jones et al. 2000) can also lead to IGC. The lower concentration of the passive film forming element leads to a less passive film in the region adjacent to the grain boundary and to accelerated IGC and IGSCC. Enrichment of certain impurities can also cause the grain boundary to be more electrochemically active. This occurs when the impurity is sufficiently enriched in the grain boundary to alter the local properties. Grain boundary impurities can alter the passive film stability as observed for sulfur in nickel or can induce IGC if they are more electrochemically active than the surrounding material as observed for phosphorus in nickel (Jones et al., 1985, 1988).

Alloy 22 can be solution treated and quenched to produce a single-phase, face-centered cubic structure. At temperatures below the solvus temperature, the equilibrium structure is a mixture of the face-centered cubic and several intermetallic phases, P, μ and σ . The precipitation of these phases at grain boundaries can alter the corrosion behavior because of their difference in chemistry from the matrix and by the depletion of chromium and possibly molybdenum adjacent to the grain boundary. This denuded zone occurs during precipitation and is "healed" once precipitation is complete. As such, a denuded or alloy depleted zone is more likely at short aging times than after long aging times. Because the P, μ and σ contain high concentrations of chromium and molybdenum their passive films should be as stable as those of the alloy. These phases are also not expected to exert a strong galvanic couple with the matrix because their compositions are not too dissimilar than the alloy. Therefore, the greatest possible effect of grain boundary precipitation on IGC and IGSCC is if a chromium or molybdenum denuded zone develops.

The P, μ and σ phases are brittle compounds, so their fracture strength can be less than the alloy. Grain boundaries with significant quantities of precipitation act as low energy paths for fracture. This process lowers the fracture strength of the alloy and the mechanical performance of Alloy 22 when significant grain boundary precipitation occurs. Precipitation may occur in the waste canister material in the following ways: 1) as a result of improper solution treating and quenching conditions of the canister following fabrication, 2) in the heat affected zone of the weld, 3) in the weld filler metal, 4) in the induction heated zone during stress modification, and 5) from long time aging at repository temperatures.

Weld filler metal will have a different microstructure and microchemistry than the base metal and heat affected zone (HAZ) adjacent to the weld. It will contain the face-centered-cubic matrix phase with σ and P precipitated in the interdendritic regions of the solidified weld (as cast) filler metal. Molybdenum segregation will occur during solidification with concentrations as high as 20% within the interdendritic region. Some of these microchemistry inhomogeneities will be eliminated by the the solution treatment given the entire canister prior to being loaded and the

closure welds being made and the induction heating cycle used to mitigate the stress on the outer weld surface. The metallurgical stability of the weld filler metal may differ from the base material if: 1) the interdendritic segregation persists and 2) if the precipitates are not dissolved following the solution treatments. The kinetics of growth of pre-existing precipitates will be different than precipitation from solid solution.

The ordering of nickel and solvent atoms on the crystal lattice can occur at temperatures of 500 C and below. This process occurs slowly in nickel-chromium-molybdenum alloys but Sridhar, et al., 1980 noted that cold work accelerates the formation rate. Long range ordering (LRO) has been proposed as a mechanism in the stress corrosion cracking of nickel alloys used in the presence of reduced hydrogen, such as in oil and gas wells containing H₂S. Lattice ordering alters the susceptibility to hydrogen-induced cracking by altering the deformation characteristics of the alloy. Under current plans, the waste canister will be solution annealed and quenched following rolling and welding. In addition, the final closure welds will have their surface stresses modified by laser peening and induction heating and quenching. These processes are intended to induce a compressive stress on the surface. However, it is also possible that material adjacent to the induction heated and quenched surfaces will be deformed during quenching because of the difference in contraction between the hot and cold sections of the canister. Therefore, the effects of cold work on long range ordering kinetics are important because LRO could occur in this deformed material in a shorter time than in the remainder of the canister material.

Grain boundary segregation of impurities, such as sulfur and phosphorus, has been demonstrated in a number of metallic alloys including many nickel- and iron-based alloys. This segregation is an equilibrium process with a chemical driving force that involves a decreased grain boundary and bulk chemical energies. These elements can enhance the IGC rate, the IGSCC rate, both from anodic dissolution and hydrogen-induced cracking processes, and lower the fracture toughness of the material. Segregation is time and temperature dependent with enrichment ratios, the ratio between the grain boundary and bulk composition at equilibrium, increasing with decreasing temperature. The kinetics of segregation are controlled by atomic diffusion such that the segregation rate decreases with decreasing temperature. Enrichment ratios as high as 10⁶ have been measured for some elements, for example, sulfur in nickel. A sulfur concentration of 400 ppm (maximum specified for Alloy 22), could result in a grain boundary concentration of 100% or one monolayer of pure sulfur with an enrichment ratio of 10⁶. This is not likely in an alloy since alloying elements reduce the chemical activity of sulfur, but there is still a significant chemical driving force for segregation such that it must be evaluated.

Impurities can also enrich on free surfaces of nickel-base alloys by thermal segregation (Burton et al., 1979) and anodic dissolution (Danielson and Baer, 1989, Baer and Danielson, 1987). It has been shown by Danielson and Baer (1989, 1987) that sulfur enrichment on the surface of nickel severely degrades the passivity of nickel in acid solutions. The kinetics for thermally activated segregation to the free surface exceed that to the grain boundaries. If sulfur and phosphorus degrade the passive film of Alloy 22 similar to that observed with nickel, it could be of greater concern than segregation to grain boundaries. For instance, an alloy with 100 ppm of sulfur corroding at 1 μm/yr will accumulate a monolayer of sulfur on the surface in 500 years if 100% of the sulfur atoms are retained at the surface. Danielson and Baer (1989, 1987) found that a monolayer or less was sufficient to degrade the passive film of nickel. The key uncertainty is whether a similar effect will occur in Alloy 22 that forms a chromium rich passive film that is more stable than the NiO film that forms on nickel.

Briant and Kuthra (1988, 1986) also noted that segregation of sulfur to the interface between a surface oxide and the metal substrate in nickel-base alloys induced spallation of the oxide upon cooling to room temperature. The segregation occurred at 800 to 1100 C which are very high temperatures relative to that expected for the waste repository. Briant, however, has noted that surface segregation still occurs at much lower temperatures, even though the process is considerably more sluggish and complex than at higher temperatures. It is not obvious whether this process will occur in Alloy 22 at temperatures below 200 C and, if it does, whether it could be more severe than enrichment by anodic dissolution and breakdown of the passive film, mentioned above.

6.2 ASSESSMENT OF CURRENT PROJECT DATA AND ANALYSIS TO SUPPORT LONG-TERM PERFORMANCE PROJECTIONS

The Project is focusing on developing the necessary models to predict the precipitation and ordering in Alloy 22 as a function of repository relevant times and temperatures. The Project is making experimental measurements of precipitation using materials aged for extended periods (up to 40,000 hours at 260, 343, and 427 C) at Haynes Alloys. These materials have been shared with the Project and they serve as an excellent source of aged material. The extent of precipitation is being measured primarily by scanning electron microscopy (SEM) and some by transmission electron microscopy (TEM) analysis, with an emphasis on grain boundary precipitation. Phase identification is being done by TEM with P, μ , σ , carbide and $\text{Ni}_2(\text{Cr},\text{Mo})$. Comparison between measurements and models is being made primarily with the SEM analysis for the start of grain boundary precipitation and for complete coverage of grain boundaries with precipitates. A general nucleation and growth kinetics model is being used and the parameters defined using the experimental data. With the assumption that no change in the precipitation mechanism, Project staff is using the model to extrapolate precipitation kinetics at lower temperatures. Extrapolation using the best fit to the current data at four temperatures shows that it will take more than 10,000 years for full grain boundary coverage at 300 C, based on the best fit of the data (DOE report, December 2000). Using the minimum slope within the uncertainty error bars of the data, extrapolation predicts full coverage following only 100 years at 300 C. Examination of welded samples is also in progress and extrapolations based on the observed phase volume fraction following welding and the kinetic growth model also gives a prediction that full grain boundary coverage will either occur in more than 10,000 years, based on the best fit to the data or less than 1,000 years at 300 C based on the minimum slope. More data and smaller uncertainty is needed to improve the confidence in the kinetic analysis. The Project staff is continuing to collect more data and to reduce the uncertainty so that it is expected that this short-coming will be overcome.

Alternate methods to microscopy have been used by the Project to estimate the extent of precipitation as a function of temperature and time. Fracture toughness, as measured by charpy tests, has been used on the basis that grain boundary precipitation of the intermetallic phases at grain boundaries embrittles the material (DOE report, June 2001). The presence of grain boundary phases alters the corrosion properties of Alloy 22 and this affect was also used by the Project to estimate the kinetics of grain boundary precipitation (DOE report, June 2001). The ASTM G28A test was used for this estimation. When this data is used to extrapolate to 10,000 years, both sets of data show that it will take longer than 10,000 years to achieve full grain boundary coverage at 300 C. However, the concern with this approach is the method used for

converting from charpy and corrosion data to the kinetic model. This was done by assuming a change in the charpy energy from 264 to 150 ft-lb and an increase in the corrosion rate from 0.8 to 2.03 mm/yr corresponds to full grain boundary coverage. The times at each temperature to achieve these changes is then plotted as a function of $1/T$ and a curve fitted to this data is extrapolated. This approach assumes only grain boundary precipitation is contributing to the change in charpy energy and corrosion rate. However, this was not proven. For these alternate approaches to be used, the Project must correlate the charpy energy and corrosion rate to the extent of grain boundary precipitation.

The kinetics of ordering reactions in Alloy 22 is being treated by the Project in a manner very similar to that of precipitation. The sluggishness of the ordering kinetics is a significant hindrance to obtaining sufficient data for a high confidence extrapolation to 10,000 years. Very small ordered domains have been observed by TEM but the volume fraction was difficult to measure. Therefore, some bounding arguments have been used to establish the extrapolation to 10,000 years. The results show that LRO will form in 10,000 years at 270 to 300 C.

The Project has assumed that the most deleterious affect on corrosion and mechanical properties is associated with complete grain boundary coverage. However, this has not been demonstrated, especially for corrosion and stress corrosion. The depletion of passive film forming elements such as chromium and molybdenum adjacent to the grain boundary will occur long before complete grain boundary coverage. In fact, this depletion is a transient phenomenon that will be eliminated with longer aging times and could be eliminated by the time complete grain boundary coverage is achieved. Depletion of these elements could lead to IGC and IGSCC as observed in 300 series stainless steels where sensitization is the result of chromium depletion during grain boundary carbide precipitation.

The Project has chosen not to evaluate either grain boundary or surface segregation effects. While the kinetics of thermally activated segregation will be very slow at repository temperatures, the potential effects of segregation, should it occur, are significant. Also, surface enrichment during anodic dissolution does not require much corrosion and is again potentially very significant should impurities such as sulfur degrade the passive film.

6.3 APPROACH, ANALYSIS, METHODS AND PLANS TO SUPPORT LONG TERM PERFORMANCE PROJECTIONS

6.3.1 Precipitation

The current effort by the Project to measure the grain boundary precipitation kinetics is progressing in the correct direction and has an excellent source of material aged to long periods of time. There are several areas where improvement is needed so that these extrapolations will have the desired confidence. The Panel recommends that the Project extend their current work to include the following:

1. Determine if chromium and molybdenum depletion occurs adjacent to the grain boundaries and if so determine the time and temperature relationship for this depletion and the impact of this depletion on corrosion and stress corrosion cracking. This effort is important because this depletion, if it occurs, will happen at shorter times than is required to form "fully covered grain boundaries". Therefore, experiments to measure the effects of aging on corrosion and stress corrosion using samples with "fully covered grain

boundaries" may not be the most severe condition since the depletion of elements that stabilize the passive film such as chromium and molybdenum, can lead to IGC and IGSCC. Intergranular corrosion may also occur as a result of grain boundary precipitates, although depletion of chromium could induce substantially greater IGC rates. Sensitized stainless steels is a case where the carbides that precipitate at grain boundaries do not contribute to IGC but their precipitation causes depletion of chromium adjacent to the grain boundaries that does induce IGC. Brossia et al. (2001) have noted IGC in crevice corrosion tests of Alloy 22 after 5 minutes of aging at 827 C. However, predictions made by the Project staff show that there would be less than 1% of the total grain boundary P phase at the grain boundary following this treatment. Clearly, complete grain boundary precipitation is not needed to induce IGC.

2. Demonstrate that the correct model is being utilized to extrapolate the data and that there is a fundamental understanding that the precipitation mechanism is the same at low temperatures as the higher temperatures where the parameters for the model are being determined. Of course, verification of the model and precipitation mechanism could be accomplished with the same analysis if this could be done at the repository temperature. But since this is not feasible, it is necessary to demonstrate the model with aging treatments at temperatures above the repository temperature. Verification that the precipitation mechanism is the same at repository temperatures as at the higher evaluation temperatures could be done with experimental or theoretical phase diagrams.
3. Identify critical volume fractions of grain boundary precipitation necessary to affect corrosion and mechanical properties and determine the time, temperature relationship for each of these critical volume fractions rather using than the more arbitrary approach of designating "starting precipitation" and "fully covered grain boundaries". The current definitions do not relate to any specific failure process, for example, loss of fracture toughness.
4. Calibrate the alternative grain boundary precipitation measurement methods used, i.e. charpy impact and corrosion, to the extent of grain boundary precipitation.

6.3.2 Ordering Reactions

The current approach used by the Project to determine the time and temperature dependence of the order reaction is similar to that used for precipitation. Ordering has been observed but only after 30,000 hours at 427 C and shorter time at higher temperatures. However, current model extrapolations for LRO indicate that it will form after 10,000 years at 270 to 300 C. The Panel recommends that this effort be given equal importance to that for precipitation because of the implications of ordering to stress corrosion cracking. The effects of deformation on LRO formation kinetics needs to be measured because it is known that deformation accelerates the LRO formation rate and that there will be residual deformation following the induction heating and quenching treatment.

6.3.3 Impurity Segregation

The Project currently has no effort to evaluate grain boundary segregation and its effects on corrosion and stress corrosion cracking. Evidence exists in many materials that segregation of impurities such as sulfur and phosphorus to grain boundaries increases the IGSCC rates,

including hydrogen-induced crack growth, and decreases the fracture toughness of materials. There is evidence for phosphorus segregation occurring in other nickel-based alloys, such as C-276, and some propose that it contributes to hydrogen-induced crack growth. It is necessary to develop the models to (a) predict the grain boundary chemistry as a function of time and temperature and (b) demonstrate whether the levels of grain boundary impurities that can be achieved in repository lifetimes can alter the corrosion and stress corrosion performance of the material (See C. Briant summary in Vol. 2). There are kinetic models that can be utilized for the preliminary predictions to determine if grain boundary segregation is likely to be an issue. Specifically, the Panel recommends that Project staff: 1) measure the effects of sulfur on passive film stability in relevant repository environments; 2) model and/or measure the rate of sulfur accumulation on the surface as a function of corrosion rate, if sulfur affects the passive film stability; and 3) evaluate the potential for grain boundary impurity segregation as a function of time and temperature and in the heat affected zone (HAZ) .

6.3.4 Grain Growth

The Project currently has no effort to evaluate the grain size as a function of temperature and time. The mechanical properties of a material are a function of the grain size, such as the well known Hall-Petch relationship, between grain size and yield strength. The Panel recommends that alloys available from Haynes be used to develop a relationship between grain size and time and temperature.

6.3.5 Alloy Specification

The Project currently has no effort to define the alloy composition within the bounds of the commercially available Alloy 22 composition. This is a concern because some elements have a sufficiently wide range of allowance that alloy stability and corrosion behavior may vary significantly from one heat of material to the next (See S. Floreen summary-Vol2). For example, iron ranges from 2 to 6 % in the Alloy 22 specification. Similarly, impurities such as sulfur and phosphorus that segregate to grain boundaries have a specified maximum of 0.02 wt% (200 wt ppm or about 400 at. ppm) while carbon a specified maximum of 0.015 wt% . Carbide precipitation is possible in Alloy 22 so higher carbon concentrations could lead to grain boundary carbide precipitation and further sensitization of the alloy. The Panel recommends the following:

- That a program heat of material with desired levels of elements within the alloy specification be procured. This must be a sufficiently large heat of material to allow it to be included in all aspects of the program. This is recommended since the current measurements are being made on a variety of heats of material. If there are heat-to-heat variations, the current program results may not correctly predict the behavior for any random heat of material.
- That some evaluation be conducted to determine the effect of variations in critical elements such as iron, phosphorus, sulfur and carbon. This may not need to be a full matrix of tests but needs to be sufficiently robust to be convincing.

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7. LONG-TERM UNIFORM CORROSION OF PASSIVE METALS

7.1 ISSUES OF IMPORTANCE TO THE UNIFORM CORROSION RESISTANCE OF ALLOY 22

The generally excellent resistance of Alloy 22 to uniform corrosion is entirely due to the protective nature of its passive film. Even though this uniform corrosion resistance is expected to persist for thousands of years, the passive film itself is amazingly thin.

Four major topics relate to the long-term uniform corrosion of Alloy 22: (1) the structure and composition of the passive film formed on Alloy 22 in aqueous solutions, (2) the uniform corrosion of Alloy 22 in the passive state, (3) the uniform corrosion of Alloy 22 in the transpassive state, and (4) measurement of the uniform corrosion rate of Alloy 22. These topics are covered in depth by Devine in the Compilation of Special Topic Reports. In this section, the Project's approach to these topics are reviewed and assessed and recommendations are made.

7.2 PROJECT'S APPROACH TO LONG-TERM UNIFORM CORROSION

7.2.1 Structure and Composition of the Films Formed on Alloy 22

The Project is using a number of characterization tools to investigate the structure, composition, and thickness of the passive films formed on Alloy 22 immersed in aqueous solutions and the oxide films formed on Alloy 22 during high temperature oxidation in air. Work is underway at the University of Western Ontario (UWO), General Electric's Corporate Research and Development Center (GECRD) and the Lawrence Livermore National Laboratory (LLNL).

One major objective of the research is to understand the time evolution of the composition and structure of Alloy 22's passive film. A brief description of the key results obtained to date at LLNL, GECRD and UWO are presented below.

At UWO, Shoesmith and colleagues are investigating the passive films formed on Alloy 22 in SCW (pH neutral) and BSW (pH 13). Samples of Alloy 22 are pre-conditioned by either (1) two weeks in air, (2) four weeks in air at 200°C or (3) four weeks in water-saturated air at 100°C. Results have been reported on TOF-SIMS used to determine the distribution of chromium, nickel and molybdenum within the passive film and to measure the thickness of the passive film formed in 1M NaCl + 0.1M H₂SO₄ (pH=1). TOF-SIMS is complemented by XPS, which identifies the oxidation states of the species in the films. TOF-SIMS indicate there is a bi-layered passive film formed on Alloy 22 in acidic chloride. The inner layer is Cr/Ni rich and the outer layer is Cr/Mo rich. The XPS analysis indicates the chromium concentration of the passive film of Alloy 22, as well as the thickness of the entire passive film, increase with applied potential (air formed film = 18Å, 29% Cr₂O₃-60NiO-11MoO₃; 200 mV = 20Å, 43Cr₂O₃-47NiO-10 MoO₃; 500 mV = 23Å, 56 Cr₂O₃-32NiO-12 MoO₃; 700 mV = 28Å, Cr₂O₃-25NiO-12 MoO₃). The inner chromium oxide layer is the key component of the film, which produces low passive corrosion rates. The continuous chromium enrichment of the inner barrier layer is held responsible for the long times required to reach steady state.

At GECRD, XPS was used to investigate the time dependency of the overall composition of the passive film of Alloy 22 in 2800xJ-13 (pH=12.2). The passive film formed on Alloy 22 immersed for two months in 2800 x J-13 (pH 12.2) at 95°C was 50Å thick. Analysis of the film's composition by XPS indicated the sample was covered by a silicate deposit that increased in

thickness with time over the two month long test period. This investigation did not determine if the passive film was layered. Nevertheless, the analysis indicates that after one month of immersion the film that lay underneath the silicate deposit was enriched in chromium and molybdenum with respect to nickel. This film composition is consistent with the film compositions reported for the passive films formed in borate buffer on Ni-Cr (Boudin et al.), Ni-Cr-Fe (Boudin et al., Lorang et al.) and Ni-Cr-Mo (Lloyd et al., Lorang et al.) alloys. The films formed on Ni-Cr, Ni-Cr-Fe and Ni-Cr-Mo were layered.

The oxide film formed on Alloy 22 during high temperature oxidation in air and the passive film formed on Alloy 22 in SCW (pH=8) at 90°C were investigated at LLNL using cross-sectional TEM, EDS and XPS.

The results indicate the oxide film formed on Alloy 22 during dry oxidation at 550°C/10,000 hrs. consisted of three layers: an inner layer that is rich in chromium, a middle layer that is rich in iron, and an outer layer that is rich in nickel. The overall thickness of the film was 500 Å.

The tri-layered oxide film formed at 550°C/10,000 hrs., in particular the presence of an intermediate layer of iron oxide, resembles the passive film that forms on Inconel 600 in neutral pH solutions (Boudin et al.). The relatively high concentration of iron in Inconel 600 helps to account for the presence of the intermediate, iron-rich layer. An Fe-rich intermediate layer was not detected in the passive film formed on Alloy 22 in an acidic aqueous solution (Lloyd et al.). The relatively high diffusivity of iron through chromium oxide at 550°C might explain the presence of an iron-rich layer in the film formed at 550°C, even though Alloy 22 contains only \approx 1% iron, and the absence of this layer in the passive film that forms at 90°C.

The chromium-rich inner layer and nickel-rich outer layer in the tri-layered oxide film formed on Alloy 22 in air at 550°C are similar to the inner and outer layers of the passive film formed on Alloy C 4 in neutral pH 0.5M NaCl. However, the passive film of C4 in 0.5M NaCl is bi-layered, as is the passive film of Alloy 22 in acidic chloride. The bi-layered passive films formed on Ni-Cr-Mo alloys are in contrast to the trilayered passive films formed on Ni-Cr-Fe alloys in aqueous solutions and the trilayered oxide film formed on Alloy 22 in air at 550°C. The intermediate layer in all cases is an iron rich oxide. While small concentrations of iron in a Ni-Cr alloy can result in a film with an intermediate, iron-rich layer, the presence of relatively large concentrations of molybdenum does not result in the formation of an intermediate molybdenum rich layer in either thermally formed oxides or passive films.

The similarities of the high temperature oxide films and the aqueous passive films of Alloy 22 suggest that the uniform corrosion resistance of Alloy 22 that is covered with a thermal oxide film will be similar to the uniform corrosion resistance of Alloy 22 that is protected by a passive film that was formed in the aqueous solution. The specific effect of the intermediate layer of iron oxide on the uniform corrosion resistance of Alloy 22 in aqueous solutions is not known. It would be of interest to learn the fate of the intermediate Fe-rich layer during immersion in acidic (SAW) and neutral/mildly alkaline (SCW) solutions.

In summary, the Project has begun to characterize the high temperature oxide films and the passive films that form on Alloy 22. Results have been obtained for the compositions of the passive films formed on Alloy 22 in several aqueous solutions and the compositions of oxide films formed in air at room temperature and 550°C. Results to date are consistent with published results for films on Ni-Cr binary alloys and Ni-Cr-Fe/Mo ternary alloys.

7.2.2 The Uniform Corrosion of Alloy 22 in the Passive State

The Project is evaluating the likelihood that waste packages will fail by uniform corrosion in less than 10,000 years by determining the average rate of uniform corrosion of Alloy 22 in a variety of solutions relevant to the repository. Average corrosion rates are derived from measurements of the change in weight of rectangular coupons (1"x2"x1/8") of Alloy 22. The tests have been ongoing at the Long Term Corrosion Test Facility (LTCTF) at LLNL for nearly 4.5 years. The LTCTF consists of a number of 2000 liter volume fiberglass tanks that each contain 1000 liters of solution. Tests are conducted at two temperatures: 60°C and 90°C. The solutions are agitated and air is moved across the solution at a rate of 150 cc/min.

After two years of immersion in the LTCTF, the mean corrosion rate of ≈ 144 coupons of Alloy 22 was $113 \text{ nm/y} = 1.13 \text{ mm}/10^4\text{y}$. The maximum corrosion rate was $794 \text{ nm/y} = 7.94 \text{ mm}/10^4\text{y}$. There was no effect of solution composition or of test temperature (60°C or 90°C) on the measured weight losses of Alloy 22 in the LTCTF.

The measurements of the average corrosion rate of coupons in the LTCTF are supplemented by a number of electrochemical measurements of the instantaneous corrosion rate of Alloy 22 in a number of aqueous solutions. The results are summarized in Table 7.2.2-I (on page 40).

Collectively, the results indicate that the uniform corrosion rate of Alloy 22 in the passive state is very low in a range of solutions. The low measured rates of corrosion indicate it is unlikely that Alloy 22 in the passive state would sustain significant uniform corrosion during 10,000 years of immersion in aqueous environments relevant to the repository at Yucca Mountain.

There is disagreement in the results from the LTCTF and from short duration electrochemical tests concerning the influence of temperature on uniform corrosion rate of Alloy 22. The corrosion rate of Alloy 22 measured by electrochemical techniques over relatively short periods of time increased with increasing temperature as well as increasing potential. In pH 3 sulfate over the temperature range of 20°C to 70°C (Bellenger, 1996) and in 1M NaCl + 0.1M H₂SO₄ over the temperature range of 25°C-85°C (Lloyd, 2001) the corrosion rate of Alloy 22 increased with increasing temperature. This is in contrast to the lack of temperature dependence of the two-year average corrosion rate of Alloy 22 in the LTCTF at 60°C and 90°C. Further work is required to determine the influence of temperature on the uniform corrosion rate of Alloy 22.

A result that might indicate the uniform corrosion rate of Alloy 22 increases with increasing time, is the ennoblement of the corrosion potential of Alloy 22. The Project is investigating the cause(s) of the $\approx 500 \text{ mV}$ increase in corrosion potential of Alloy 22 during 4.5 years of immersion in SAW at 90°C in the LTCTF. Similarly large increases in corrosion potential of Alloy 22 coupons have not been observed in the other test solutions in the LTCTF. Short time electrochemical tests have demonstrated that the uniform corrosion rate of Alloy 22 increases with increasing potential in the passive range (Bellenger, 1995; Lloyd, 2001). Consequently, it is possible that the large increase in corrosion potential of Alloy 22 in SAW in the LTCTF could be accompanied by increases in the uniform corrosion rate. However, as already mentioned, the average corrosion rate of Alloy 22 test coupons in the LTCTF is low and the same in all of the solutions tested.

The ennoblement of corrosion potential of Alloy 22 immersed for 4 years in SAW at 90°C was first reported in June 2001 (Summary Alloy 22 Corr. Pot. Data, June 21, 2001). The corrosion potential of some samples of alloy 22 had risen from initial values of $\approx -100 \text{ mV}$ to $+390 \text{ mV}$ vs Ag/AgCl. More recent results indicate that a similar rise in corrosion potential occurs in only ≈ 80 days, at which time the corrosion potential is over 300 mV vs Ag/AgCl and continuing to

slowly rise (Lian, 2002). Additional measurements indicate the corrosion potential of platinum in SAW at 90°C is ≈ 400 mV vs Ag/AgCl and is fairly constant over the 80 day period of the test. Collectively, the results of the 80 day long bench top tests of the corrosion potentials of Alloy 22 and platinum in SAW at 90°C and of the corrosion potential of Alloy 22 immersed for 4.5 years in SAW at 90°C in the LTCTF suggest the corrosion potential of Alloy 22 in SAW at 90°C asymptotically approaches the corrosion potential of platinum. If so, the ennoblement of the corrosion potential of Alloy 22 might be a consequence of a decrease in its corrosion rate to very small values approaching the exchange current density of the oxygen reduction reaction. That is, the ennoblement of the corrosion potential might indicate a large decrease in corrosion rate of Alloy 22, rather than an increase in corrosion rate.

The corrosion potential of Alloy 22 in SAW at 90°C was found to increase slowly with time during the first 3-4 weeks, resulting in an increase of ≈ 100 mV. Over the next 2 weeks the corrosion potential increased sharply by ≈ 300 mV. Finally, over the next two weeks, the rate of change of the corrosion potential decreased, resulting in an additional increase of ≈ 100 mV.

Simultaneous measurements were made over a period of 167 hrs. of the corrosion potential and of the corrosion rate of Alloy 22 in SAW by LPR (Lian, 2002). The results indicate that as the corrosion potential increased from an initial value of ≈ -100 mV to $\approx +200$ mV, the corrosion rate decreased from an initial value of $\approx 3 \mu\text{A}/\text{cm}^2$ to $\approx 0.04 \mu\text{A}/\text{cm}^2$ ($\approx 2.8 \text{ mm}/10^4\text{y}$). This is an important result, which indicates that the ennoblement of the corrosion potential of Alloy 22 in SAW at 90°C is accompanied by a decrease, rather than an increase, in corrosion rate.

In view of the results by Lloyd et al that the concentration of chromium in the inner (barrier) layer of the passive film of Alloy 22 in 1M NaCl + 0.1M H₂SO₄ slowly and continuously increases with time, it is possible, if not likely, that the increase in corrosion potential and the decrease in corrosion rate of Alloy 22 with increasing time in SAW at 90°C is also caused by chromium enrichment of the passive film. As shown in Table 7.2-II, chemical analyses indicates very high concentrations of chromium in the passive films of coupons of Alloy 22 immersed in SAW for 4.5 years. The high chromium concentration in the passive film on Alloy 22 following 4.5 years in SAW strongly supports the idea that the ennoblement of the corrosion potential of Alloy 22 in SAW at 90°C is caused by chromium enrichment of the passive film, which produces a more protective film that causes the corrosion rate to decrease and the corrosion potential to increase.

The Project is further evaluating the hypothesis that the ennoblement of the corrosion potential of Alloy 22 in SAW at 90°C is the result of chromium enrichment of the passive film and/or an increase in thickness of the passive film by determining the time evolution of the passive film's composition and thickness during immersion in SAW at 90°C.

In summary, the results obtained to date by the Project and published results of other researchers indicate that Alloy 22 has a very low corrosion rate in the passive state. The ≈ 500 mV increase in corrosion potential of Alloy 22 in SAW at 90°C is accompanied by a decrease in the uniform corrosion rate. The increase in corrosion potential and decrease in corrosion rate is most likely caused by a chromium enrichment of the passive film. The results to date indicate it is unlikely that uniform corrosion of Alloy 22 in the passive state will result in failure of the waste packages in the repository at Yucca Mountain in less than 10,000 years.

7.2.3 Uniform Corrosion Alloy 22 in the Transpassive State

To date the Project has not investigated the environmental and metallurgical factors that might cause a relatively high rate of uniform corrosion of Alloy 22 in the transpassive state.

A recent set of experiments by the Project relates to the transpassive corrosion of Alloy 22 (Summary of Recent Information Relevant to WAPDEG PM, November 2001). Samples of Alloy 22 were immersed for 24 hrs. in aerated, unaerated, and deaerated SAW at 90°C. At the end of the 24 hr. period, the samples of Alloy 22 were cyclically polarized. Some of the results of these tests are presented in Table 7.2.3-I.

Two facts indicate the transpassive potential was associated with oxidation of Alloy 22. First, the potential of oxygen evolution in these solutions was in the range of 800mV-1200mV vs Ag/AgCl. Second, the solution turned color from clear to yellow-green.

Recall from the discussion in Section 7.2.2 that the corrosion potential of Alloy 22 in SAW at 90°C appears to reach a maximum value of 400 mV vs. Ag/AgCl. If the corrosion potential cannot exceed 400 mV, transpassive corrosion of homogenized Alloy 22 will not occur unless a combination of Fe^{+3} from the corrosion of steel structures close to the waste packages and radiolysis of the water increase the oxidizing power of the solution on the surface of the waste package.

7.2.4 Measurement of the Uniform Corrosion Rate of Alloy 22

The Project is using a combination of measurements of weight change and electrochemical techniques to measure the uniform corrosion rate of Alloy 22 in environments relevant to the Nuclear Waste repository at Yucca Mountain. These measurements were described in Section 7.2.1.

Measurements of changes in the weights of specimens immersed for long periods of time in the LTCTF have been performed and provide a measure of the average corrosion rate of Alloy 22. The measurements of the change in weight of the corrosion coupons in the LTCTF are due, in part, to an increase in weight caused by the precipitation on the sample's surface of a film of silicate. To account for the weight gain caused by the silicate film, a weight equivalent to a corrosion rate of 0.063 $\mu\text{m/y}$ is subtracted from the weight of each test coupon. The current techniques employed by the Project to measure uniform corrosion rate are consistent with industry's standards and practices.

In some early reports, the Project recorded the minimum and maximum current densities at the corrosion potential during the potentiodynamic polarization of the sample. These current densities were incorrectly identified as upper and lower bounds of the corrosion rate. This is inappropriate and has been discontinued.

The Project is supplementing the weight change measurements of average corrosion rate of coupons in the LTCTF with measurements of the instantaneous corrosion rate by the LPR technique.

7.2.5 Modeling of the Passive Film and Uniform Corrosion Rate of Alloy 22

The Project is modeling the long-term uniform corrosion behavior of Alloy 22 in the repository at Yucca Mountain by a combination of the Point Defect Model (PDM) of Passivity (Chao, 1981; Lin, 1981; Chao, 1982) and the Mixed Potential Model (MPM) (Macdonald, 1992, 1994, 1999). The combination of the Point Defect Model and the Mixed Potential Model is called the General Corrosion Model (GCM) (Macdonald, 1999; 2001).

In addition, predictions of the long-term uniform corrosion rate as a function of time are performed by the use of an empirical model (Waste Package and Drip Shield Degradation, June 2001).

The passive film formed on Alloy 22 consists of two layers. The compositions of the two layers depend, to a large extent, on the pH of the solution. According to the PDM, the inner layer of the passive film forms by the generation of oxygen vacancies at the film/metal interface. At steady state, the rate of film growth into the metal at the film/metal interface is balanced by the rate of dissolution of the inner layer at the interface between the inner and outer layers.

The PDM suggests that the outer layer of the passive film grows by the precipitation of cations that have migrated through the inner layer and passed into the solution. Note that the outer layer need not form by precipitation of species from the solution and onto the inner layer. In particular, oxide films formed during high temperature oxidation are multi-layered and in some cases the morphology of the outer layer resembles the morphology of the outer layer formed in aqueous solutions. Clearly, the outer layer of the films formed during high temperature oxidation did not form as a result of a precipitation process.

According to the PDM chromium enrichment of the inner layer of the passive film results from the selective dissolution of nickel at the film/metal interface, the rapid oxidation of chromium to chromium oxide, and the fast migration rate of nickel through the chromium oxide inner layer.

In addition to predicting the structure of the passive film, the PDM calculates the rate of growth of the passive film at steady state.

The corrosion potential and corrosion rate are calculated with the GCM. The GCM uses the MTM to combine the steady-state passive film growth rate, as calculated by the PDM, with the rates of the hydrogen ion and oxygen reduction reactions, as calculated by Butler-Volmer equations fitted with values of parameters appropriate to hydrogen ion and oxygen reduction, respectively.

Because of the lack of information on the kinetics of the reduction reactions on Alloy 22 in environments relevant to Yucca Mountain, preliminary calculations have been performed using values for the kinetics of the reduction of hydrogen ions and oxygen on 304 stainless steel in pressurized water at 288°C. The results predict that the uniform dissolution rate of Alloy 22 will be low enough that failure of the waste package by uniform corrosion will not occur in less than 10,000 years. The total corrosion loss of the wall of the Alloy 22 waste package in 10,000 years is calculated as 1.8 mm.

The Project is also calculating Pourbaix diagrams for Alloy 22 in the solutions and at temperatures relevant to the repository at Yucca Mountain. As of this date, the Project has not generated any Pourbaix diagrams of Alloy 22. The intent is to use the Pourbaix diagrams to predict the stability of the passive films formed on Alloy 22. The thermodynamically stable films will be compared to the films actually present on Alloy 22. The films that form on Alloy 22 are identified by the techniques described in section 7.2.1.

7.3 ASSESSMENT AND RECOMMENDATIONS

7.3.1 Structure and Composition of the Passive Films and Oxide Films of Alloy 22.

The Project is using a number of characterization tools to investigate the structure and composition of the passive films formed on Alloy 22 immersed in aqueous solutions and the oxide films formed during high temperature oxidation in air. The work to date represents a small

fraction of the total amount of work that is required to fully characterize the composition, structure, and thickness of the films that form on Alloy 22 in air and in the different aqueous solutions that might contact the waste package in the repository at Yucca Mountain. Although only a relatively small amount of experiments have been conducted, some very informative results have already been obtained. On the negative side, at this time the overall effort, which is being conducted at three different laboratories, appears disjointed. This may be the result of the early stage of the research and the relatively small amount of results that have been presented to date. With time, as more results come forward, the different components of the overall program might show themselves to be well coordinated.

For example, Shoesmith and colleagues have characterized very well the composition and thickness of the bi-layered films that form on Alloy 22 in air and at a variety of potentials in 1M NaCl + 0.1M H₂SO₄. These results are consistent with the published work of others on the passive films of Ni-Cr binary alloys, Ni-Cr-Fe ternary alloys, and C4, a Ni-Cr-Mo alloy. Collectively, the results reveal the strong effects of alloy composition and solution chemistry (especially pH) on the structure and composition of the passive films formed on Ni-Cr-X alloys. However, 1M NaCl + 0.1M H₂SO₄ is not relevant to the repository at Yucca Mountain and so these results do not have a direct impact on the performance of Alloy 22 waste packages.

The experiments at GECD&D use XPS to analyze the overall composition of the films that form on Alloy 22 in SCW (pH 12.2). More information would be provided if the compositions were determined by a depth profiling technique such as AES. This would allow a direct comparison of the layered films formed in alkaline water (at GECD&D) with the films formed in mildly alkaline water (experiments conducted at LLNL in SCW pH 8) and in neutral water (experiments to be conducted at UWO in SCW pH 7) and in strongly acidic water (experiments conducted at UWO in 1M NaCl + 0.1M H₂SO₄).

While coordination between the film characterization experiments performed at UWO, GECD&D and LLNL does not appear to be strong, the results obtained at each laboratory have made use of multiple experiments that were very well coordinated. The effective coordination of multiple experiments is responsible for the high value of the information that has been obtained at each laboratory. For example, chromium enrichment of the passive film was found to be the reason that a long time was required for Alloy 22 to reach a steady state passive corrosion rate. This explanation was obtained by coordinating the TOF-SIMS analyses of passive films of Alloy 22 with measurements of the oxidation rate of Alloy 22.

A second example of valuable information obtained from well coordinated experiments is the XPS analyses of the passive films formed by anodic polarization of Alloy 22 in simulated concentrated water (SCW) at pH 11 and 60°C and 90°C. The results of coordinated polarization experiments and passive film analyses indicate the pronounced anodic oxidation peak between 200 and 400 mV vs SCE is due to the oxidation of Mo(IV) to Mo(VI) within the passive film.

In general, the Panel recommends better coordination of the generally excellent work underway and planned at UWO, LLNL and GECD&D.

The Panel specifically recommends the following.

1. The Panel recommends the Project carefully coordinate the analytical work at the different laboratories so as to insure that the extensive amount of work that is planned provides a comprehensive description of the films that form on Alloy 22.
2. The Panel recommends the Project seek to identify if critical values of potential, temperature, anion concentration and anion identity exist where the passive film

undergoes a significant (discontinuous) change in either structure or composition. Such experiments have been proposed by the Project.

3. The Panel recommends that changes in structure/composition of the high temperature oxide films as a result of immersion in the various solutions relevant to the repository at Yucca Mountain be investigated. Changes in the films need to be investigated at a range of potentials and temperatures. Such experiments have been proposed by the Project and some work is underway.
4. Finally, surface segregation of sulfur and transpassivity are the two most likely factors that would cause significant rates of uniform corrosion of Alloy 22. Therefore, changes in the structure and composition of the passive film as a function of surface segregation of sulfur and as a consequence of highly oxidizing potentials should be investigated. This is the Panel's most important recommendation for work related to uniform corrosion of alloy 22.

7.3.2 Uniform Corrosion Rate of Alloy 22

The Project plans to continue measurements of the average uniform corrosion rate of test coupons of Alloy 22 in the LTCTF. In addition, the Project intends to periodically measure, by LPR method, the instantaneous corrosion rate of coupons of Alloy 22 in the LTCTF. The Panel supports the LPR measurements since they will indicate time dependent changes in the uniform corrosion rate.

The Project is systematically investigating the causes of the ennoblement of the corrosion potential of Alloy 22 in SAW at 90°C. In a relatively short period of time, the Project has acquired significant understanding of the cause(s) of the ennoblement of corrosion potential. To date, the results reveal a correlation between an increase in corrosion potential and a decrease in uniform corrosion rate. The Project is currently trying to correlate the changes in corrosion potential and corrosion rate with changes in the structure, composition, and thickness of the passive film.

The Panel has the following recommendations related to the uniform corrosion rate of Alloy 22 in the passive state.

1. The Panel supports the Project's efforts to understand the cause(s) of the ennoblement of the corrosion potential of Alloy 22 in SAW. In particular, the panel recommends testing multiple samples of Alloy 22 and removing selected samples after the first 3 weeks of immersion, removing a second group after a total of ≈ 7 weeks of immersion and removing a third group after 12 weeks of immersion. The Project's data of corrosion potential vs. time show sharp changes in slope at times of three weeks, seven weeks and 12 weeks of sample immersion. The structure and composition of the passive film of each group of samples should be determined in an effort to correlate changes in the corrosion potential with changes in the structure and/or composition of the passive film. Such experiments already appear to be part of the Project's plans.
2. The Panel recommends determination of the mechanism of enhancements of the uniform corrosion rate of Alloy 22 that are caused by the formation of tetrahedrally close packed phases (TCP) and Long Range Order (LRO) be investigated. The objective is to mechanistically justify the value of the general corrosion rate enhancement factor, which the Project uses to account for the increase in uniform corrosion rate caused by the

presence of TCP phases and LRO. The Panel recommends that a group of samples of Alloy 22 be heat treated to develop LRO and that a second group of samples be heat treated to form TCP phases. Then, for both groups of samples, perform a combination of corrosion rate measurements and analyses of the structure and composition of the passive films.

3. Similarly, the Project has accounted for microbiologically influenced corrosion by a general corrosion rate enhancement factor of 2. The panel recommends that mechanistic understanding of the influence of MIC on the uniform corrosion rate be obtained. This might require identification of the chemistry of the solution that is adjacent to the metal surface as a result of presence of biofilms. It might also require analyses of the structure and composition of passive films formed in the presence of biofilms.
4. The Panel recommends testing the uniform corrosion rate of coupons in the LTCTF at temperatures higher than the present maximum of 90 °C . Higher test temperatures are warranted (1) by the increase in oxidation rate of Alloy 22 with increasing temperature, which was observed in short duration electrochemical tests, and (2) by the knowledge that salts with deliquescence points of $\approx 25\%$ RH, might contact the surface of the waste package. The presence of salts with low deliquescence points would place the waste package in contact with an aqueous phase at higher temperatures.
5. The Panel recommends testing the uniform corrosion rate of Alloy 22 at high passive potentials for long periods of time. Short time electrochemical tests indicate the uniform corrosion rate of Alloy 22 increases with applied passive potential. High corrosion potentials might be established on waste canisters of Alloy 22 as a result of the combined effects of Fe^{+3} corrosion products from steel structures in the vicinity of the waste package and radiolysis of the water on the surface of the waste package. Increases in corrosion potential of samples of Alloy 22 in the LTCTF have occurred as a result of Fe^{+3} introduced into the water by corrosion of steel components of the test apparatus and/or stainless steel test coupons (Lian, 2002).
6. Uniform corrosion of Alloy 22 is unlikely to cause failure of the waste containers in less than 10,000 years. However, one of the two likely causes of high rates of uniform corrosion of Alloy 22 is surface segregation of sulfur. The Panel recommends investigating the influence of surface segregation of sulfur on the uniform corrosion rate of Alloy 22. The Panel recommends that two causes of surface segregation of sulfur be investigated: equilibrium segregation due to high temperature heat treatments and anodic segregation resulting from uniform corrosion of Alloy 22. The Panel recommends the determination of critical bulk sulfur concentrations below which heat treatments and anodic segregation do not cause significant increases in the uniform corrosion rate of Alloy 22.

7.3.3 Uniform Corrosion Alloy 22 in the Transpassive State

Alloy 22 will undergo high rates of uniform corrosion in the transpassive state. The Panel recommends the following.

1. Determination of the likelihood of radiolysis of the water causing transpassive dissolution of fully homogenized Alloy 22. This should be done for the range of solution

compositions relevant to the repository at Yucca Mountain. In particular, the full range of solution pH should be investigated.

2. Determination of the combinations of radiolysis of water, composition of the water, in particular, solution pH and concentration of Fe^{+3} , and metallurgical factors, including surface segregation of sulfur, grain boundary segregation of phosphorus, and precipitates of chromium rich and molybdenum rich phases, that might interact synergistically to initiate transpassive dissolution at relatively low potentials. Results in the literature for Ni-Cr alloys suggest that such factors might initiate transpassivity locally, resulting in the formation of oxidizing corrosion products (e.g., Cr(VI) species) that lead to high rates of uniform dissolution of the alloy.

7.3.4 Measurement of the Uniform Corrosion Rate of Alloy 22

The Panel finds that the measurements by the Project of the uniform corrosion rate of Alloy 22 are consistent with current standards and practices.

The Panel has no specific recommendations related to measurements of the uniform corrosion rate. The Panel does support the Project's plans to use electrochemical impedance spectroscopy for additional characterization of the electrochemical behavior of samples removed from the LTCTF.

7.3.5 Modeling of the Passive Film and the Uniform Corrosion Rate of Alloy 22

The Panel recommends the following.

1. Measurement of the parameters of the Butler-Volmer equations describing the rate of hydrogen ion and oxygen reductions on Alloy 22. These kinetic parameters will serve as input into the General Corrosion Model.
2. Measurement of the steady state corrosion rate of Alloy 22 to determine if it is potential independent, as predicted by the Point Defect Model.
3. Further development of the Point Defect Model or a new model of passivity to predict the non-steady state performance of Alloy 22 (Urquidi-Macdonald, 2001). The primary purpose is to have a single model that can predict long-term, steady state corrosion rates in the passive state and that can be verified by short term, laboratory tests. In particular, the effect of potential and temperature on uniform corrosion rate in the passive state.

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8. LOCALIZED CORROSION

8.1 INTRODUCTION

As discussed in detail in the last chapter, many engineering alloys, including common alloys such as stainless steels and aluminum alloys as well as the proposed waste package materials Alloy 22 and titanium Grade 7, are useful because of passive films, which are thin (nm scale), oxide layers that form naturally on the metal surface and greatly reduce the rate of corrosion of the alloys. Such passive films, however, are often susceptible to localized breakdown resulting in accelerated dissolution of the underlying metal. If the attack initiates on an open surface, it is called pitting corrosion; at an occluded site it is called crevice corrosion. These closely related forms of localized corrosion can lead to accelerated failure of structural components by causing perforation or by acting as an initiation site for cracking.

Intergranular corrosion is another technologically important form of localized corrosion that can occur in alloys having regions at or near grain boundaries with different composition than the bulk of the grain. The classic example of intergranular corrosion is sensitization of stainless steels, which often occurs during welding or heat-treatment as a result of the precipitation of chromium carbides on grain boundaries and the resultant depletion of chromium from the nearby matrix of the neighboring grains. Intergranular corrosion of sensitized stainless steel occurs as a result of localized attack of the chromium-depleted region that separates the stainless steel grains. Alloy 22 has a very low carbon content and does not undergo carbide precipitation or sensitization during welding. Sensitization of Alloy 22 will only occur under extreme thermal

conditions as a result of phase precipitation. Phase formation will be covered in the section of this report describing degradation modes; this chapter will not discuss intergranular corrosion. This chapter will highlight the critical factors in the field of localized corrosion, address the susceptibility of the waste package materials to localized corrosion, describe how the Yucca Mountain Project is addressing the localized corrosion, assess this effort, and make recommendations.

8.1.1 Localized Corrosion Phenomenology and Controlling Parameters

Localized corrosion has been studied for several decades by many researchers. Detailed information is available in a book (Szklańska-Smiałowska 1986) and several conference proceedings (Staehle, Brown et al. 1974; Frankenthal and Kruger 1978; Turnbull 1987; Isaacs, Bertocci et al. 1990; Frankel and Newman 1992; Natishan, Kelly et al. 1995). Pitting and crevice corrosion are complex processes that are influenced by many different parameters, including the environment, metal composition, potential, temperature, and surface condition. Important environmental parameters include pH and aggressive ion, inhibitor, and oxidizer concentration. Other phenomenological aspects of localized corrosion include the stochastic nature of the processes and the stages of localized attack, including passive film breakdown, metastable attack, stable growth, and arrest. In order to understand how the Project is addressing localized corrosion, a detailed understanding of the phenomenology is critical. A brief summary of these issues is given below and a more detailed description is provided in the Compilation of Special Topic Reports.

Classical pitting corrosion (caused by passive film breakdown) will only occur in the presence of aggressive anionic species. Chloride ions are usually, although not always, the cause. The susceptibility to pitting tends to vary with the logarithm of the bulk chloride concentration (Leckie and Uhlig 1966). Crevice corrosion is also frequently associated with the presence of chloride ions. As discussed in a previous chapter, the waters in Yucca Mountain contain chloride, and the environment on the waste package might be rich in chloride.

The presence of oxidizing agents in a chloride-containing environment is extremely detrimental and will further enhance localized corrosion. Oxidizing agents increase the likelihood of localized corrosion by increasing the local potential and providing cathodic reactant. On the other hand, inhibiting ions such as sulfates, nitrates, chromates, and molybdates act to reduce the susceptibility of some materials to localized corrosion. This phenomenon is discussed in a Special Topics Report. The effect of these oxyanions on localized corrosion is of particular importance to the behavior of waste packages in a Yucca Mountain repository since the environment is predicted to be rich in such anions.

Electrochemical studies of localized corrosion have found that characteristic potentials exist. Stable pits form at potentials noble to the pitting potential, E_P , and will grow at potentials noble to the repassivation potential, E_R , which is less noble than E_P . During upward scanning in a cyclic polarization experiment, a stable pit starts growing at E_P where the current increases sharply from the passive current level and, upon reversal of the scan direction, repassivates at E_R where the current drops back to a low value. Corrosion experts generally consider that materials exhibiting higher values of E_P and E_R are more resistant to pitting corrosion, and cyclic polarization experiments are commonly used for this purpose. A correlation has been found such that metals with low experimentally determined pitting and repassivation potentials have a higher tendency to form pits naturally at open circuit (Leckie and Uhlig 1966). Crevice formation and

repassivation potentials can be found for samples with crevices. These values are typically lower than the corresponding potentials for pitting, which indicate that crevice corrosion occurs more readily than pitting, and is harder to stop once started. The difference between the corrosion potential and some critical potential is being used as a design criterion for the proposed waste package. This is discussed in more detail below.

Alloy composition and microstructure can have strong effects on the susceptibility of an alloy to pitting and crevice corrosion (Szklaarska-Smialowska 1986). Titanium alloys and the chromium-containing nickel-based alloys, including Alloy 22, are extremely resistant to corrosion (Evans 1994; Agarwal 2000). Except for iron, the alloying elements in Alloy 22 (having a typical composition of 21.5% chromium, 13.5% molybdenum, 3% tungsten, 3% iron) provide enhanced passivity and localized corrosion resistance.

Temperature is also an important factor in localized corrosion since many materials will not pit or crevice-corrode at a temperature below a certain value (Brigham and Tozer 1973; Brigham and Tozer 1974; Qvarfort 1988; Qvarfort 1989; Arnvig and Davison 1993; Laycock, Moayed et al. 1995; Arnvig and Bisgard 1996). Temperature will play a critical role in the behavior of the waste package since the repository will likely be hot for many years and then slowly cool.

The exact condition of a surface can have a large influence on the localized corrosion behavior of a material. In general, the susceptibility to localized corrosion increases as the roughness of the surface finish increases. On the other hand, protective surface films can reduce the likelihood for localized corrosion. There is no plan to provide special surface finishes or treatments to the waste package canisters or drip shield. The surface condition will be a consequence of all of the prior processing and handling, extended exposure to high temperature air when the drift is closed, and possible contamination of the surface by dust or precipitated products from drips.

The growth of a pit generates an occluded morphology that is essentially a crevice, so active pits and crevices are basically identical. Both are usually acidified and rich in chloride. The cathodic reaction typically occurs at a location on the boldly exposed surface where the concentration of cathodic reactant is higher. The phenomenological aspects of pitting apply equally to crevice corrosion. The difference between pitting and crevice corrosion is in the initiation phase. The occlusion associated with a crevice provides a ready barrier to transport, so initiation of crevice corrosion is easier. Alloys are usually resistant to pitting corrosion under conditions in which they are resistant to crevice corrosion, but the inverse is certainly not true. It is likely that the waste package will be much more susceptible to crevice attack since Alloy 22 resists pitting, but crevices will exist between the waste package and the supporting rails, beneath surface deposits, including dust or biofilms, and between the Alloy 22 outer can and 316L NG inner can.

Localized corrosion growth tends to decelerate with time owing to the increasing size of the localized corrosion site. This increasing dimension results in an increase in diffusion length or ohmic path, so the rate decreases regardless of whether the dissolution is limited by mass transport or ohmic drop. For ideal geometries, the size varies with time according to $d \propto t^n$, where $n \approx 1/2$.

Pitting and crevice corrosion are often considered to be autocatalytic; once the attack initiates, it tends to propagate because of the aggressive acidic chloride conditions that are generated within the site. However, this is not always the case. Metastable pits are small pits that initiate, grow to a certain size, and then repassivate, typically within seconds or fractions of a second. Numerous metastable pits micrometers in size can form at potentials far below the breakdown potential

associated with the initiation of stable pits or above the breakdown potential during the incubation time before a stable pit initiates.

Larger pits and crevices can also stop growing, which is called pit arrest, death, stifling, or repassivation. Repassivation might occur if a sudden event, such as loss of a pit cover, caused a sudden enhancement of transport and dilution of the local environment to the extent that the rate of dissolution in the pit or crevice would be insufficient to replenish the lost aggressive environment. Localized corrosion is often under cathodic control, growing as fast as cathodic current consumes the generated electrons. So stifling will also occur if the available cathodic current limits the anodic reaction to the extent that the local anodic current density decreases below that required for stability.

8.1.2 Review of Susceptibility of Waste Package Materials to Localized Corrosion

Alloy 22 and other corrosion resistant nickel-based alloys. Among the nickel-based alloys, Alloy 22 is one of the most corrosion resistant to many environments because of its high chromium, molybdenum, and tungsten contents. It has a high value of every pitting index and a high critical crevice temperature. Pitting is extremely difficult to sustain in Alloy 22, although it is susceptible to crevice and under-deposit corrosion under extreme conditions of acidity, chloride concentration, potential, and temperature. An example of the environment required to produce pitting corrosion on a boldly exposed surface is saturated sodium chloride at 80°C and very high potential (maybe above the potential for transpassive dissolution) (Macdonald 2001). This suggests that the critical solution for stabilization of pits and crevices in Alloy 22 is extremely aggressive, and the rate of dissolution in a localized corrosion site is usually insufficient to sustain attack unless a transport barrier pre-exists, such as in a crevice.

Localized corrosion of Alloy 22 will occur under certain very aggressive conditions. Pitting of Alloy 22 is often associated with welds and has been reported in boiling ASTM G 28 B tests (Rebak 2001). Alloy 22 will also pit at very high temperatures (163°C) in chloride solutions containing very high concentrations (2.5%) of dissolved lead (Barkatt and Gorman 2000), although it is immune at a lower lead concentration (0.5%) (Gorman 2001). Similar observations were made in solutions containing mercury (Barkatt and Gorman 2000; Gorman 2001).

As mentioned above, crevice corrosion of Alloy 22 can be initiated in hot chloride solutions at high potentials. Experiments on creviced samples in 5 M lithium chloride with either 0.05 or 0.5 M (nitrate + sulfate) produced crevices only at temperatures higher than 80°C (Kehler, Ilevbare et al. 2001). Higher crevice initiation potentials were required in the solution with higher oxyanion concentration or if the sample was first aged 6 months in lab air. The initiation potential was found to be a strong function of temperature, decreasing with increasing temperature above 80°C. In another study, the crevice repassivation potential in 0.5 and 4 M chloride solutions containing 1.78 mM oxyanions decreased by about 100 mV for welded Alloy 22 samples and by about 600 mV for samples aged at 870°C relative to unwelded and unaged samples (Dunn, Cragolino et al. 2000). These observations highlight the role of electrolyte, temperature, potential, surface condition, and microstructure in the localized corrosion process for Alloy 22. It should be noted that stabilization of localized corrosion for Alloy 22 requires maintenance of aggressive conditions in an occluded space, which might not be possible in the repository environment.

The localized corrosion resistance of Alloy 22 has been compared to that of similar alloys by several authors. Alloy 22 was compared to Alloy 625, which has less molybdenum, and thus a

less severe critical crevice solution, lower crevice initiation potential, and lower critical crevice temperature (Kehler, Ilevbare et al. 2001). The rates of metastable pitting/crevicing were lower for Alloy 22 than for Alloy 625 (Kehler, Ilevbare et al. 2001). The critical crevice temperature in ASTM G-48 solution is listed as being considerably lower than that of Alloy 276 in one report (Agarwal 2000) and considerably higher in others (Hibner 1987; Rebak and Crook 1998). In general, it is among the most corrosion resistant of all of the nickel-based alloys, although the susceptibility depends on the environment. Some newer alloys, such as Alloys 59 and 2000, have higher chromium and molybdenum contents and are probably more resistant to localized corrosion than Alloy 22 in chloride solutions.

Titanium grade 7 and other alpha titanium alloys. Titanium Grade 7, like Alloy 22, is extremely corrosion resistant owing to the formation of a protective passive film (Cotton and Hanson 1994; Been and Grauman 2000). In fact, titanium Grade 7 is much more resistant to localized corrosion than Alloy 22 in the likely waste package environments. However, it is susceptible to hydrogen uptake and embrittlement, as discussed in another section of this report.

Pitting of titanium alloys in chloride solutions only occurs at extremely high potentials, well beyond the stability of water. On the other hand, pitting corrosion can occur in fluoride solutions and crevice corrosion is possible in hot halide or sulfate containing environments (Been and Grauman 2000). Bulk environment pH is critical for crevice corrosion of commercially pure titanium; it does not occur when the $\text{pH} > 10$, but can initiate when $\text{pH} < 7$, with the crevice pH going to < 1 (Been and Grauman 2000). A critical temperature for crevice corrosion of titanium and titanium alloys has also been observed (Been and Grauman 2000).

Titanium Grade 7, containing 0.2 % palladium is extraordinarily resistant to localized corrosion, withstanding crevice corrosion at higher temperatures (up to 200°C) and lower pH's (down to pH 1) than commercially pure titanium (Been and Grauman 2000; Shoesmith 2000; Shoesmith 2001). Fluoride ions can enhance crevice corrosion susceptibility, but titanium Grade 7 remained immune to a range of aggressive environments (up to 1.6% Cl^- and 100 ppm F^-) (Schutz and Grauman 1986). Titanium Grade 7 is the most resistant of the titanium alloys, a result of palladium enrichment at the surface (Shoesmith 2000).

8.2 DESCRIPTION OF THE YUCCA MOUNTAIN PROJECT APPROACH TO LOCALIZED CORROSION

Determination of the susceptibility of the proposed waste package design to localized corrosion resistance has been based on in-house experimentation at Lawrence Livermore National Laboratory and the published work of other labs. This section will review the Project work supporting the design to protect waste packages from localized corrosion and the planned activities. It was assembled based on published documents (Farmer and McCright 2000; Lee 2000; Pasupathi 2000; Dobson 2001) as well as meetings, email, and phone conversations with Project personnel.

8.2.1 Basis of Project Model: ΔE Approach

The Project is using the ΔE approach for the prediction of the waste package susceptibility to localized corrosion. As described above, characteristic potentials are associated with localized

corrosion. The initiation of localized corrosion typically occurs above a certain potential, which will be called the breakdown potential, E_B , although it is often referred to as a pitting or crevice potential depending upon the form of attack that occurs. Another potential, which will be referred to as the repassivation potential, E_R , is the potential below which a stable form of localized corrosion (pitting or crevice corrosion) repassivates or stops growing. E_R is typically lower than E_B for a given form of localized corrosion. The ΔE design approach evaluates the difference between the open circuit potential (E_{OC}) and either E_B or E_R . If the conditions are such that the waste package E_{OC} will remain far below E_B (i.e. $E_B - E_{OC}$ is large), it can be considered that there is a low probability for localized corrosion to initiate. Since E_R is typically lower than E_B , consideration of $E_R - E_{OC}$ is a more conservative measure. In other words, if E_{OC} is predicted to remain far below the potential at which stable localized corrosion will repassivate, then there is a low likelihood that stable localized corrosion will ever form.

The waste package design cannot avoid crevices; they will exist between the waste package and supports, between the outer barrier (Alloy 22) and the inner barrier (316 stainless steel), and under deposits (including dust or biofilms) on the waste package surface. Since crevice corrosion typically initiates and repassivates at lower potentials than pits, consideration of the repassivation potential for crevices in the ΔE measure, or $E_{R,CREV} - E_{OC}$, would be an extremely conservative approach for determining the likelihood of localized corrosion.

A measured value of $E_{R,CREV}$ might depend on details of the method used to measure it (Wilde 1974), although it has been shown that E_R is independent of the extent of prior growth for pits in stainless steel and other corrosion resistant alloys after the passage of large charge densities (Sridhar and Cragolino 1993; Dunn, Cragolino et al. 2000). A Japanese standard for a method to measure $E_{R,CREV}$ has recently been agreed upon, and is described in a Special Topics Report.

The Project approach is based on the generic measure of $E_{CRIT} - E_{OC}$, where E_{CRIT} is the critical potential, the definition of which is discussed below. This approach requires knowledge of several factors. Clearly, the values of E_{CRIT} and E_{OC} must be known. Both can be strong functions of environmental parameters such as chloride concentration, oxy-anion concentration, and temperature. See the chapter on waste package environment for a discussion of these factors. Of particular interest is the possible generation of oxidizing species over time that would increase E_{OC} and thus decrease ΔE .

Values of E_{CRIT} and E_{OC} can be measured for any given environment. These values will depend on the nature of the sample surface. The finish applied to the external surfaces of the canisters, defects inflicted during handling, and possible long term high temperature exposure during the initial years will all influence the sample surface in a way that could affect the values of E_{CRIT} and E_{OC} . Welding will change the microstructure in a way that apparently has a deleterious effect on localized corrosion resistance (Dunn, Cragolino et al. 2000). The open circuit exposure of the waste package to the lower temperature aqueous environment might also influence the values of E_{CRIT} and E_{OC} .

E_{CRIT} and E_{OC} will be distributed values with an average and a range. Any overlap of the distributions would be a cause for concern. If E_{CRIT} is a conservative measure, such as $E_{R,CREV}$ as described above, and is known for the exposure conditions, then any E_{OC} value below the lowest measured critical potential would, with high probability, be safe from localized corrosion. As will be described below, the value of ΔE determined by the Project approach using their data and definition is expected to be quite large (a large fraction of a volt). As a result, the Project has predicted that localized corrosion will not occur, and the localized corrosion module of the Total System Performance Assessment is never turned on. The Project has not articulated clearly in

any publication the minimum value of ΔE determined by their methods that would be sufficiently large to warrant the assumption that localized corrosion will never occur. When asked to provide such a value, Project personnel provided an answer of 200-400 mV.

Even given a sufficient separation of the E_{CRIT} and E_{OC} distributions, it is possible to ask if there exist reasonable localized corrosion phenomena that might occur at potentials far below E_{CRIT} . For instance, if metastable pitting is possible at low potentials, an accumulation of metastable pitting damage in a concentrated region, such as a crevice, over very long periods of time might integrate to a much larger rate of consumption than that resulting from passive dissolution. However, metastable pitting is probably not possible at potentials below E_{CRIT} if a conservative value is used, such as $E_{\text{R,CREV}}$.

8.2.2 Generation of Data

As described above, the ΔE approach requires determination of E_{CRIT} and E_{OC} . Project researchers are aware of the importance of understanding the conditions under which localized corrosion might occur and check for its presence in experiments that they perform for other purposes. Primarily, however, two types of experiments have been used to address localized corrosion susceptibility: cyclic potentiodynamic polarization experiments and immersion tests. Other experiments also indirectly examine localized corrosion resistance. This section will summarize the experimental work relevant to localized corrosion.

Cyclic Potentiodynamic Polarization Experiments. Most of the reported electrochemical testing for localized corrosion susceptibility has been cyclic potentiodynamic polarization (CPP) tests on nominally uncreviced samples. CPP experiments provide information regarding the behavior of a sample over a wide range in potential. The potential was scanned at 0.6 V/h from a value just below the E_{OC} to either a specific potential or a potential at which a specified value of current density was measured, such as 50 mA/cm². The scan direction was then reversed and the potential scanned back to the original E_{OC} . From CPP curves, it is possible to identify the various critical potentials described above, such as the breakdown and repassivation potentials. The samples have typically been disks pressed against the cell using a polymeric gasket. This type of seal is designed to minimize crevice corrosion, but it does not eliminate it; it is impossible to avoid crevices altogether. (Simple immersion of samples into a solution avoids crevices but can lead to waterline attack in some cases. This might not be a problem for Alloy 22, and waterline immersion might be the best approach for crevice-free exposure.) Any time that a breakdown potential is observed in a CPP curve, it is necessary to examine the sample to determine the form of the attack. The breakdown and repassivation can then be categorized as being associated with pitting or crevice corrosion. If one is interested in specifically investigating crevice initiation and repassivation potentials, it is best to use a sample with a controlled crevice configuration such as generated by the multiple crevice former described in ASTM G 78 (ASTM G78). CPP experiments on intentionally creviced Alloy 22 samples have been performed at the University of Virginia under contract to DOE in support of the Project (Kehler, Ilevbare et al. 2001).

Most of the Project CPP experiments were performed in the various predicted and accelerated environments. These environments have high oxyanion concentrations and do not cause localized corrosion of Alloy 22 and titanium Grade 7. A few experiments on Alloy 22 in pure chloride solutions have been reported in order to show the beneficial effects of the inhibiting oxyanions. The experiments at the University of Virginia were performed in solutions containing

very high chloride concentrations and varying chloride/oxyanion concentration ratios. These results are discussed below.

CPP experiments also provide a value of E_{OC} . E_{OC} can be measured during the initial immersion, or taken from the curve as the zero-current potential where the current changes polarity (where CPP curve points to minus infinity in a semilog plot). Zero-current potentials are an instantaneous E_{OC} , but can be different than the original E_{OC} owing to the initial cathodic polarization. The zero-current potential on the reverse scan is typically much different because of changes in the electrode and electrolyte. It should be clear that any value of E_{OC} is dependent on the surface conditions and environment. So the E_{OC} of a waste package could change considerably with time and be much different than the zero-current potential in a CPP experiment. Nonetheless, it is possible to determine values for E_B , E_R , and E_{OC} from a single CPP curve, and these values have been used to determine ΔE .

Long Term Corrosion Test Facility experiments. Ongoing experiments in the Long Term Corrosion Test Facility are examining the long-term immersion behavior of a range of materials, including Alloy 22 and titanium Grade 7, with several different configurations, including samples with intentional crevice formers, in a number of different environments. The primary purpose of these experiments is to determine corrosion rate by weight loss and to examine the sample surfaces for evidence of localized corrosion. The Long Term Corrosion Test Facility is a lab at Lawrence Livermore National Laboratory with multiple exposure tanks constructed of fiberglass-reinforced Hetrion 522 polymer, each with a capacity of 2000 liters and a solution volume of 1000 liters. Each tank holds a number of sample racks containing test samples of varying configuration. Some of the predicted and accelerated environments are being tested, including those designated as simulated concentrated water, simulated acidified water, and simulated dilute water. Currently, the temperatures of the test solutions are 60 and 90°C; tanks capable of higher temperature are being installed. Different alloys are exposed in a given tank, but they are all from a given class of alloys, such as titanium, nickel, or stainless steel. Samples in the Long Term Corrosion Test Facility are exposed above the solution, at the waterline, and immersed in the solution. All of the samples exposed in the Long Term Corrosion Test Facility are examined for localized corrosion when they are removed from the tanks, although one particular sample design is specifically used to test for localized corrosion resistance. The crevice corrosion samples use a standard Teflon multiple crevice former (ASTM G78), which is pressed against part of the sample using a spring.

As of July 2001, Project staff had made no electrochemical measurements in the Long Term Corrosion Test Facility, although corrosion potential and corrosion rate measurements by the linear polarization technique are planned. Recently, the Project has started to make electrochemical measurements on samples removed from the Long Term Corrosion Test Facility after long periods of exposure. U-bend samples have been removed from the test rack and tested on a bench in a separate lab using solution taken from the same tank. This approach should provide data identical to what would be measured directly in the exposure tanks.

8.2.3 Interpretation of Data

None of the Alloy 22 samples exposed at open circuit to any of the test environments has exhibited any form of localized corrosion to date. These test environments contain considerable concentrations of inhibiting oxyanions, the test temperatures are not as high as those that might be seen by the waste package, and the possible effects of oxidizing radiolysis products are not

addressed. Nonetheless, these data are supportive of the localized corrosion resistance of Alloy 22 in the anticipated Yucca Mountain environments. The observations showing no evidence of localized corrosion, at levels down to those observable by atomic force microscopy, are not subject to misinterpretation. On the other hand, the creviced samples exposed to the Long Term Corrosion Test Facility have exhibited a slightly higher weight loss than the nominally uncreviced "weight loss" samples (Pasupathi 2000). There was no evidence for localized corrosion on the creviced samples, but also no explanation for why the weight loss was higher. The intentionally creviced samples were initially more highly polished than the uncreviced samples to generate a tighter crevice fit, but the uniform corrosion rate of smoother samples would be expected to be lower.

The Project used CPP experiments to determine values of E_B , E_R , and E_{OC} . The determination of these potentials from CPP curves is straightforward. However, interpretation of their meaning and the decision of which should be used as the critical potential in the ΔE determination is less clear, as will be discussed in the next section.

8.2.4 Application of Data in Model

Localized Corrosion Initiation. The Project approach is based on the generic measure of $E_{CRIT} - E_{OC}$, where E_{CRIT} is the critical potential. Unfortunately, the Project has not clearly defined the meaning of critical potential in their usage and different values have been identified in different documents. Part of the problem results from the fact that the test environments used in the experiments do not typically produce localized corrosion in Alloy 22 or titanium Grade 7. Alloy 22 exhibits transpassive dissolution above a breakdown potential. Typical transpassive dissolution, including what is usually observed for Alloy 22 in these environments, does not result in a current hysteresis during cyclic potentiodynamic scanning. Instead, the transpassive attack stops or "repassivates" at or close to the transpassive potential, where the breakdown initiated (Farmer and McCright 2000). For a typical metal/environment system that does exhibit localized corrosion, a positive current hysteresis is observed and E_R is lower than the E_B (see Figure 1 in the appendix section on localized corrosion phenomenology). In this case, E_R is the more conservative value to use in the ΔE approach. Since transpassive dissolution rather than localized corrosion is observed for Alloy 22 in the test environments, the Project has considered the transpassive breakdown potentials to be the critical potentials for the ΔE calculation.

Identification of E_{CRIT} is complicated by the presence of a rather large anodic nose in the upward scan of the CPP curve for Alloy 22 in some solutions, such as simulated concentrated water. This nose is likely associated with the oxidation of one or more elements in the passive film, such as molybdenum, which can exist in multiple oxidation states in passive films. This phenomenon is a transient effect, and the current decreases after the peak of the nose. There is no evidence that this current is the result of localized corrosion or that this oxidation process has a deleterious influence on the passive film.

A slight positive hysteresis is observed upon scan reversal at high potentials in the transpassive region in some solutions, such as simulated concentrated water, although the hysteresis is not evident until lower potentials, which is not typical for localized corrosion. Some, but not all, samples that exhibited this type of behavior were examined after the experiments and found to show signs of crevice corrosion at the gasket (Farmer 2001). Not all samples were examined for crevice attack, but this type of behavior was conservatively assumed to be evidence of crevice corrosion, and the potential at which the current increased during the upward scan was assumed

to be E_{CRIT} in the ΔE calculation. It is quite possible, however, that any localized corrosion that might have occurred was actually initiated at a higher potential in the transpassive region.

In the latest Analyses and Model Report, the critical potential for Alloy 22 is considered to be the transpassive potential, which is extremely high (Farmer and McCright 2000). In contrast, the Abstraction, which defines the model for the Total System Performance Assessment, uses the lowest potential limit of the current nose for curves that exhibit such a nose (Lee 2000). Even though this potential is not associated with localized corrosion or any other form of breakdown, it is much lower than the transpassive potential, and thus much more conservative. The use of these potentials in the ΔE calculation means that the prediction for the presence or absence of localized corrosion is based only on data unrelated to localized corrosion. Project staff have not explored other environments, including more aggressive environments from which extrapolations could be made. The implications for this approach on the usefulness of the data are discussed below.

The actual model described in the Abstraction determines ΔE for Alloy 22 from each polarization curve using the zero current potential on the upward scan as E_{OC} and the potential at which the current nose first appears, or the transpassive potential for curves that do not exhibit a nose, as the critical potential (Lee 2000). The values of ΔE for Alloy 22 in the various environments have been fitted to an equation of the form:

$$\Delta E(\text{mV}) = 1260 - 0.313 T + 8.15 \log[\text{Cl}^-] - 188 \text{ pH} + 11.8 \text{ pH}^2 + \varepsilon \quad [1]$$

where temperature T is in $^{\circ}\text{C}$, $[\text{Cl}^-]$ is in mole/l, and ε is an error variance, which has a normal distribution and a mean of 0. It is interesting that this equation does not include a term describing the influence of inhibiting oxyanions, and is weakly dependent on temperature and bulk chloride concentration, despite the strong effect of these parameters on localized corrosion. The strongest dependence is on pH, and the function exhibits a minimum at about pH 8. These dependencies reflect the fact that the breakdown is associated with transpassive dissolution rather than localized corrosion.

The polarization curves for titanium Grade 7 show a breakdown and current increase at 800-1500 mV Ag/AgCl, which is probably the result of oxygen evolution at specific sites such as palladium clusters or fractures in the TiO_2 film (Shoesmith and Ikeda 1997). This again is not localized corrosion but the data have been treated in a similar fashion as for Alloy 22 (Lee 2000), with the fitted equation taking the form:

$$\Delta E(\text{mV}) = 2050 - 1.17 T + 14.1 \log[\text{Cl}^-] - 48.9 \text{ pH} + \varepsilon \quad [2]$$

where ε is an error variance. This function is weakly dependent on T and chloride concentration and decreases about 50 mV with each increasing pH unit (Lee 2000).

Growth of Localized Corrosion. Although it is a moot point in the current model because localized corrosion is predicted never to occur, the Project has developed a means to handle the growth stage of localized corrosion. If localized corrosion initiates in Alloy 22, Project staff predict that the growth will be constant with time at a rate that is log-uniformly distributed between 12.7 and 1270 $\mu\text{m}/\text{y}$, with a mean of 127 $\mu\text{m}/\text{y}$ (Farmer and McCright 2000). In one respect, this is a very conservative approach, since the rate of localized corrosion propagation typically slows with time, following a $d \propto t^{1/2}$ type of relationship (Frankel 1998). (Of course, conservatism here is irrelevant since the localized corrosion model is never utilized.) The Project has made no measurements of localized corrosion rate; the value of 127 $\mu\text{m}/\text{y}$ is the general (not localized) corrosion rate of alloy C-276 in dilute HCl at a few degrees centigrade below its boiling point (Sedriks 1996). In more concentrated HCl (10-20%) at a temperature that is a few

degrees higher, the corrosion rate of alloy C-276 is reported to be above 7620 $\mu\text{m/y}$ (Sedriks 1996). It is not clear that the rate of localized corrosion propagation can be related to the general corrosion rate determined in dilute HCl, since the environment within a pit or crevice would be quite concentrated.

For titanium Grade 7, the rate of localized corrosion growth is also assumed to be constant with time, if it were to occur at all (which is not predicted). The model assumes that the rate is uniformly distributed between 490 and 1120 $\mu\text{m/y}$ (Dobson 2001).

8.2.5 Alternative Approaches to Prediction of Waste Package Localized Corrosion

Other organizations have studied waste package performance and have developed different predictive models. These alternative approaches provide a valuable context for evaluation of the Project model.

Center for Nuclear Waste Regulatory Analysis. The Center for Nuclear Waste Regulatory Analysis (CNWRA) at Southwest Research Institute, funded by the US Nuclear Regulatory Commission, has a vigorous activity studying the corrosion prediction of materials related to waste disposal. They have been strong proponents of the ΔE design approach for localized corrosion, but have taken a slightly different approach.

CNWRA has provided some of the best evidence that repassivation potentials are independent of the extent of prior localized corrosion growth after sufficient growth or depth of attack (Sridhar and Cragolino 1993; Dunn, Cragolino et al. 2000). This allows the definition of a conservative value that is independent of experimental method. They make this value more conservative, as described above, by using creviced samples and thereby determining $E_{R,CREV}$. Much of the work was performed on Alloy 825, which was initially selected as a candidate container material and is less resistant than Alloy 22. The approach was validated by long-term potentiostatic experiments on Alloy 825 at potentials above and below $E_{R,CREV}$ (Dunn, Cragolino et al. 2000). Creviced samples initiated localized attack at potentials far below those at which non-creviced (waterline immersed) samples exhibited passivity breakdown. However, no attack was observed after 10^8 s (38 mo) on creviced samples for potentials below or even just above (~ 50 mV) the highest repassivation potential.

CNWRA experiments on Alloy 22 show that $E_{R,CREV}$ is considerably higher than that for Alloys 625 and 825 for chloride concentrations below 1 M (Dunn, Pan et al. 2000). It decreases with temperature and chloride concentration, and an expression was generated to express the relationships (Cragolino, Dunn et al. 2001):

$$E_{R,CREV}(\text{mV SCE}) = 1300 - 13.1 T + (2.3 T - 362.7) \log [\text{Cl}^-] \quad [3]$$

This relationship is valid for $[\text{Cl}^-] > 1$ M and temperatures between 80 and 105°C (Cragolino, Dunn et al. 2001). The effects of oxyanions have not been considered despite their strong inhibiting action.

CNWRA has developed a mixed potential model to predict E_{OC} of a passive metal metal (Cragolino, Mohanty et al. 2000). This model was originally developed for the old waste package design with a carbon steel outer pack, but has been applied to the new design using some different values (Dunn, Pan et al. 1999). It assumes a passive current density that is distributed between 6.3×10^{-8} and 2.0×10^{-7} A/cm², independent of potential, $[\text{Cl}^-]$, T, and time. This is a considerable simplification. The electrochemical kinetics of the oxygen and water reduction cathodic reactions are calculated assuming values for kinetic parameters. The values of E_{OC} generated by the mixed potential model are then compared to values of $E_{R,CREV}$, which are

distributed owing to spatial variations in temperature and [Cl⁻]. When E_{OC} is predicted to be higher than E_{R,CREV}, localized corrosion is assumed to initiate instantaneously. Once initiated, the penetration rate is assumed to be constant with time and equal to 250 μm/yr (Dunn, Pan et al. 1999). The constant rate of penetration is a conservative estimate, similar to that made by the Project.

University of Virginia. As mentioned above, the University of Virginia investigation studied the breakdown and repassivation of creviced Alloy 22 samples in 5 M lithium chloride brines containing nitrate and sulfate ions at a range of temperatures (Kehler, Ilevbare et al. 2001). The following equation is the result of a multiple regression analysis of the repassivation potentials measured:

$$E_{R,CREV}(\text{mV SCE}) = 2410 - 358 \log\left(\frac{[\text{Cl}^-]}{[\text{I}]}\right) - 20.41 T \quad [4]$$

where [I] represents the total molar concentration of inhibition oxyanions and T is in °C. Overlap of E_{OC} (~-45 to -195 mV SCE at 95°C) and E_{R,CREV} values indicated that there is a non-zero probability of crevice corrosion in solutions where ([Cl⁻]/[I]) = 100 or 10 at 95°C (Kehler, Ilevbare et al. 2001). The probability of attack approaches zero as the temperature is lowered. Extrapolation of Eqn. 4 to a molar ratio of 1, which is similar to the values predicted for the waste package environment, results in an E_{R,CREV} value that is far above the E_{OC} values that have been measured in the Long Term Corrosion Test Facility. This is consistent with the lack of evidence for localized corrosion in these environments over a long exposure period.

Electric Power Research Institute. A recent report sponsored by the Electric Power Research Institute (EPRI) takes a very different approach to localized corrosion prediction of waste package materials (Shoesmith 2000). Relative humidity rather than potential is considered to be the critical parameter. Of course, relative humidity is linked to temperature. As the temperature of the waste package decreases with time in the repository, the relative humidity will increase, eventually reaching a critical humidity at which an aqueous phase will form. There could be a period when the temperature is cool enough so that an aqueous phase would exist on the waste package (assuming failure of the drip shield), but hot enough so that the temperature would be above the critical crevice temperature in the local environment that forms on the surface. The critical crevice temperature is assumed to be 100°C based on the fact that Alloy 22 has survived for years in the Long Term Corrosion Test Facility at 90°C with no localized corrosion. The EPRI model assumes that crevice corrosion will definitely occur in the waste package environment when the temperature is in the critical range (Shoesmith 2000), which is a conservative assumption that ignores the inhibiting effects of the oxyanions likely to be present. This is in contrast to the assumptions of the Project model, which result in the prediction of no localized corrosion. The amount of time that a waste package will spend in this critical temperature range depends on its position in the repository, the waste package heat output, and ventilation period, and was calculated to vary between about 170 and 1100 years (Shoesmith 2000). The extent of damage is then determined by localized corrosion growth kinetics as the waste package cools through the temperature range in which growth is possible. The depth of attack, d, is assumed to follow a power law:

$$d(\mu\text{m}) = B t^n \quad [5]$$

where B is temperature independent and normally distributed between 5 and 100 with a mean of 55, t is time in years, and n is assumed to be uniformly distributed between 0.1 and 0.5.

Localized corrosion growth tends to follow a parabolic law, with n ≈ 0.5, which is predicted for growth limited by either transport or ohmic effects (Frankel 1998). Distributing n between 0.1

and 0.5 is a simple mathematical means to handle the possibility of repassivation. By setting $n \ll 1$, this growth model is much less conservative than the Project and CNWRA models, but it is more realistic. In the EPRI model, the contribution of localized corrosion to the failure distribution is relatively minor because of the limited time during which it will act (since it will repassivate below the critical crevice temperature) and the prediction that the rate will decrease with time (Shoemith 2000).

8.2.6 Work Planned for the DOE Project

The Project plans to address many different aspects of localized corrosion of the waste package and drip shield, according to information presented to this Panel at formal meetings and during informal discussions. These plans appear to have been influenced by the approaches taken by other labs as they incorporate some of the aspects discussed in the last section. A number of different activities have been discussed and presented; only a select few will be mentioned here.

- There seems to be a trend to treat the critical potential and E_{OC} separately, and to study breakdown in a wider range of solutions than those anticipated to form on the waste package. The breakdown potential will be examined in solutions with higher ratios of chloride/oxyanions, and higher temperature measurements in autoclaves will be performed.
- A mixed potential model to predict E_{OC} is already being developed by the Project. It is based on the Point Defect Model, and the developer of the Point Defect Model, D. Macdonald, is doing the work under subcontract. The goal is to have a prediction of E_{OC} evolution with time, which can be compared with critical potentials determined in a range of conditions, as is done in the CNWRA approach.
- Long term potentiostatic testing will be performed under a range of conditions to validate the critical potential approach, as has been done at CNWRA.
- The reactions occurring in the transpassive region will be examined to distinguish the extent of oxygen evolution and possible localized corrosion from transpassive dissolution.

8.3 ASSESSMENT AND RECOMMENDATIONS

8.3.1 Project Approach

The ΔE design criterion for the prediction of localized corrosion is viable and conservative if applied properly. However, the way in which the Project determines ΔE is inferior to other approaches, such as those described in section 4.5.5 above. The Project determines both E_{CRIT} and E_{OC} from CPP curves measured in solutions in which Alloy 22 and titanium Grade 7 do not exhibit localized corrosion. The fact that ΔE is positive in the environments predicted to form on the waste package supports the choice of these materials. However, it is inappropriate to base a prediction for localized corrosion resistance for an environment that is not exactly defined solely on data that are unrelated to localized corrosion. These data, and the results of the Long Term Corrosion Test Facility, only prove that Alloy 22 and titanium Grade 7 are extremely resistant to the tested environments; they do not allow prediction of the behavior in other environments. It is possible, though not likely, that a slightly different environment would cause

localized corrosion in Alloy 22. This is the major liability in the current approach of design based on experiments in a limited number of environments for service conditions that are not completely defined.

The Panel recommends that the Project determine ΔE in environments that cause localized corrosion, i.e. testing must be done in a range of more aggressive environments than those predicted to form. Furthermore, a conservative measure of E_{CRIT} should be sought, such as $E_{R,CREV}$, using a technique that allows for considerable active crevice growth prior to repassivation. Given $E_{R,CREV}$ values for a range of aggressive exposure conditions, it should be possible to extrapolate back to less severe environmental conditions.

The $E_{R,CREV}$ values could be used in two different ways. A range of possible waste package environments could be considered and the probability of achieving such conditions determined. Extrapolated values of $E_{R,CREV}$ could then be determined for the different environments with a range of probabilities. Alternatively, the Project could establish the boundary in environment space (E, T, pH, $[Cl^-]$, $[I]$, etc.) separating possible localized corrosion (breakdown associated with localized corrosion observed) from immunity to localized corrosion (passivity and transpassive breakdown only). The probabilities of achieving the various environments on that boundary could then be determined.

Furthermore, changes in the surface of the waste package over time will influence E_{OC} considerably. Evidence for changes in E_{OC} with time has been observed on samples exposed to the Long Term Corrosion Test Facility for 4 years. E_{OC} for some samples has increased by hundreds of mV relative to values measured on fresh samples in new solutions, a magnitude that comprises much of the ΔE margin. Determination of E_{OC} from the zero-current point on a potentiodynamic polarization curve is inappropriate for long term prediction. Experimental and theoretical (mixed potential model) approaches should be taken to determine E_{OC} . Comparison of these measured and predicted values of E_{OC} with the measured or extrapolated values of $E_{R,CREV}$ would comprise a valid approach to the determination of ΔE .

8.3.2 Issues to be Addressed

Other issues related to localized corrosion have not been addressed sufficiently. Some of these issues are included in the Project plans, whereas others have not been included to date.

Temperature. Temperature is a critical factor in localized corrosion with higher temperatures being more likely to cause localized corrosion. The Panel recommends that $E_{R,CREV}$ and E_{OC} values used for ΔE be determined at higher temperatures and most particularly at all temperatures to which the waste packages might be exposed in the presence of an aqueous layer.

Propagation and arrest. The Panel recommends that studies of localized corrosion propagation and arrest be undertaken to supplement work on initiation because these factors will control the accumulated extent of damage from localized corrosion should it occur. Experiments in aggressive environments provide the opportunity to study growth and arrest behavior. Since there is a chance that the waste package surface will be exposed only to a moist dust environment rather than to dripping or full immersion, the possible influence of such an exterior environment on limiting localized corrosion growth should be studied.

Metal surface condition. The Panel recommends that the effects of metal surface condition on localized corrosion be examined. The metal surface condition can have a large influence on the localized corrosion behavior. In general, the susceptibility to localized corrosion increases as the roughness of the surface finish increases. On the other hand, protective surface films can reduce

the likelihood for localized corrosion. Currently, the Project does not plan to provide special surface finishes or treatments to control the waste package or drip shield surface condition prior to emplacement; the surface condition will be a consequence of all prior processing and handling. Once emplaced, the waste package and drip shields will be exposed to air at high temperatures when the drift is closed.

Metallurgical condition. The structure of Alloy 22 might change during long-term aging at moderate temperatures, and will certainly change locally as a result of the multipass weld required to seal the canister. The Panel recommends that the influence of such structural changes on the susceptibility to localized corrosion be addressed.

Oxidizing agents. The Panel recommends that environments containing possible oxidizing agents, such as peroxide or ferrous/ferric, be investigated. The possible effects of radiolysis should be reevaluated for the current waste package design and expected condition of spent fuel.

Relevant exposure conditions. The Panel recommends that localized corrosion behavior be examined for the most relevant conditions that can result in wet environments in contact with metal surfaces: moist dust surface associated with humid air exposure or scale and deposits formed by evaporated drips. Full immersion of metal surfaces is a highly unlikely condition in the repository. It is unlikely that the thin aqueous layer on a waste package will be able to support the cathodic reactions needed to maintain localized corrosion to the same extent as possible in bulk solutions. This has not been addressed by anyone in the field of localized corrosion. The Panel recommends that analysis of the initiation, propagation and arrest of crevice corrosion and pitting under the conditions listed above be completed.

8.4 CONCLUSIONS

- The lack of evidence for localized corrosion after long periods of exposure in the anticipated waste package environments indicates that Alloy 22 and titanium Grade 7 are resistant to this form of corrosion in the selected environments.
- The ΔE design approach for the prediction of localized corrosion is viable and conservative if applied properly.
- The current Total System Performance Assessment model uses data from uncreviced, freshly prepared samples in a few anticipated environments in which Alloy 22 and titanium Grade 7 do not typically exhibit localized corrosion. Therefore, the ΔE values used in the current Total System Performance Assessment model are unrelated to localized corrosion. This is not an appropriate approach for the prediction of localized corrosion.
- The Project should follow an approach for determination of ΔE that is similar to that taken by other organizations. E_{CRIT} should be determined in aggressive environments that cause localized corrosion. E_{OC} should be measured and modeled separately.
- Other issues should be addressed. The effects of temperature, surface condition, metallurgical condition and oxidizing agents, including radiolysis should be clarified. Propagation and arrest of localized corrosion should be studied in more detail. Localized corrosion should be studied in the relevant exposure conditions: moist dust surface associated with humid air exposure or scale and deposits formed by evaporated drips.

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9. STRESS CORROSION CRACKING

Stress corrosion cracking may compromise the integrity of the waste package; the Project staff is addressing this integrity threat in the design of the waste package and in their research program. It is planned to mitigate stress corrosion cracking of the waste package through the use of the highly stress corrosion cracking resistant Alloy 22 and by control of residual tensile stresses. Research to date shows that nickel base Alloy 22 is highly resistant to stress corrosion cracking in the environments expected in the repository. The Project plans to relieve residual tensile stresses introduced during fabrication by a stress anneal of the entire canister prior to filling and final closure. In the vicinity of the final closure welds, beneficial residual compressive stresses will be introduced into the outer surfaces of the waste package by laser peening or local induction annealing heat treatments.

The mitigation method, experimental approach, and modeling efforts for stress corrosion cracking are consistent with the state of the art and appropriate research work generally is underway to verify the models. However, the Panel has identified a few deficiencies with the current program, as described below.

9.1 DESCRIPTION OF STRESS CORROSION CRACKING

9.1.1 Definition of Stress Corrosion Cracking

Stress corrosion cracking is a corrosion damage mode where slow crack growth in a metal or metal alloy is caused by the conjoint action of a tensile stress and a cracking environment. The metal is virtually undamaged over most of the surface while fine cracks propagate through it. The more general term environmentally assisted cracking encompasses stress corrosion cracking as well as corrosion fatigue (a result of cyclic loading) and hydrogen induced crack growth and embrittlement. Corrosion fatigue is not a relevant failure mode for the waste package because the stresses on the package will be static and cyclic loading is required for corrosion fatigue crack propagation. Hydrogen induced crack growth and embrittlement are discussed elsewhere in this document.

All engineering alloys are susceptible to stress corrosion cracking, but the environments that cause the cracking are alloy specific. Chloride and sulfur containing environments are the most common environments associated with stress corrosion cracking of stainless steels and nickel base alloys. Stress corrosion cracking of these alloys also has been reported in other halide

environments, in environments containing sulfur species, in caustic, and even in high purity water at high temperatures.

9.1.2 Relevance of Stress Corrosion Cracking to Repository Life

Stress corrosion crack propagation rates are low in comparison to rates for other crack propagation processes, such as brittle fracture, hydrogen embrittlement, or overload failure. Nevertheless, they are very fast from the standpoint of the desired life of a repository. For example, Roy (2000) reported a time-average crack growth rate of 5×10^{-9} mm/s over a one-year period for precracked specimens of Alloy 22 tested in a simulated tuff repository environment. The test solution was designed to simulate concentrated Tuff repository brine that had been acidified by microbial activity. This crack growth rate corresponds to through wall penetration of the canister in about 150 years. An order of magnitude higher crack growth rate was reported for another heat of Alloy 22 in shorter-term tests in this environment (Roy 1999).

Gerald Gordon (Waste Package Department Materials Team Lead, CRWMS/M&O) stated in a June 2000 presentation to the Under Secretary of the U.S. Department of Energy that the "Only potential viable mechanism that could lead to early through-wall penetration (of the waste package) is SCC." While some may disagree with this statement, there can be little argument that stress corrosion cracking is one of the primary potential failure modes of the waste package. Stress corrosion cracking has the potential to compromise the integrity of the waste package long before the design life of the repository has been reached.

9.2 PROCESSES AND CONTROLLING PARAMETERS

Three factors must be present simultaneously for stress corrosion cracking to occur; tensile stresses must be present in the metal, a cracking environment must be present, and the metallurgy (composition, microstructure, etc) must be susceptible to stress corrosion cracking. The stress corrosion cracking may be transgranular (cracking through the grains in the alloy) or intergranular (cracking between the grains) depending on the environment and the metallurgy of the alloy. Each of the three controlling factors is briefly discussed. The discussion encompasses both stainless steels and nickel base alloys because the two families of alloys are closely related and there is a continuum in the stress corrosion cracking behavior between the two. There is significantly more information on the behavior of stainless steels and Type 316 stainless steel is the primary candidate for the inner shell of the waste package. Therefore, it is useful to compare the stress corrosion cracking behavior of Type 316 stainless steel with that of Alloy 22.

9.2.1 Effect of Stress

Stress is defined as the load applied to a component divided by the cross sectional area and has units of Newtons per square meter (Mega-Pascals (MPa)) or pounds force per square inch (psi). As the load increases or the cross sectional area decreases, the stress in the component increases. In general, the likelihood of initiation of stress corrosion cracking and the rate of propagation of stress corrosion cracking increases with increasing magnitude of the tensile stress. Stress corrosion cracking will not occur in the presence of compressive stresses: the introduction of compressive stresses in the surface of a component by shot peening or other methods is a common procedure to prevent the initiation of stress corrosion cracking.

The stress in a metal can be applied or residual in nature. Residual stresses are introduced in a structure during fabrication, welding, or as a result of mechanical damage. In the case of the outer barrier of the waste package, the primary source of applied stress is the weight of the waste package applied at the supports. The primary source of residual stress is the final closure welding of the lid of the outer barrier. The Project plans to anneal the outer barrier following fabrication to minimize the residual stresses introduced prior to final closure welding. The Project also plans to perform a local induction annealing treatment on the closure weld. Further discussion of this issue is given under the section of the report on critical technical issues. Residual stresses also may be introduced in the outer barrier of the waste package following placement as a result of rock fall or failure of rock bolts in the tunnels if the drip shield were to fail catastrophically.

The residual stresses introduced in the outer barrier of the waste package by the final closure weld have been analyzed using a finite element modeling technique and measured using stress relaxation techniques. The results of the analysis are summarized in ANL-EBS-MD-000005 REV 00 ICN 01 (2000). At the metal surface, radial residual stresses may exceed 20% of the yield strength and residual hoop stresses may exceed 50% of the hoop stress.

The concept of a threshold stress is commonly used in conjunction with the process of initiating stress corrosion cracking. Below this threshold stress, the metal is considered to be immune to stress corrosion cracking, while cracking will readily initiate above this stress. Gordon (2000) and Andresen (2001) reported on the results of constant load stress corrosion cracking tests of Alloy 22 and 316 NG stainless steel and 304 stainless steel in 20% basic saturated simulated repository water at 105 to 125°C. Annealed Alloy 22 was resistant to crack initiation for the reported test duration of 2500 hours up to stresses of 2.1 times the yield strength of the alloy. The yield strength is defined as the stress level at which the metal exhibits a specified magnitude of permanent plastic deformation. A variety of other metallurgies and exposure conditions for Alloy 22 also were evaluated (including creviced, welded, and cold worked and ordered) and no crack initiation was observed for the reported test duration of 2500 hours up to stresses of 2.0 times the yield strength of the alloy. In these tests, 316 NG was resistant to crack initiation whereas 304 stainless steel that was heat-treated to produce grain boundary precipitation (sensitized) readily failed.

It is not uncommon in stress corrosion cracking initiation studies for typical engineering alloys to be resistant to stress corrosion cracking at stresses up to the yield strength yet these same alloys readily failure in service at stresses well below yield. The discrepancy between laboratory stress corrosion cracking initiation studies and field experience is the result, in part, of the presence of surface discontinuities (defects) in service equipment that locally concentrate the stress. These defects may be introduced in the mill, during component fabrication, or in service. Mill defects include non-metallic inclusions present in the alloy, defects introduced by the rolling process, or grain boundary attack as a result of cleaning (pickling) the metal surface with an acid. Weld defects are the most common type of fabrication defect. Time is another difference between laboratory tests and field behavior where long service times can lead to the development of environmental conditions that promote localized corrosion. Pits in the metal surface, formed as a result of localized corrosion, can act as stress concentrators and promote stress corrosion cracking initiation. Pitting can be especially deleterious because the acidic environments that develop within pits are frequently more potent cracking environments than the bulk environments.

The stress concentrating effect of a defect is proportional to the size of the defect and inversely proportional to its radius. For very sharp defects, i.e., ones with small radii, the stress at the tip of

the defect exceeds the yield strength of the material, even for relatively short defects. Under these conditions, the average stress in a component or structure is not an accurate driving force parameter for crack initiation or growth. The stress intensity factor K is commonly used as a driving force parameter for crack propagation in structures containing defects. This parameter is proportional to stress and the square root of the flaw size and has units of $\text{MPa m}^{1/2}$ ($\text{ksi in}^{1/2}$).

Ongoing research is being conducted by the Project to identify a threshold value of K , below which initiation of cracking at a pre-existing defect would not occur. This threshold value of K is referred to as K_{ISCC} . A K_{ISCC} value greater than $25 \text{ MPa m}^{1/2}$ has been estimated for Alloy 22 in concentrated saturated environments that simulate expected repository conditions. This K_{ISCC} value is considerably higher than values estimated for stainless steels in similar test environments, demonstrating the superior stress corrosion cracking performance of Alloy 22 over the stainless steels.

Research also has been conducted to investigate the relationship between the magnitude of the stress intensity factor, K , and crack growth rates above K_{ISCC} . As described in the introduction to this section, Roy (2000) reported a time-average crack growth rate of 5×10^{-9} mm/s over a one-year period for precracked double cantilever beam specimens of Alloy 22 tested in a simulated tuff repository environment. In these tests, the K varied between 39 and 45 $\text{MPa m}^{1/2}$. Andresen (2001) performed crack growth tests on compact type specimens of Alloy 22 at 110°C in aerated concentrated high-pH salt environments characteristic of concentrated Tuff Repository groundwater. Crack length was monitored in-situ using a reversing DC potential drop technique. Under static load conditions, very low rates of crack growth (5×10^{-10} mm/s) were measured for 20% cold worked Alloy 22 specimens at a stress intensity factor of $30 \text{ MPa m}^{1/2}$. Crack growth rates under cyclic loading (minimum/maximum load (R ratio) of 0.7 and frequency of 0.001 Hz) were an order of magnitude higher for annealed and 20% cold worked specimens.

9.2.2 Effect of Environment

Stress corrosion cracking of nickel base alloys has been observed in a number of environments, including halides (chlorides, bromides, iodides, and fluorides), sulfur containing environments (sulfides, sulfur oxyanions, and thiosulfates), caustic, and even high temperature water (Sridhar 1992). Cracking susceptibility generally increases with increasing concentration of the deleterious species and with increasing temperature. In the more benign environments, cracking may only occur in microstructures associated with grain boundary precipitation and this type of cracking is generally intergranular.

Laboratory testing of nickel base alloys is commonly performed in very potent artificial cracking environments, such as boiling magnesium chloride solutions, because of the high resistance to cracking of nickel base alloys and the need to accelerate the cracking process. Actual environments encountered in the field generally are less concentrated than the test environments and contain both cracking accelerators and cracking inhibitors. Therefore, alloys that may crack in laboratory testing may perform well in actual applications. For example, service experience indicates that alloys containing above 30% nickel are resistant to chloride stress corrosion cracking in most environments encountered in the chemical process and other industries (Sedricks 1992); whereas, Copson (1959) found that 50% nickel was necessary to impart resistance to cracking in tests in boiling magnesium chloride.

In studies of the effect of environmental factors on stress corrosion cracking of high-level radioactive waste containers, Dunn (1999) reported that precracked double cantilever beam

specimens of 316L stainless steel experienced extensive transgranular stress corrosion cracking at 110°C in 40% MgCl₂ solution but were resistant to cracking at 90°C in a 5% NaCl solution at a pH of 2.7. The latter environment is an aggressive concentrated simulated repository environment, but never the less, is a significantly less potent cracking environment than concentrated boiling magnesium chloride. Alloy 22 experienced minor cracking and grain boundary attack in the MgCl₂ solution and no cracking in the NaCl solution.

Minor constituents in the environment also may influence cracking behavior. Thomas et al (2001) characterized secondary-side intergranular stress-corrosion-cracking in Alloy 600 tubing from once through and recirculating steam generators with a wide range of local operating conditions. High-resolution transmission electron microscopy was used to identify the corrosion products and environmental impurities along deeply attacked grain boundaries. Despite the diverse operating histories of the samples, several common characteristics of secondary-side intergranular stress corrosion cracking were identified, including the presence of environmental impurities all the way to the crack tips. Lead was found in nm-wide oxidized zones at the leading edges of attack in four of six cases, including three where lead contamination in the aqueous environment was not reported. These results suggest that lead may be a contributing factor in many cases of secondary-side intergranular stress corrosion cracking in steam generators. Copper and minor sulfur were also found in the attacked grain boundaries in several samples.

9.2.3 Effect of Metallurgy

The composition and microstructure of an alloy can have a dramatic effect on susceptibility to stress corrosion cracking. In the case of stainless steels and nickel base alloys, it is well established that resistance to stress corrosion cracking in chloride environments increases with increasing nickel content. As described above, Copson (1959) developed the well-known time to failure curve for stressed steel wires of stainless steels and nickel base alloys in boiling concentrated magnesium chloride. The curve shows that alloys containing about 10 weight percent nickel exhibited a maximum in stress corrosion cracking susceptibility, while alloys containing more than about 50% nickel were resistant to cracking. Nickel may be beneficial in terms of either controlling the deformation mode or moving the corrosion potential away from the cracking range (Sridhar 1992). Alloy 22, which contains approximately 56% Ni, is highly resistant to chloride stress corrosion cracking.

Relatively little research has been performed to investigate the effects of other alloying elements on the stress corrosion cracking resistance of nickel-base alloys in chloride environments. In stainless steels, molybdenum at concentrations above 1.5% has been shown to be beneficial in mitigating chloride stress corrosion cracking, regardless of the cation present (magnesium or sodium). Alloy 22 contains 13% molybdenum. On the other hand, tungsten (an alloy addition to Alloy 22), and phosphorus (an impurity in Alloy 22) have been shown to be detrimental to chloride stress corrosion cracking performance of stainless steels. Other impurities in Alloy 22, such as sulfur and carbon, have been found to have a variable effect on chloride stress corrosion cracking of stainless steels (Sedriks 1992).

Alloy 22 is a metastable alloy, as described in the section of this report on alloy stability. When properly heat-treated, the alloy exhibits primarily a single-phase face centered cubic microstructure that is resistant to stress corrosion cracking and other forms of corrosion. Short-term exposure at high temperatures during welding or heat treatment or long-term exposures at

lower temperatures during service can lead to the formation of a variety of different types of precipitates at the grain boundaries, which can degrade stress corrosion cracking performance.

9.3 PROPOSED SCC LIFE PREDICTION MODELS

9.3.1 Threshold Stress Intensity Model

The stress corrosion cracking process is commonly broken down into two stages; the initiation stage and the propagation stage. One model proposed by the Project Staff for stress corrosion cracking initiation is the threshold stress intensity model referred to as SCC Model A (ANL-EBS-MD-000005 REV 00 ICN 01 [October 2000]). This model assumes that there is a threshold stress intensity factor, referred to as K_{ISCC} , below which a stress corrosion crack will not propagate even in the presence of a potent cracking environment and metal susceptible to stress corrosion cracking. The parameter K_{ISCC} is considered to be a material property, but it is a function of the exposure environment; the value decreasing with increasing potency of the environment. In order to apply the model, the driving force for crack initiation (applied stress intensity [K]) is compared with the value of K_{ISCC} . The applied K is a function of the flaw orientation and size, the dimensions of the structure and the magnitude of the stress. Crack initiation is assumed to occur only if the applied K is larger than K_{ISCC} .

9.3.2 Slip Dissolution/Film Rupture Model

The slip dissolution/film rupture model has been successfully applied to predict stress corrosion cracking behavior in a number of alloy-environment systems of practical engineering significance including pipeline steels in underground environments (Parkins 1977) and stainless steels and nickel base alloys in light water reactor environments (Andresen and Ford 1994). The model is based on the slip dissolution/film rupture mechanism and the environments in which this mechanism applies are passivating environments. Slip dissolution refers to the process of dislocations (defects in the crystal lattice) 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 unfilmed metal to corrode. The crack advances by anodic dissolution (corrosion) at the crack tip and 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. The maximum rate of crack advance can be calculated from Faraday's law, based on the corrosion kinetics:

$$V = (i_a M) / (z F \rho)$$

Where i_a is the anodic current density on a bare metal surface, measured electrochemically, M is the atomic weight of the metal or alloy, z is the valence change associated with the metal oxidation reaction, F is Faradays constant, and ρ is the alloy density. For potent cracking environments, crack growth rates of the order of 10^{-6} mm/s are typical for common engineering alloys, which corresponds to penetration in less than one year.

Penetration rates for stressed susceptible alloys in potent cracking environments usually are much lower than the maximum Faradaic rate because of the development and maintenance of passive films at the crack tip. Rupture of the films as a result of crack tip creep and repassivation of these films are contributing factors in determining the rate of crack advance. Ford and Andresen (1988) developed a model to account for these processes:

$$V = (\dot{\epsilon}_{ct} / \dot{\epsilon}_t)(MQ_f)/(zF \rho \epsilon_f)$$

Where $(\dot{\epsilon}_{ct} / \dot{\epsilon}_t)$ is the strain rate at the crack tip, ϵ_f is the strain required to fracture the passive film at the crack tip and Q_f is the oxidation charge per film rupture event.

The oxidation charge per film rupture event (Q_f) is equal to the integral of the current density (i_t) over the time period between the events (t_f). The parameter t_f is equal to the fracture strain divided by the crack tip creep rate $[\epsilon_f / (\dot{\epsilon}_{ct} / \dot{\epsilon}_t)]$. The parameter i_t follows a power law relationship:

$$i_t = i_0 [t/t_0]^{(-n)}$$

Where n is the power law exponent and i_0 is the current density on a bare metal surface at short times following film rupture (t_0). The crack propagation equation can then be reformulated:

$$V = A (\dot{\epsilon}_{ct} / \dot{\epsilon}_t)^n$$

Where A and n are material constants that are a function of the potency of the cracking environment. These constants can be derived from first principles (mechanical properties of the alloy and passive film) and electrochemical testing but can be determined from fitting crack growth rate data. Ford (1988) established an empirical relationship between A and n for 304 stainless steel in 288°C water.

$$A = 7.8 \times 10^{-3} n^{3.6}$$

Ford and Andresen (1988) also derived a relationship between the crack tip creep rate, the stress intensity factor (K_I). For constant load conditions, the equation becomes:

$$V = \bar{A} (K_I)^{\bar{n}}$$

For 304 stainless steel in 288°C water, an empirical relationship between \bar{A} and A , and \bar{n} and n were established.

$$\bar{A} = A(4.1 \times 10^{-14})^n$$

$$\bar{n} = 4n$$

Further details of the derivation are given in Ford 1988, Andresen 1994 and in (ANL-EBS-MD-000005 REV 00 ICN 01).

This model predicts that the crack velocity is proportional to the applied stress intensity factor raised to an exponent \bar{n} . In general, susceptibility to stress corrosion cracking decreases with

increasing n , primarily because of the effect of n on \bar{A} . On the other hand, the crack velocity becomes much more sensitive to changes in K with increasing n because of the power law relationship. These effects are shown graphically in Figure 1 for $n = 0.1$ and $n = 1$.

9.4 DATA AND MODEL APPLICATION

9.4.1 Threshold Stress Intensity Model

The Project Staff has evaluated the likely range in the stress intensity factor for the Alloy 22 outer barrier of the waste package. This range is based on the expected residual stresses and flaws present in the package. Only residual stresses were considered based on analyses, which indicate that other loads on the waste package, such as dead weight loads, produce insignificant stresses. A finite element model was used to estimate the residual stresses in the barrier caused by the closure welding process. It was assumed that the primary source of crack like flaws in the outer barrier is the welding process and both surface breaking flaws and those near surface flaws that may be exposed by general corrosion were evaluated. The distribution of flaws was estimated from industrial experience with similar welding processes. The as-welded condition, as well as two methods of stress reduction, was evaluated. The Project plans to reduce residual tensile stresses in the waste package by means of a stress anneal and water quench of the entire Alloy 22 waste canister, followed by an induction anneal or laser peening of the final closure welds.

The estimates of K_{ISCC} are based primarily on tests with pre-cracked wedge loaded double cantilever beam specimens exposed in simulated concentrated repository environments. The crack extension is measured by compliance methods and fractographically. In five to eight month tests, the mean value of K_{ISCC} was estimated to be $33 \text{ MPa m}^{0.5}$ with a standard deviation of 1.77 in acidified (pH 2.7) brine at 90°C (Roy 1998). In a subsequent publication (Roy 2000), no cracking was detected in one-year exposures in this environment at K values of 18 to $33 \text{ MPa m}^{0.5}$. At higher stress intensity factors, crack growth rates were an order of magnitude lower than reported in the previous study.

K_{ISCC} values also were estimated from crack growth tests performed on precracked compact tensions specimens in a simulated concentrated basic (pH 13.4) repository water at 110°C (DTW: I1000810412251.010). A reversing DC potential drop technique was used to measure crack growth and the load on the specimens was periodically cycled to promote crack growth. In one test performed at an applied K_I of $30 \text{ MPa m}^{0.5}$, the crack arrested when the load cycling was stopped. It was concluded that the K_I value used in the test was very near the K_{ISCC} .

9.4.2 Slip Dissolution/Film Rupture Model

The slip dissolution model is assumed to turn on when the applied stress on the outer canister is above a threshold stress value (σ_{th}). As in the threshold stress intensity model, residual stress from fabrication is the primary source of stress assumed in the evaluation. The estimate of the threshold stress has evolved, as stress corrosion cracking data on Alloy 22 and other corrosion resistant alloys have become available. In ANL-EBS-MD-000005 REV 00 ICN 01 (October 2000), the σ_{th} was assumed to be between 10 and 40% of the yield strength. The lower bound was based on data for 304 and 316 stainless steels while the upper bound was based on data for more cracking resistant Fe-Cr-Ni alloys in aggressive environments such as boiling magnesium

chloride. This threshold stress has been increased to 80 to 90% of the yield strength based on data from U-bend and slow strain rate tests on Alloy 22 in simulated relevant and bounding repository environments (TDR-MGR-MD-00007 REV 00, June 2001).

Current estimates of n for Alloy 22 range from 0.84 to 0.92, based on crack growth tests of this alloy under cyclic loading at 110°C and a K_I of 30 MPa (m)^{1/2} in a concentrated mixed salt solution (ANL-EBS-MD-000005 REV 00 ICN 01). This compares with an n value of 0.54 for 304 stainless steel in 288°C water. The variability of n as a function of environmental factors has not been established. The values of A and n estimated from this crack growth testing are converted to \bar{A} and \bar{n} values for constant load conditions using the correlations established for stainless steels at 288°C in high-purity water. Crack velocity as a function of stress intensity factor for n values of 0.54, 0.84 and 0.92 are shown in Figure 1. Note that the calculations shown in Figure 1 were based on the equations using \bar{A} and \bar{n} for constant load conditions. The times required to penetrate a canister wall as a function of stress intensity factor and n based on these crack velocities are shown in Figure 2. These data indicate that the predicted canister life drops below 10,000 years for K_I values above about 10 MPa (m)^{1/2}, even for the least conservative value of n (0.92).

9.5 IMPORTANT TECHNICAL ISSUES

Described below are the important technical issues identified by the Panel that are associated with the Project staff's approach for mitigation of stress corrosion cracking of the waste package. Specific issues relevant to stress corrosion cracking initiation and growth models, stress mitigation techniques, and alloy stability are identified.

9.5.1 Threshold Stress Intensity Model

An important critical issue with the threshold stress tests is the sensitivity of the crack growth measurement techniques. This issue is not specifically discussed in the cited references. In similar testing, a Nuclear Regulatory Commission contractor (Cragolino 2001) has estimated a crack detection sensitivity of 10 to 30 μ m, based on fractographic examination of the specimens. Considering the higher sensitivity estimate and a test duration of one year, a pre-existing 5 mm deep crack could propagate through the wall of an Alloy 22 waste package in 2000 years. In other words, the canister could failure in one fifth of the design life at a stress intensity factor where no crack growth is expected to occur, based on the threshold stress intensity model. The predicted failure time would be less than 1000 years for the lower sensitivity estimate. It is not unlikely that the large discrepancy in the crack growth data reported by Roy in the two citations is the result difficulties encountered in confidently measuring such small amounts of crack extension.

Elastic compliance is the second technique used by the Project Staff for measuring crack extension in the double cantilever beam specimens. This technique involves comparing the slope of a load deflection curve measured on the specimen before and after exposure. The measurement is performed by loading the specimen in a mechanic test frame and measuring the crack opening displacement using a clip gage or LVDT. Guidelines for the use of compliance to determine crack length are given in Annex A2 of ASTM E 647 (Standard Test Method for Measurement of Fatigue Crack Growth Rates) and relate ASTM procedures. The accuracy of the technique is dependent on a number of factors including the calibration resolution, linearity of

the equipment, and the reproducibility of accurately placing the displacement measuring gages. The accuracy is not explicitly indicated in the ASTM references, but given the macroscopic nature of the measurement it is unlikely to be more accurate than direct observation of the fracture surface. In fact, calibration of the technique is normally based on fractographic observations.

Reversing DC potential drop is the third technique used by the Project staff for measuring crack extension. Andresen (2001) does not specifically identify a sensitivity for the technique but he claims the ability to accurately measure crack growth rates of 5×10^{-10} mm/s. This rate corresponds to 158 mm of crack growth in 10,000 years.

9.5.2 Slip Dissolution/Film Rupture Model

Issue 1 – Threshold Stress. The slip dissolution model, as developed by Ford (1988), does not contain a threshold stress or stress intensity factor. It assumes that crack propagation will occur if a crack like defect is present and there is dynamic strain at the crack tip. The Project staff developed the threshold stress component in the application of the slip dissolution model to the waste package. This use of a threshold stress, determined based on crack initiation tests for smooth specimens, is not conservative.

In engineering applications, stress corrosion cracks occasionally initiate from smooth free surfaces in the absence of defects in instances where a very potent cracking environment is present. More commonly, the environments are less potent and the metals are more resistant to stress corrosion cracking. Under these circumstances, stress corrosion cracking, if it does occur, initiates from defects. Common initiation sites for stress corrosion cracking include weld defects, areas of mechanical damage, metallurgical defects, and regions of localized corrosion. Stress corrosion cracking of underground pipelines is one example of the discrepancy between laboratory tests on smooth specimens and field experience. Stress corrosion cracking tests on smooth tensile specimens of line pipe steels in field cracking environments invariably produces threshold stresses near the yield strength. On the other hand, stress corrosion cracking has been found at operating stress as low as about 50% of the yield strength. This discrepancy is partly the result of residual stresses in the line pipe but surface defects play a role. Threshold stresses generally drop 20 to 30% when actual pipe surfaces, which contain small pits and inclusions, are used in the testing.

Issue 2 – Crack Growth Predictions. In the application of the slip dissolution model to Alloy 22, the calculation of A and the conversion from n to \bar{n} and A to \bar{A} are based on empirical relationships developed for 304 stainless steel in 288°C water (ANL-EBS-MD-000005 REV 00 ICN 01 (October 2000)). It is not intuitively obvious that these conversions should be applicable. The deformation behavior at the crack tip is a critical aspect of the slip dissolution model and the behavior of nickel base alloys is quite different than that of stainless steels. The stacking fault energy of nickel base alloys is three to four times larger than that of 304 stainless steel (Gordon 1977) and deformation behavior is closely related to the stacking fault energy of a metal.

Stacking faults are created in face centered cubic iron and nickel base alloys by alteration in the sequence of the stacked layers of atoms, producing hexagonal close packed regions enclosed by partial dislocations. Because stacking faults are internal surfaces, energy is required for their creation and growth. Stacking faults occur much more readily in low stacking fault energy alloys such as 304 stainless steel than high stacking fault energy alloys such as Alloy 22. Low stacking fault energy alloys exhibit planar deformation along slip planes, creating stress concentrations at

inhomogeneities in the microstructure, such as grain boundaries and inclusions. High stacking fault energy alloys, such as Alloy 22, exhibit non-planar slip, with the development of dislocation tangles. The slip behavior and dislocation distribution influence work hardening and creep behavior and therefore would be expected to affect the parameters in the slip dissolution model.

Issue 3 – Sensitivity to Crack Growth As in the threshold stress intensity model, a critical issue in establishing the magnitude and variability of the constants in the slip dissolution model is the sensitivity of the crack growth measurement techniques. Andresen (2001) does not specifically identify a sensitivity for the reversing DC potential drop technique but he claims the ability to accurately measure crack growth rates of 5×10^{-10} mm/s. This rate corresponds to 158 mm of crack growth in 10,000 years, which is well below the sensitivity necessary for establishing the constants under non-accelerated testing conditions. In TDR-MGR-MD-000007 REV 00 (June 2001) it was stated that "the measured growth rate on 20% cold worked Alloy 22 samples was approximately 4×10^{-10} mm/s, a rate that is near the lower limits of such measurements" in what appears to be the same or similar tests.

9.5.3 Stress Mitigation

As described above, the Project plans to reduce residual tensile stresses in the waste package by means of a stress anneal and water quench of the entire Alloy 22 waste canister, followed by an induction anneal or laser peening of the final closure welds. In the pulp and paper industry, early stainless steel suction rolls were made from Type 316 or CF-8M (the cast equivalent) materials (or early austenitic stainless steels with significant amounts of ferrite; i.e. Alloy 63). As part of the manufacturing process, they were solution annealed and water quenched to remove sensitization and sigma phase. Premature failure problems were found with some of these rolls. Research studies revealed that these failures were caused by high tensile residual stresses induced during the quenching process. It was found that slow air or furnace cooling after annealing was required to minimize tensile residual stresses in the large diameter, heavy section rolls. Slow cooling, however, sensitized Type 316 or CF-8M materials. For this reason, stainless steel alloys were developed that could be slow cooled without being sensitized. Today, typical suction rolls are made of proprietary grades of duplex stainless steels that are not sensitized by slow cooling after solution annealing.

In the fabrication of nuclear waste containers, the quenching process after solution annealing could produce unacceptably high tensile residual stresses. On the other hand, slow cooling could lead to the initiation and growth of deleterious grain boundary precipitates.

9.5.4 Alloy Stability

The Project's future corrosion test plans include the evaluation of the stress corrosion cracking resistance of aged and welded and aged microstructures in simulated repository environments in the Long Term Corrosion Test Facility. The specimens will be aged to produce grain boundary precipitation, but currently there are no plans to evaluate the different stages of aging. The early stages may be more deleterious than later stages. For example, the potential for chromium and molybdenum depletion near the precipitates may be greater early in the aging process, and this depletion may be healed later in the process. Further details are given in the section of the report on Alloy Stability.

9.5.5 Environmental Considerations

Minor constituents in the repository environment may influence cracking behavior. In a study of secondary-side intergranular stress corrosion cracking in Alloy 600 tubing from once-through and recirculating steam generators, lead was found at the leading edges of cracks in several instances including three where lead contamination in the aqueous environment was not reported.

9.6 RECOMMENDATIONS

9.6.1 Threshold Stress Intensity Model

There are at several possible approaches to the resolution of the problem of crack growth sensitivity and the definition of K_{ISCC} . The most conservative approach is to assume that crack propagation will occur for all positive values of K , i.e., assume that K_{ISCC} is zero. The problem is then reduced to a calculation of the probability that a flaw will exist in the waste package that is large enough to extend below the compressive stress layer introduced by the stress mitigation techniques. The influence of general and localized corrosion on the stress distribution in the canister will have to be evaluated to establish the time at which the flaw will experience positive values of K . At this time, the crack growth model would be turned on.

There are a few methods to improve the sensitivity to crack extension. The exposure times and number of replicate tests could be increased in the current design of the double cantilever beam tests to improve sensitivity. For example, a 10-year exposure period and a crack detection sensitivity of 10^{-4} m would provide a threshold stress intensity factor that would correspond to a 20,000-year life. A second approach is to use the electric potential drop (EPD) technique and accurately establish a maximum sensitivity to crack growth. Some form of accelerated testing in conjunction with detailed posttest examination would be required since confirmation of crack growth, even for EPD measurements, typically is based on fractographic evidence.

Another resolution path to establish a conservative value of K_{ISCC} is by accelerating the test and extrapolating back to the expected repository conditions. Since stress is incorporated in K , it cannot be an accelerating factor. The frequency of cyclic loading is a possible acceleration factor. Tests could be performed at several frequencies and the data extrapolated to constant load conditions. Environmental factors such as temperature and solution concentration also are available for acceleration. It is prudent to use at least two methods of acceleration to ensure that the cracking mechanism does not change as a result of the acceleration. Extrapolation with the two methods should give the same estimate of K_{ISCC} at the expected repository conditions.

9.6.2 Slip Dissolution/Film Rupture Model

Issue 1 – Threshold Stress. The Pane recommends that the Project abandon the threshold stress component of the slip dissolution model for the welds, which will contain flaws. Considering the incorporation of K_I in the slip dissolution model, it seems obvious that the model should be coupled with the K_{ISCC} threshold stress intensity model. The threshold stress model may be applicable for the unwelded portions of the waste package if it can be demonstrated that flaws will not be present and that localized corrosion, which can produce stress concentrators, is unlikely to occur. It is reasonable to continue the stress corrosion cracking tests on smooth

specimens since they are relatively inexpensive to run and provide useful data for screening test environments. Attention should be given to the use of realistic surface finishes for the specimens.

Issue 2 – Crack Growth Predictions. The Panel recommends that the Project develop sufficient crack growth rate data for Alloy 22 to confidently establish A , n , \bar{A} , and \bar{n} values for this alloy. The development of the model parameters specific to Alloy 22 may actually improve the predicted likelihood that the canister will survive the 10,000-year repository life. As described above, the current model, which uses the constants derived from data for 304 stainless steel, predicts inadequate performance for the Alloy 22 canister for moderate K_I levels above the threshold stress or threshold stress intensity factor.

Issue 3 – Sensitivity to Crack Growth. The panel recommends that the Project establish the maximum sensitivity of the electric potential drop technique to crack growth, using a combination of accelerated testing and fractography. Accelerated testing also may be necessary to establishing value of A , n , \bar{A} , and \bar{n} for Alloy 22 if it is found that the sensitivity is inadequate. As in the threshold stress intensity testing, it is prudent to use at least two methods of acceleration to ensure that the cracking mechanism does not change as a result of the acceleration. Extrapolation with the two methods should give the same estimate of the constants at the expected repository conditions.

9.6.3 Alternative Stress Corrosion Cracking Models

The Panel recommends that alternative models for stress corrosion cracking be considered by the Project. Alternative models can provide validation and support for the Project approach. Alternative models also may be required if the current models are found to be deficient.

9.6.4 Stress Mitigation and Alloy Stability

The panel recommends that the issue of heat treatment for stress mitigation and alloy stability be thoroughly evaluated. Two approaches can be employed to minimize tensile residual stresses induced by cooling after solution annealing. The first is to slowly cool the fabricated containers as is done for suction rolls in the pulp and paper industry. This approach would require the use of a nickel base alloy that is not susceptible to sensitization during the slow cooling process. The second is to carefully design and control the quenching process so that minimal levels of tensile residual stress are produced at or near free surfaces during the quenching operation. The selected approach should be verified by finite-element thermal and stress analysis and by experimental measurements on prototype containers.

The Panel also recommends that the effects of early stages of ordering, grain boundary segregation, and impurity segregation on stress corrosion cracking be evaluated. These processes may be dependent on the composition of the alloy, so the role of heat-to-heat variation on stress corrosion cracking behavior should be evaluated for the different stages of aging.

9.6.5 Environmental Considerations

The Panel recommends that the issue of the effects of minor constituents, such as lead, in the repository environment on stress corrosion cracking be evaluated in the testing program.

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10. HYDROGEN EFFECTS

10.1 INTRODUCTION

The high strength and excellent resistance to corrosion of high performance nickel-chromium-molybdenum alloys such as Hastelloy C-276 and Inconel X-750 are attractive characteristics of materials of construction for engineering systems where chemical stability is important (Latanision, 1985). Although these alloys were originally intended for service in high temperature applications they have become widely used in hostile aqueous environments such as deep sour gas wells. The latter contain, in addition to hydrocarbons, acid gases such as CO₂, H₂S and various brine components at temperatures up to 450F and at pressures often in excess of 20 ksi (138Mpa). It was once considered that such nickel-base alloys were resistant to chloride induced transgranular stress corrosion cracking. Recent work, however, shows that these alloys are susceptible to such embrittlement in high temperature (400F, NACE solution – 5%NaCl, 0.5% acetic acid saturated with H₂S) chloride environments (Berkowitz and Kane, 1980), (Asphahani and Tawancy, 1981), (Asphahani, 1978). In addition, such alloys are susceptible to low temperature intergranular hydrogen embrittlement in 25C NACE solution (Berkowitz and Kane, 1980), (Asphahani, 1977), (Coyle, Kargol and Fiore, 1981), (Sridhar, Kargol and Fiore, 1980). Moreover, the resistance to hydrogen embrittlement and to (chloride) stress corrosion cracking appears to have quite different functional dependence on metallurgical history. In short, resistance to hydrogen induced cracking does not correlate with resistance to (chloride) stress corrosion cracking. Indeed, in the case of deep sour gas wells, for example, there is no single material that resists both hydrogen embrittlement and stress corrosion cracking at the strength level required.

10.2 THE PHYSICAL METALLURGY OF HYDROGEN SUSCEPTIBILITY

In service environments ranging from high purity water to deep sour gas wells, the corrosion and embrittlement characteristics of nickel base alloys have been found to be intimately related to the physical metallurgy of the alloys, Intergranular corrosion, stress corrosion cracking and hydrogen embrittlement have been associated with, for example, grain boundary microstructure and microchemistry, solute segregation, ordering phenomena, etc. (Latanision, 1985). The evolution of microstructure and corresponding structure-property- relationships are integral to performance of alloys under service conditions.

The hydrogen embrittlement of Hastelloy C-276 serves as a useful guide to the behavior of nickel-chromium-molybdenum alloys. Berkowitz and Kane (1980), for example, have shown that embrittlement susceptibility is increased by aging treatment conducted in the range of 200-500C following cold work. No failures were observed in C-ring specimens exposed to 25C NACE solution that was not galvanically coupled to mild steel, implicating hydrogen as a prerequisite to failure. Similar observations were made by Blanchet, et al., (1977) with respect to the intergranular cracking of Inconel 600 in high temperature water. Moreover embrittlement resistance decreased with the time or temperature of aging treatment: short times at high

temperature or long times at low temperature decreased resistance to embrittlement.. Cold worked samples that were unaged were found to exhibit high resistance to intergranular embrittlement.. There is a remaining concern in downhole applications that alloys strengthened by cold work may age and embrittle in service at downhole temperatures. Based on the evidence that tramp elements in the alloy could markedly increase susceptibility to embrittlement (Latanision and Opperhauser, 1974), it was proposed that grain boundary impurity segregation might play a major role in embrittlement.. Auger electron spectroscopy studies of aged and unaged C-276 samples charged with hydrogen revealed phosphorus segregation to the grain boundaries that correlated with the aging treatments. Experimental low-phosphorus heats were examined in the same experimental conditions and showed resistance to embrittlement when bulk phosphorus levels were lowered substantially below commercial limits. This work demonstrated that intergranular hydrogen embrittlement was intimately associated with phosphorus segregated grain boundaries.

It should be emphasized that while many such studies of hydrogen embrittlement have been conducted on C-276, the mechanism by which cracking occurs remains the subject of considerable controversy. One school (Berkowitz and Kane, 1980) argues that the observed phosphorus segregation to the grain boundaries in embrittled alloys has the effect of stimulating the absorption of atomic hydrogen at the grain boundaries. Phosphorus is one of many metalloids (others include sulfur, antimony, tin, arsenic, etc.) which are electrocatalytic poisons for the (atomic) hydrogen recombination reaction and, therefore, limit the formation of molecular hydrogen while simultaneously increasing the population of atomic hydrogen on an electrode surface, thus increasing the likelihood that adsorbed atomic hydrogen will become absorbed. While metalloid segregated grain boundaries might be expected to serve as preferential sites for atomic hydrogen absorption into solids, soluble metalloid salts or gases are also known to stimulate hydrogen absorption from electrolytes on a more general scale. Another school (Asphahani and Tawancy, 1981), (Coyle, Kargol and Fiore, 1981) on the other hand argues that ordering, which occurs upon aging, prompts planar slip and may in turn enhance crack nucleation at emergent slip steps, increase internal stress concentration at dislocation pile-ups and/or promote transport of hydrogen by a dislocation drag mechanism.

Gdowski (1991) has summarized the literature in 1991 with respect to hydrogen effects in Ni-Cr-Mo alloys on behalf of the Project. He has correctly identified the variables that affect susceptibility: alloy composition, cold work, aging, impurities, temperature, stressing direction and the environment. Not all nickel-chromium-molybdenum alloys are equivalently susceptible, for example. There remains to the present date, no information of which we are aware on the susceptibility of Alloy 22. It appears that hydrogen susceptibility has been discounted as a potential degradation mode because the waste containers are expected to have sufficient strength with Alloy 22 in the annealed condition (1), and other alloys in this family have shown resistance to hydrogen embrittlement when in this condition. There is, however, no evidence to support this conclusion for Alloy 22. Given that susceptibility is dependent on specific alloy composition, there is no basis for assuming that Alloy 22 will behave similarly. Moreover, it is likely that residual stresses will be introduced into the waste package during fabrication; for example, during welding and quenching operations. Finally, it must be recognized that embrittlement will not occur without a source of hydrogen. While it may seem unlikely that hydrogen would be present in an otherwise oxidizing environment, there is no doubt that the chemistry in local corrosion cells may produce hydrogen under such conditions (see for example Shively, et al. (1967).) Likewise, the potential for microbiologically influenced corrosion chemistry and/or

trace element geochemistry at the site that may produce hydrogen and stimulate its absorption has not been fully explored.

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11. CONTRIBUTING FACTORS

In this section, several contributing factors to the long-term performance of waste packages are presented. The topics are presented in two categories: (a) Design and Fabrication Factors and (b) Corrosion, Chemistry and Metallurgy Factors. Each of the topics has been drawn from a Special Topic Report prepared for the Panel by individual Panel members or subject matter experts who assisted the Panel in gathering information. Full versions will be available in a "Compilation of Special Topic Reports" for the Waste Package Materials Performance Peer Review.

The purpose of each Special Topic Report was to gather information on a relevant factor to the long-term performance of waste packages. Authors of the reports were selected for their expertise and background on the particular topic. The Panel used these reports as background and input to the review. Any views and comments expressed in the reports do not necessarily reflect the opinion and findings of the Panel.

11.1 DESIGN AND FABRICATION FACTORS

The design and fabrication details can have a great effect upon corrosion and mechanical behavior of waste packages. The Panel notes a gap between the design/fabrication effort and the materials/corrosion effort on the Project. The former needs to recognize and control the effects of fabrication processes on metallurgical structure and residual stresses, and the latter needs to express findings in useable guidelines to direct design and fabrication decisions. For example, thermal treatments need to be selected with awareness of their effects upon metallurgical structure. Waste packages can be fabricated to meet the relevant specification regarding mechanical performance but have a detrimental microstructure for corrosion performance. The condition of the metal surface, i.e. surface roughness, residual stresses, oxide films and surface contaminants, can adversely affect corrosion performance.

The materials performance and corrosion work to date has focused primarily on supporting performance assessment. The Panel concludes that it is time to balance this effort with work to support design and fabrication of the waste packages. In particular, work is required on weld and weld repair processes. This is not a recommendation to end the science program, but rather to redirect and balance the science effort to support design and manufacture/fabrication for long-term performance. Many of same scientist/engineers and experimental/modeling procedures are appropriate to address the important issues with regard to the fabrication of durable waste packages.

Fabrication processes affect the surface condition, metallurgical condition, and stress patterns of the waste packages. Welds are a primary area of concern. The effects of other fabrication processes, such as solution annealing, assembling of dual cans, and induction heating are also important. Tight areas of contact (crevices) between metals are potential trouble spots for corrosion.

11.1.1 Fabrication Processes and Metallurgy: Sub-Panel Meeting

[after Wong-Special Topic Report]

The objective of this meeting was to obtain technical input on metallurgical issues associated with the waste package fabrication process from a group of international materials and corrosion experts. The experts agreed that the fabrication processes proposed for the waste package are in the main routine methods that are widely used in many industries. However, the tolerances required for the waste package were viewed as a critical aspect in the manufacturing process. There was a great deal of discussion on the effects of mis-alignments between the inner and outer shells of the waste package, since these could lead to significant bending moments in the circumferential welds of the waste package. The Project staff noted that machining tolerances were also deemed the "rate-determining" step in the waste package fabrication sequence, based on discussions by fabricators at the 2000 Waste Package Fabrication Workshop sponsored by the Nickel Development Institute.

There was a significant amount of discussion about waste package welding and its effects on material performance. Many experts noted that, from a metallurgical perspective, the welds are the areas of the waste package that would most affect long-term performance. Of all the fabrication processes described, it was viewed that welding would have the greatest impact on the metallurgical condition of the waste package.

There was a fair amount of discussion on laser peening (local induction annealing was mentioned, but the experts focused the discussion on laser peening). A presentation described industrial applications of laser peening (developed by Toshiba). The presentation concentrated on methods for laser peening the core shroud welds in-situ in the containment vessel of a boiling water reactor nuclear power station. As a result of laser peening, residual surface compressive stresses, approximately 2 to 3 mm in depth, are produced in the shroud welds. This laser peening system by Toshiba has been in production since 1999 and has been used in two nuclear power stations in Japan.

Evaluation of corrosion resistance at the transition area between the peened and non-peened regions at the surface of the welds was noted to be important. Examples were cited from the French experience with laser peening processes in steam generator tubing, where there were

numerous failures at these transition regions. The effects of applied stress on the transition areas between peened and non-peened also need to be evaluated.

The waste package design contains features that may cause some areas of the container to be susceptible to localized corrosion. If trunion rings for handling waste packages were seal-welded bands, the potential full circumferential crevices at both ends of every waste package would be created. It was also suggested that, based on the waste package design presented, waste package positioning strategies should be exercised to help avoid crevice corrosion conditions. For example, it was noted that the waste package should be placed on the emplacement pallet in such a manner that avoids having any weld regions in contact with the pallet.

In evaluating and modeling an alloy's susceptibility to localized corrosion, it is necessary to determine the critical potential by a conservative method. The experts from Japan described a measurement technique, known as the step-down potential method or E_{R-CREV} technique, for determining the critical potential. [Special Topic Report, M. Akashi]

11.1.2 Development of Weld Procedures

[after Lippold-Special Topic Report]

The quality and durability of the closure weld and its postweld processing are critical to the Project's goal to ensure that nuclear waste storage canisters will survive their design lifetime in the emplacement environment. The two primary issues regarding long-term integrity of the welds in the Alloy 22 corrosion barrier are the level and nature of residual stresses associated with the closure welds and the stability of the weld metal microstructure. If tensile residual stresses in and around the welds are determined to be life limiting relative to corrosion performance, then the mitigation techniques must be evaluated very carefully to ensure that adequate stress relief can be achieved in practice. This will require the production and testing of full-scale mockups. A weld repair procedure must be developed and validated.

The weld development activities and metallurgical studies involving Alloy 22 and the ERNiCrMo-10 filler metal have been limited to date, and no irresolvable technical issues have been identified. The Panel concludes that a substantial weld development and validation effort is required to support the waste package fabrication program. The gas tungsten arc weld process and procedure selected by Project staff is adequate for the initial development and prototype stage, but it has inherently low productivity and requires the use of complicated postweld processing to reduce residual stresses. Further optimization of this process is required for Yucca Mountain repository and the Panel encourages consideration of other processes. The most significant metallurgical issue associated with welding involves the long-term stability of the weld metal and the potential negative effects with respect to corrosion resistance. A secondary issue is the weldability of the filler metal and its resistance to cracking during fabrication. Both of these issues need to be evaluated in more detail.

Current Status of Weld Program: The current closure weld approach employs "off-the-shelf" technology to complete the weld by using the multipass, gas-tungsten arc welding (GTAW) process. The process is reliable and well proven, but completion of the closure weld will require multiple weld passes and hours of welding time to complete. This will increase the potential for weld defects such as lack-of-fusion, weld misalignment, shielding gas interruptions, and so forth. To account for this, a robust weld monitoring system must be in place and a repair welding procedure must be developed.

Following completion of the closure, the welds will be subjected to laser peening and local induction stress relieving to eliminate tensile residual stresses. It will be difficult to determine the efficacy of these techniques once they have been performed. Further investigation on the application and implementation of these techniques is required.

Weld Filler Metal Qualification: The ERNiCrMo-10 filler metal has been used in the early development studies because it is the matching composition to the C-22 base metal. It is possible that better long-term performance can be achieved by the use of an alternate filler metal. To date, there has been little work to evaluate filler metal composition as it affects both weldability and long term metallurgical stability. The weld metal microstructure of the matching ERNiCrMo-10 filler metal varies significantly from that of the base metal due to solidification and segregation effects. For example, there is considerable segregation of Mo to interdendritic regions (up to 18 wt%) in the microstructure, and both σ and P phases are present in the as-welded condition. The effect of postweld annealing on the weld microstructure has not been established, nor is the long-term stability of the weld metal relative to long range ordering. Considerable work is needed to better characterize and quantify the microstructure and its stability.

A filler metal qualification program should also be put in place in order to better quantify the behavior of the filler metal with respect to its weldability. In highly restrained joints, nickel-base filler metals are known to be susceptible to a number of cracking phenomena including solidification cracking, weld metal liquation cracking, and solid-state "ductility-dip" cracking. Little or no weldability test data exists for ERNiCrMo-10 or comparable filler metals. Weldability test techniques now exist that can be used to develop a database that will allow the weldability of the filler metals to be quantified. This will ultimately allow selection or designation of filler metal compositions that optimize weldability. Any filler metal development program designed to improve another property, such as corrosion or long term stability, should be coupled with weldability testing to ensure that an improvement in one property does not create a deficiency in another.

Evaluation of Alternate Welding Processes: The Panel recommends that the Project continue to evaluate alternate welding processes for the closure weld. While the GTAW process is reliable and dependable, it is very slow and results in high levels of residual stress that must subsequently be relieved by peening or induction heating. Electron beam welding is attractive because it can utilize a much simpler weld joint (a square-butt configuration) and can be conducted in a single pass, thus reducing the weld time significantly. It also has inherent disadvantages, including high equipment cost and maintenance requirements, and how to deal with weld defects that may occur. A "single shot" process such as friction welding is also very attractive from a metallurgical, residual stress, and productivity standpoint. Because friction welding is a solid-state process, many of the concerns regarding long term metallurgical stability resulting from segregation during weld solidification are minimized. However, because of the size of the canisters, the friction welding equipment needed would far exceed the capabilities of what is currently commercially available. There may also be other "hybrid" processes that are applicable. For example, coupling GTAW with laser welding has been shown to greatly improve penetration and productivity. These alternatives would require considerable development, but all would significantly improve productivity and would have a benefit with respect to reduction of residual stresses and improved metallurgical stability.

11.1.3 Composition Effects within the Chemical Specification for Alloy 22

[after Floreen-Special Topic Report]

The chemical composition of heats of commercially available Alloy 22 can vary within the specified range for each element. The Panel recommends that the effects of alloy composition within the specified ranges of Alloy 22 be determined. Composition specifications for Alloy 22 are relatively broad, and the microstructure and properties of Alloy 22 are likely to be sensitive to chemistry and processing history within the specified composition. Consequently, some heats may behave better or poorer than others. By determination of this behavior and optimizing these variables, it may be possible to achieve better behavior with this alloy. The author bases much of the following discussion on his experience with Alloy 625 while working at Knolls Atomic Power Laboratory.

Alloys such as Alloy 22 were not designed for prolonged service at intermediate temperatures. Consequently, little thought was given to controlling the composition so as to prevent the precipitation of undesirable phases. Often, the composition specifications are left fairly broad to make melting and alloy production easier, and to prevent competitors from making another alloy too close to the one being considered. The result is that heats of the same alloy can have widely different properties, even though the compositions fall within the specifications for the alloy. This variability due to compositional factors was recognized when Alloy 625 was being examined for various applications. When the magnitude of the variability became evident, an experimental program was undertaken to determine how to tighten the composition limits. Alloy 22 is not identical to Alloy 625, but is similar enough so that the Alloy 625 results can provide examples of the changes that can happen with changes in composition.

Alloy 625 Experience: Compositional Variability for Time- Temperature- Transformation (TTT) Diagrams: For Alloy 22, the Project has concluded that the carbides and the intermetallic compounds obey the same kinetics and precipitate at the same time. This is counter to the experience with Alloy 625. Carbides generally precipitate much sooner in nickel base alloys; because the kinetics are controlled by carbon diffusion while the intermetallics require substitutional element diffusion. In Alloy 625, the carbides come out over an order of magnitude sooner than the other phases. Several different carbides precipitate, which is common.

The Project staff working with Alloy 22 apparently found another TTT diagram in the literature that looked similar to theirs, and they appear to have concluded that the TTT diagram was independent of chemistry variations. This is too optimistic. In Alloy 625, the diagram can be shifted significantly by changes in Nb content in particular. Experience with Alloy 718 TTT diagrams also showed wide variation in reported precipitation kinetics. Examination of seven TTT curves from the literature showed that several had resemblance to each other, but others were far different. There are probably several reasons for these differences, but a primary reason was likely to be the differences in alloy chemistry between the test materials.

Several practical consequences follow from the above. If it takes about an hour to start to form intermetallics in Alloy 22 at high temperatures, then these phases should not be present in properly processed heats. Thus these detrimental phases should not appear at all or until late in the life of the repository. Carbides however, may be present to start with and will come out sooner during service life.

Alloy 625 Experience with Weld Metal: Weld metal is likely to be more sensitive to compositional variations than base plate. For example, the TTT curves for Delta phase in Alloy 625 base plate and in gas tungsten arc weld metal made the standard Alloy 625 filler metal differ greatly. The TTT curve for the weld metal was shifted to the right by more than an order of magnitude in time. This resulted directly from the segregation of the alloying elements in the

cast structure of the weld. Carbides and/or intermetallic phases can be formed during solidification of the weld metal. Typically they will be in interdendritic regions where the final stages of solidification occur. The impact strength of GTA weldments was dramatically improved by switching from conventional Alloy 625 filler to a low (Si+Fe) wire. The improvement again resulted from a reduction in second phase particles. Huntington Alloys developed this improved wire chemistry.

An Approach to Determine Composition Effects: The goal is to narrow the chemistry ranges so that detrimental phases are kept to a minimum while maintaining satisfactory mechanical properties and corrosion resistance. Reducing the Mo, W, Fe C levels would be a fruitful approach but other elements may also be important.

An approach to examining the effects of composition is an experimental program using small heats with systematic changes in chemistry. A set of vacuum melted ingots weighing on the order of 50 pounds could be hot rolled to plate stock, and this would provide a substantial supply of test material. The effects of thermal exposures could then be determined, along with spot checks of the mechanical properties and corrosion behavior. In addition, autogenous GTA weld beads could be made on test coupons and examined before and after thermal exposures to provide information on how to optimize the filler metal chemistry. It would also be useful to make several heats of weld wire with modified compositions to check the weldability. This type of chemistry adjustment is common practice in industry, where experience shows that altering the composition of an alloy can significantly improve its performance in certain applications.

One other chemistry variable that deserves mention is the level of tramp elements, e.g. S, P, O etc. Should these elements be problematic, the best thing to do is to minimize their amounts. That is, use good melt practice, e.g. VIM- V AR with selected melt stock. The performance benefit should be well defined, because this will increase the cost.

11.1.4 Residual Stress in Stainless Steel Cylinders from Quenching

[after Jaske-Special Topic Report]

In the fabrication of waste packages, the quenching process after solution annealing could produce unacceptably high tensile residual stresses. Two approaches can be employed to minimize tensile residual stresses induced by cooling after solution annealing. The first is to slowly cool the fabricated containers as is done for suction rolls. This approach would require the use of a corrosion resistant alloy that is not susceptible to sensitization or other detrimental metallurgical processes during the slow cooling process. The second is to carefully design and control the quenching process so that minimal levels of tensile residual stress are produced at or near free surfaces during the quenching operation. The selected approach should be verified by finite-element thermal and stress analysis and by experimental measurements on prototype containers.

11.1.5 Corrosion Product Passive Films: Effect of Surface Finish

[after Rapp-Special Topic Report]

Results are described for films grown on Alloy 690 in pressurized water reactor environment. While the environment studied (pressurized water at 325C at 155 atm pressure with pH= 7.2, containing additions of LiOH and H₃BO₃) is not directly relevant to the Yucca Mountain Project,

the alloy composition and the nature and growth mechanism and kinetics of the passive film may be relevant.

Admittedly, the composition for the passive film formed in flowing pressurized water at 325 C should not necessarily mimic that for thin-film atmospheric corrosion by an aerated aqueous film at much lower temperature. The former passive film might exhibit a higher dissolved proton content (OH^- ions), thereby supporting the inward growth of the chromium-rich corrosion product by anion diffusion. Because of the simultaneous dissolution of the corrosion product, the passive films reached constant (limiting) thicknesses, on the order of 70-100 nm, and constant compositions (enriched in Cr, but with significant Ni and Fe), after about 144 hours. Significantly, an electropolished surface provided a tightly adherent, fine-grained product film with an important reduction in the growth rate of the passive film, while a peened (deformed) surface exhibited faster growth kinetics and a thicker corrosion product.

In attempting to draw inferences from this study that are useful to the YMP, the importance of the electropolished surface preparation stands out. This advantage (compared to a deformed surface) should be realized whether the corrosion product film grows dominantly by outward cation grain-boundary diffusion over cation vacancies, or else by inward anion grain-boundary diffusion over anion vacancies. As shown in a study of the high-temperature gaseous sulfidation of Mo, any corrosion product grown by anion diffusion must form initially a fine-grained, tightly adherent product with a columnar morphology. The fine scale grains result naturally because a given metal grain at the metal-scale interface offers multiple and redundant possible epitaxial orientations for the nucleation of a new product grain. However, the differing orientations for these scale grains cannot support grain intergrowth, i.e. their impingement stifles grain growth. Therefore, the repeated nucleation of new grains, all being epitaxial, but with differing orientations, continues the reaction, but leads to the formation of a columnar morphology. The excellent adherence results from the continued epitaxial contact at the metal-scale interface. In contrast, for scales grown by cation diffusion with vacancy annihilation at the metal-scale interface, an eventual malfunction (tangling) of the interface dislocations whose climb normally results in vacancy annihilation can lead to void formation, poor adherence, and impurity segregation at the metal-scale interface.

11.2 CORROSION, CHEMISTRY AND METALLURGY FACTORS

11.2.1 Localized Corrosion: Phenomenology and Controlling Parameters

[after Frankel-Special Topic Report]

Pitting and crevice corrosion are terms that describe a set of complex processes that are influenced by many different parameters, including the environment, metal composition, potential, temperature, and surface condition. Important environmental parameters include aggressive ion concentration, pH, and inhibitor concentration. Other phenomenological aspects of localized corrosion include the stochastic nature of the processes and the stages of localized attack, including passive film breakdown, metastable attack, stable growth, and stifling. This section will discuss the phenomenology and controlling parameters in localized corrosion in general. It will be divided into discussions on pitting and crevice corrosion. Much of the phenomenology will be described in relation to pitting because the understanding usually was

developed vis-à-vis pitting. However, the phenomenology is largely applicable to crevice corrosion as well; the term "crevice corrosion" can simply be substituted for "pitting" in much of the following discussion. This is important since crevice corrosion will likely be more of a concern than pitting corrosion for the WP. The crevice corrosion section will discuss aspects unique to that phenomenon. Much of this section is taken from recent review articles [G. S. Frankel 1998, 2001].

Stages of Pitting: Pitting can be considered to consist of various stages: passive film breakdown, metastable pitting, pit growth, and pit stifling or death. Any of these stages may be considered to be the most critical. For instance, once the passive film breaks down and a pit initiates, there is a possibility that a stable pit will grow. The full range of available spectroscopic and analytical techniques has been applied to the study of the structure and composition of passive films in a hope to predict and understand pit initiation. To those who prefer the surface science approach, for example, it is often assumed that alloying affects localized corrosion via changes in the composition and structure of the passive film. According to this view, pit growth is considered to be well understood and to offer little in the way of fundamental understanding of the phenomenon of pitting. On the other hand, others feel that pit growth is pivotal and often controls the pitting process, since pits will not initiate if they cannot grow at least for a short while. It is considered that the passive state is required for pitting to occur, but details of the passive film composition and structure play a minor role in the pitting process. This view is supported by the fact that many observations of pitting tendency can be fully accounted for by growth considerations. Furthermore, pit growth is critical in practical applications of failure prediction. Finally, the metastable pitting stage may be thought to be the most important since only pits that survive this stage become stable growing pits. Metastable pits exist on the edge of stability. Studies of metastable pits can therefore provide insight into fundamental aspects of pitting since both initiation and stability are key factors in metastable pitting.

Crevice Corrosion: The growth of a pit generates a morphology that is essentially a crevice, so active pits and crevices are basically identical. Both are usually acidified and rich in chloride. The cathodic reaction is typically removed to a location on the boldly-exposed surface. As mentioned above, the phenomenological aspects of pitting apply equally to crevice corrosion. The difference between pitting and crevice corrosion is in the initiation phase. The occlusion associated with a crevice provides a ready barrier to transport, so initiation of crevice corrosion is easier. Alloys are usually resistant to pitting corrosion under conditions in which they are resistant to crevice corrosion, but the inverse is certainly not true. It is likely that the WP will be much more susceptible to crevice attack since Alloy 22 resists pitting, but crevices will exist between the WP and the supporting rails, beneath surface deposits and between the Alloy 22 outer can and 316L NG inner can.

Accelerated corrosion in a crevice can initiate at potentials well below the pitting potential, and after considerable periods of exposure with no prior evidence of crevice attack. It has long been accepted that crevice corrosion involves passive dissolution followed by oxygen depletion, acidification and chloride enrichment. However, whether these phenomena are causal, directly resulting in initiation of crevice corrosion, or are simply consequences of the active crevice corrosion process is still a matter of debate. Similarly, ohmic potential drops have been shown to stabilize crevice corrosion under certain circumstances, and will likely exist in all crevices and pits. The question of causality can equally be raised for ohmic potential drops. Other

mechanisms for crevice initiation have also been suggested. Proper comparison of quantitative theories to experiments should allow determination of the real crevice initiation mechanism.

References

G. S. Frankel, *J. Electrochem. Soc.*, **145**, 2186 (1998)

G. S. Frankel, in *Passivity of Metals and Semiconductors; Vol. Proceedings Volume 99-42*, edited by B. Ives, J. L. Luo, and J. R. Rodda (The Electrochemical Society, Pennington, NY, 2001), p. 445.

11.2.2 Water Composition within Yucca Mountain

[after Nagy-Special Topic Report]

An excellent review of water compositions is presented in four topic areas. Recommendations in each area are presented in the full Special Topic Report.

Bounding compositions of seepage waters: The corrosion resistance of the waste package metals will depend on the composition of the water that may come into contact with the waste package. Waters extracted from Yucca Mountain (YM) show variability in pH and elemental concentrations and also age, all of which reflect different sources of water, flow pathways, and flow velocities. A key question, therefore, is to ask whether or not any limits can be placed on the range of water compositions expected to contact the WP.

While the general composition of seepage waters at YM can be obtained within ranges of values, there is no specific composition that occurs uniformly throughout the UZ. In this sense, an approach that considers families of waters (in terms of cation and anion compositions), such as that used by Rosenberg et al. (2001) is appropriate. Because the primary concern is the effect on corrosion of such waters upon evaporation at the WP surface, exact initial starting compositions are not needed because these will change as evaporation proceeds. Instead, the ratios of corrosive elements are more important to determine.

An alternative approach to using actual water samples from YM is to place theoretical bounds on YM water composition taking into consideration equilibria and kinetics of relevant mineral/water reactions. For example, one bound would be provided by water in equilibrium with the proposed repository or overlying rock units under ambient conditions (including temperature and PCO_2). The closest approach to the composition of such water might be that of a measured pore water. Perched waters may approximate such water in some cases depending on recharge and discharge conditions in the perched water horizon. The initial source of any water is precipitation. Thus, a second bound on the composition of YM water might sensibly be a local relatively young ground water, which has equilibrated rapidly with dust and aerosols. A third end member, important for understanding changes in the repository after waste is emplaced, would be water in equilibrium with a suite of fracture minerals, which may have a different bulk composition from that of the tuff. It is interesting to note that the reported pore water compositions from the Topopah Springs tuff are at the high end of the range of Ca plus Mg concentrations, but fall within the range of pore water compositions in the Paintbrush tuff in terms of having higher Cl and SO_4 concentrations. High Cl and SO_4 has been considered to be a result of evaporation. However, high concentrations, especially in the welded tuff, may be related to volcanic gases (HCl and H_2S) present at the time of formation of the tuff unit and either trapped in the volcanic ash via adsorption or as fluid inclusions.

Redox reactions in the bulk rocks are unlikely to be important as this is a highly oxidizing environment. Mn minerals in the fractures and tuff contain most Mn in the IV oxidation state. Fe in the minerals is also in the III oxidation state. Reducing environments could be artificially produced as a result of waste emplacement and subsequent reactions involving microbes or acidic gas generation.

Effects of fractures on composition: Results and interpretations from many studies, both tracer and modeling have indicated that water moves at the fastest rate through fractures at YM, despite the fact that many of these fractures are filled with secondary minerals. Therefore, the likely scenario for dominant water movement away from and back towards the waste package during the heating and cooling cycles of the waste is through fractures. In this regard, chemical interaction of heated water and fracture material may result in new water compositions distinct from those based on current analyses, depending on the temperature of the contacting water, the rates of reaction of the fracture minerals with this water, and the time the water is in contact with the fracture minerals.

The silicate and carbonate minerals found in fractures were also observed to form upon evaporation of synthetic J-13 and UZ waters in contact with finely-ground Topopah Spring tuff at 75°-85°C along with various salts. In particular amorphous silica and calcite were observed upon incomplete evaporation of synthetic J-13 water, and smectite clays upon evaporation of synthetic UZ water. This suggests that evaporation of simulated YM water may be related to the process of formation of the fracture minerals. Conversely, fracture mineralogy that involves trace elements (Mn and Fe oxides) may be important to consider in evaporative simulation experiments.

Trace element bounds and analysis: In addition to chloride salts, certain trace elements can contribute to WP metal corrosion, such as mercury (Hg), lead (Pb), fluorine (F), and arsenic (As). Analysis of these elements in the YM environment should include both concentrations in sampled waters as well as concentrations in the rocks, and particularly in fracture minerals and dust particles that may settle on the WP. However, few analyses have been performed on the subsurface rocks and waters, and some of these are questionable due to either contamination (e.g., a source of dissolved Pb in the J-13 well may be from lubrication fluids) or due to inadequate analytical techniques (i.e., detection limits too high to measure actual concentrations). In general, the trace elements listed above are associated with volcanic gases and ash, and may largely arise from these sources at Yucca Mountain. Hg concentrations in natural waters are typically between 0.01 to 10 ppb, and a current source worldwide is from atmospheric pollutant deposition. Dissolved Pb can be derived from the burning of fossil fuels, but more likely originates from the tuff itself. Pb is found in the fracture-lining Mn-oxide minerals, for example. The likely sources of F are the tuff and aerosols. Arsenic is found in general in ground waters where its concentration can range from 1 to 10 ppb, with higher concentrations being typical in the arid western parts of the United States. Perfect et al. (1995) reported a concentration of ~ 1 ppb in YM ground water. The most readily available form of As may be associated with Fe-oxide minerals in the fractures.

These four trace elements could all come into contact with the WP, although to variable extents. Likely mechanisms include deposition of infiltrating water onto the WP, reaction of water with dust particles on the WP surface, and deposition of heated water from the overlying rock during the thermal evolution of the repository. It is not clear how soluble these trace elements might remain in evaporating fluid as solid phases precipitate on the WP. For example, the majority of

the Pb could be precipitated as PbCO_3 or PbSO_4 solids. Arsenic or mercury, on the other hand, could remain as a relatively easily adsorbed and desorbed component of a wet mineral coating.

Likelihood of Formation of Silica Deposits on Waste Package: Passivation of the WP metal surfaces may occur if upon evaporation of drip water, thin layers of noncorrosive solids (e.g., silicates) are formed. Si concentrations of measured YM waters are above equilibrium with opal-CT the metastable silica phase in the fractures and tuff. Calculations of the masses of each phase that formed upon evaporation would depend on the assumption of equilibrium, because necessary kinetic information is rare for silicate minerals. As a consequence, it is likely that incorrect proportions and an incorrect sequence of mineral precipitation might be calculated. Thus, calculations may not simulate which mineral phase actually formed closest to the WP surface. While amorphous silica could form in a thin layer inaccessible to flowing fluids, excessive drying of such a layer could cause it to crack. Also, if phyllosilicate clays form, these will occur as small crystallites on the order of a few nanometers to micrometers in diameter. Clay layers can act as relatively impermeable membranes, but they will contain grain boundaries along which fluid can move. Clays flocculate at high pH indicating that they may settle on the WP surface as a randomly oriented aggregate of tiny crystals rather than a stacked layer of flat particles.

11.2.3 Localized Corrosion: Chemistry and Radiolysis Effects

[after Turnbull-Special Topic Report]

Optimum conditions for localized corrosion: For the Alloy 22 waste package material, localized corrosion will arise when the conditions are optimum for pitting or crevice attack. Crevice attack will almost always occur in less aggressive conditions than pitting corrosion because it is easier to form the local chemistry conditions conducive to passivity breakdown. The crevice geometry may be induced by physical deposition of particles or produced at the toe of a weld by inadequate welding.

The optimum environmental conditions for generating passivity breakdown will be high temperature, high oxidizing conditions in a sufficiently conducting environment with a high ratio of chloride ions to other anions (to avoid competitive anion effects). The concept of a sufficiently conducting environment has to account not only for the solution conductivity but the thickness of the solution layer as the potential drop in a thin liquid layer may limit crevice propagation rates. In that context, the absence of a generally wetted surface would certainly limit propagation of crevice attack as the anodic and cathodic areas would not be well separated and the effective cathodic area would be small, although perhaps sufficient to initiate breakdown.

For a significant crevice chemistry change when the passive current is very low, as for this alloy, the crevice geometry has to be very constrained. Increasing the temperature will increase the passive current density. However, long, tight crevices in the waste package, whether associated with a weld or deposits in a simple way, seem unlikely. Nevertheless, evaporation/boiling will assist in concentrating the solution when the geometrical conditions are less favorable.

Formation of an insoluble carbonate scale is known from seawater studies to retard the cathodic reduction of oxygen. However, when the main reactant, hydrogen peroxide, can be produced within the pores at the metal surface this may not be limiting although it would depend on whether it altered the effective area of the cathode. Calcareous scales in seawater simply limit the oxygen diffusion rate without much change in the effective area.

The pH in a crevice of a corrosion resistant alloy such as Alloy 22 will fall due to hydrolysis of chromium and molybdenum cations coupled with ionic strength effects due to a high salt concentration. Although the solubility of metal ions decreases with increasing temperature, this is not so limiting when the pH is low for the temperature range of interest, the major factor being geometric parameters.

Any direct dripping onto the hot surface will obviously outweigh dust considerations because the evaporation process will concentrate salts, form scale deposits and may create conditions conducive to sustained wetting at quite elevated temperature with the upper limit determined by the composition of the evaporated solution. Whilst wetting itself will have little impact on heat transfer, a wetting and drying cycle leading to developed carbonate/silicate scales would impede heat transfer.

Source of surface water on waste package: There are two potential sources of water to the waste packages: condensation from the atmosphere associated with dust particles containing deliquescent salts with a sufficiently low critical relative humidity (i.e. the RH value at which condensation will occur) and direct dripping onto the waste packages if no drip shield is present (or if the drip shield fails). Any direct dripping onto the hot surface will obviously outweigh dust considerations because the evaporation process will concentrate salts, form scale deposits and may create conditions conducive to sustained wetting at quite elevated temperature with the upper limit determined by the composition of the evaporated solution. Whilst wetting itself will have little impact on heat transfer, a wetting and drying cycle leading to developed carbonate/silicate scales would impede heat transfer.

Factors affecting the water chemistry: The author notes that it is imperative in dealing with these issues that the evolution of the water chemistry over the long timescales involved is perceived to be determined by the interaction of a number of processes defined by the details of the system; i.e. thin liquid layer with deposits of some kind that may be porous and themselves contributing to the chemistry, elevated temperatures (affected possibly by the build up of deposits); radiolysis with the distribution of products of the latter being temperature and chemistry sensitive; corrosion reaction byproducts (e.g. elevated pH in cathodic regions); interaction with CO₂ of the atmosphere. Such a statement is necessary to balance the tendency to transfer information to the waste package system from bulk solution experiments often in poorly related chemistry and temperature conditions. The challenge is to establish the best conceptual physical picture possible for the likely chemistry and to model and/or design experiments to validate those ideas and to consolidate the details.

Radiolysis: The radiolysis of pure water due to gamma radiation generates primary products of H, OH, HO₂, e⁻(aq), H⁺, H₂, H₂O₂ and secondary products of O₂, O₂⁻, and additional H₂O₂. Species such as e⁻(aq), H, H₂ are reducing agents (i.e. can be oxidized, thereby lowering the corrosion potential) and OH, HO₂, H₂O₂, O₂, and O₂⁻ act as oxidizing agents. In a single phase, pure water, closed system the net effect is neutral (with H₂, H₂O₂ being by far the dominant species, of near equal concentrations) but in an open system exposed to air, a net oxidizing condition of the bulk solution is suggested. In a practical system it will be the balance of kinetics and transport that determine the local conditions at the metal surface, and the net effect in terms of oxidizing characteristics has to be determined.

Thin liquid layers on surface: This situation is for a thin liquid layer (typically about 200 μm) with no significant scaling deposits, except that associated with residues of dust particles. The situation of a porous layer or a crevice is discussed below. The likely chemistry associated with absorption of water and dissolution of salts in dust particles has been described by Frankenthal

but will include sulfate, acid sulfate, nitrate anions and ammonium and sodium cations with some carbonaceous residue.

Porous deposit on the surface: The underlying physical picture is of a surface exposed to a drying environment leading to evaporation and the development of an insoluble scaled surface with the water-filled pores rich in salts. The thickness of the porous layer is difficult to predict, as it will depend on the extent of dripping of water onto the surface and the temperature and time domains in which this might occur. The distinctive feature is that oxygen replenishment of the solution at the pore base will be constrained as oxygen may be consumed by reaction with radiolysis products as it progresses along the pore. This again requires quantitative modelling, accounting for the salt concentration also, but the net effect might be expected to be essentially towards a more benign situation compared to the thin liquid layer scenario described above as the concentration of reducing species at the metal-solution interface could be higher because of the reduced oxygen level.

The chemistry of the groundwater that will drip onto the surface can reasonably be characterized. However, if we adopt the dripping scenario, there may be a washing away of products from radiolysis in the initial stages before a scale is formed and prediction of the chemistry would be difficult. It is in the later stages when a scale is formed and water filled pores are present that are not so readily washed out that may prove to be most important.

Crevice solution: The situation in a crevice as far as radiolysis should have parallels with deposit pore chemistry to an extent since oxygen depletion in the crevice solution will occur readily. If coupling to the external surface were put aside, the chemistry would be essentially neutral from the viewpoint of radiolytic factors being typical of an oxygen-free situation. When considering coupling to the external surface the latter should be perceived as a spatially continuous or semi-continuous wetted surface. If a porous scale deposit were present then the driving force may be less than for a thin liquid layer for the reason indicated. The interesting question is to consider the worst case, which is that of a thin but very conducting liquid layer with highly oxidizing conditions.

When both oxidizing and reducing species are considered together in the crevice (because of high chloride the quantities will be high also), the net effect will depend on the efficiency of the electrochemical reactions and the impact of coupling to the external surface. Prediction requires specific electrochemical data relevant to the substrate. However, since the potential associated with the external surface exposed to aerated solution should be higher with little H_2 around, there should be a net oxidation of reducing species in the crevice leading to enhanced acidification.

Impact of water chemistry and radiolysis on the bulk corrosion potential: Experimental evidence from crevice studies in stainless steels imply that the main impact of radiolysis is on the external potential with little evidence of mitigating internal cavity chemistry. Since the water chemistry of relevance is a complex function of radiolysis, temperature and exposure history simple statements are usually not possible but it is legitimate to ascertain what species/reactions are most important in determining the potential, at what concentrations do these become significant relative to behavior in unirradiated solutions and what set of conditions will yield the highest potential at a specific temperature. For Alloy 22 alloy, the corrosion potential will most likely be determined by a redox potential as the passive current is expected to be very small.

The corrosion potentials attained in irradiation tests do not respond markedly to increase in dose rate (albeit at relative low dose rates overall). A several hundred milli-volt increase in corrosion potential was observed with radiation dose rate of 1000, 20,000 and 200,000 Rad/hr. In practice this lack of dependence on dose rate is known to extend up to 1,000,000 Rad/hr.

Note inserted by Panel: To put this into perspective, the following are the expected gamma radiation levels in the repository. The waste package and surrounding environment will be subjected to a flux of neutrons and gamma rays from the stored radioactive waste. The peak gamma flux is about 1000 rad/hr at the time of emplacement of waste packages. This gamma flux decreases by a factor of 100 to 10 rad/hr after about 200 years and another factor of 100 to 0.01 rad/hr after about 400 years. Based on data above, the radiolysis effect has not been sufficiently studied or analyzed at the lower gamma fluxes that will exist after the initial emplacement. Also note that radiolysis effects on the environment will only occur when waste packages are wet.

Herbert et al argue that this follows from the lack of dependence of corrosion potential on H_2O_2 concentration once the level exceeds about 0.5 ppm (1.5×10^{-5} M) and considered to be associated with the requirement to achieve a surface coverage of adsorbed OH. Marsh et al suggest that the irradiation induced rise in corrosion potential is not determined by H_2O_2 but by other oxidizing species such as O_2^- and OH radicals.

Impact of scale formation on surface temperature: An important issue is the extent to which the surface temperature of the waste packaging can rise due to formation of a surface film which at one level is just a thin liquid layer but when dripping occurs for a period of time may be a relatively thick scale. This is simply the solution of a heat transfer problem in which definition of the heat transfer coefficient between the fluid and the heat transfer surface is required. Solution to the heat transfer problem in the absence of a deposit but with a thin liquid layer suggests that the presence of a layer up to 500 μm thick (at which thickness water will probably stream) has little impact on the heat transfer coefficient. However, no calculations were made assuming a deposit.

11.2.4 Passive Films and the Long-Term Uniform Corrosion Resistance of Alloy 22

[after Devine-Special Topic Report]

The generally excellent resistance of Alloy 22 to uniform corrosion is entirely due to the protective nature of its passive film. Even though this uniform corrosion resistance is expected to persist for thousands of years, the passive film itself is amazingly thin.

Four major topics are reviewed and related to the long-term uniform corrosion of Alloy 22: (1) the structure and composition of the passive film formed on Alloy 22 in aqueous solutions, (2) the uniform corrosion of Alloy 22 in the passive state, (3) the uniform corrosion of Alloy 22 in the transpassive state, and (4) measurement of the uniform corrosion rate of Alloy 22.

Results to date indicate that the passive film of Alloy 22 in acidic solutions is thin ($\leq 20 \text{ \AA}$) and bi-layered. The passive films that form on iron-chromium and other nickel-chromium alloys are also thin and bi-layered. Investigations of the passive films formed on nickel-chromium-molybdenum alloys in acidic solutions and nickel-chromium and nickel-chromium-iron and nickel-chromium-molybdenum alloys in neutral and mildly alkaline solutions indicate the compositions of the passive films are strong functions of the composition of the alloy and the pH of the solution. In acidic solutions, the outer layer of the passive film is depleted of nickel. In neutral and mildly alkaline solutions, the outer layer of the passive film is enriched in nickel. For excellent uniform corrosion resistance, a nickel base alloy must contain a critical minimum concentration of ≈ 20 a/o chromium. The inner layer of the passive films of alloys with greater than or equal to the critical chromium composition is nearly pure chromium oxide. The inner

layer of passive films of alloys with less than the critical concentration of chromium is a mixed nickel-chromium oxide, which is less protective than pure chromium oxide.

The mechanism of formation of a multi-layered passive film on Alloy 22 is expected to be a strong function of solution pH. In acidic solutions, the outer layer of the passive film of Alloy 22 is rich in molybdenum and chromium. The outer layer forms by the preferential dissolution of nickel in acidic solutions. The enrichment of molybdenum in the outer layer is a consequence of the relatively low solubility of molybdenum in acidic solutions.

No investigations have been conducted on the formation of passive films on Alloy 22 in neutral and mildly alkaline solutions. However, examinations of films formed on nickel-chromium and nickel-chromium-iron alloys and C4 (Ni-18Cr-10Mo) in mildly alkaline solutions suggest that a multi-layered film will form on Alloy 22 in mildly alkaline solutions and that the inner layer of the film will be enriched in chromium and the outer layer of the film will be enriched in nickel. The high nickel concentration of the outer layer appears to be the result of the faster mobility of nickel through the inner layer. The distribution of molybdenum in the film will depend on the relative mobility of molybdenum in the inner layer film and the solubility of molybdenum species in water.

For the first several hundred years in the repository, the temperature of the waste package will be too high for water to come into contact with the waste package. By the time an aqueous phase contacts the waste package, the surface of Alloy 22 will be covered with an air-formed oxide film. The oxide film on the surface of Alloy 22 will primarily be the result of oxidation that occurs during the thermomechanical processing of the waste package. Included in the thermomechanical processing is a thermal treatment intended to introduce a residual stress pattern in the waste package that will increase resistance to stress corrosion cracking. The favorable residual stress distribution is to be created by an isothermal heat treatment at 1150°C/3.5 hours, followed by a water quench of the entire Alloy 22 waste package. After the canister is filled with nuclear waste and closed, a favorable residual stress pattern will be introduced in the vicinity of the final closure welds by either an induction anneal (1000°C-1100°C/ \approx 30 sec. and cooled to 600°C in less than 10 min.) or laser peening.

The influence of the oxide formed at high temperature on the corrosion resistance of Alloy 22 in aqueous solutions at \leq 100°C is not known. However, preliminary results suggest that the film formed on Alloy 22 in air at room temperature is as protective against aqueous corrosion as is the passive film.

In summary, uniform corrosion of Alloy 22 is unlikely to cause failure of the waste containers in less than 10,000 years. However, surface segregation of sulfur and transpassivity are the two most likely factors that would cause significant rates of uniform corrosion of Alloy 22. Both of these topics are reviewed in the Special Topic Report.

11.2.5 Inhibition of Localized Corrosion by Non-Halide Anions

[after Newman-Special Topic Report]

Localized corrosion of stainless steels or nickel-base alloys is inhibited by non-halide anions (excepting aggressive sulfur compounds) according to well-defined rules. A number of anions will inhibit pitting if their concentration is comparable with that of chloride. A few appear to be relatively ineffective, such as bicarbonate. Hydroxide anions are more effective owing to their higher mobility in corrosion sites and perhaps also their simple mode of action. When the temperature is increased or a crevice is introduced, the required amount of inhibitor increases.

The most persuasive explanation of these inhibitor effects is based on Galvele's pitting theory and involves competitive electromigration of anions into a dissolving pit nucleus.

Nitrate in particular shows inhibition of pitting over a range of potentials. Artificial-pit studies show that nitrate only stifles pit dissolution when an anodic salt film has been precipitated, i.e. at high potentials. To some extent, sulfate shows analogous behavior, but only in a critical range of concentration. Since there is a large amount of nitrate in Yucca Mountain, this kind of phenomenon is very important for the corrosion assessment.

Lack of discrimination between possible crevice-corrosion initiation mechanisms (metastable pitting or passive dissolution) is hindering the crevice corrosion assessment in this area.

It should not be assumed that fluoride is an aggressive anion. It may be an inhibitor of localized corrosion.

Localized corrosion can be inhibited very effectively if the oxygen reduction reaction is shut off. This may occur naturally in Yucca Mountain.

11.2.6 Passivity-Induced Ennoblement

[after Frankel-Special Topic Report]

It is possible that an extremely passive metal, such as Alloy 22, when exposed to a relatively mild environment for long periods of time, such as the waters in Yucca Mountain, will exhibit a continually improving passivity, perhaps as a result of a continually thickening passive film. In this case, the OCP should continue to rise with time, albeit at a rate that might vary inversely with time. For want of a better term, this phenomenon will be called passivity-induced ennoblement. The purpose of this document is to consider the implications of passivity-induced ennoblement for an alloy that exhibits a critical potential in the given environment.

If the passive film were to improve continuously, the OCP would increase with time, eventually reaching the transpassive potential after a very long period. This potential would pose an upper limit to the OCP, and the limiting corrosion rate would be given by the rate of the cathodic reaction at the transpassive potential. In potentiostatically-controlled experiments where the potentiostat supplies whatever current is required, it is possible for the alloy to dissolve at high rates at potentials equal to and above the transpassive potential. At open circuit, however, high rate transpassive dissolution is only possible under oxidizing conditions in which a cathodic reaction is available to consume the electrons at an equally high rate. However, it was assumed that the cathodic reaction (hydrogen evolution) was unchanged during the potential ennoblement. If the cathodic kinetics remain unchanged, then a higher passive current density would lead to a decrease in potential out of the transpassive region. The OCP might oscillate near the transpassive potential, but the rate of dissolution would remain so low that this should not be considered a form of degradation.

The considerations are somewhat different for the case in which the alloy is susceptible to localized corrosion. As in the case of transpassivity, passivity-induced ennoblement would be limited to the breakdown potential. Localized corrosion growth at open circuit would require sufficient cathodic current, and this might limit the extent of growth. However, since localized corrosion is a local phenomenon by definition, it is possible that cathodic current from a large exposed passive area could be used to consume the current produced by localized attack at a much smaller area. This means that a low cathodic current density across the surface of a sample could be accompanied by a relatively high rate of anodic attack if the anodic area were small. On the

other hand, sustained localized corrosion growth would depend on the development of an oxidizing cathodic reaction to consume the electrons at a high rate.

The repassivation potential might be considered as the critical potential for designing against localized corrosion using the ΔE criterion. Since the repassivation potential is below the breakdown potential, it is more likely that passivity-induced ennoblement will drive the potential above the repassivation potential. This condition would be considered to be a failure according to the criteria used by the DOE Yucca Mountain Project, in that ΔE would be negative. Any initiated localized corrosion might continue to propagate at a potential above the repassivation potential. However, if the cathodic kinetics were unchanged, the problem remains as to how localized corrosion could propagate to any considerable extent under open circuit conditions. It is clear that any mixed potential model for the corrosion potential and corrosion rate must carefully consider the cathodic kinetics. It is possible that cathodic kinetics could change with time. Changes in the reversible potential for oxygen reduction are not important because the potentials of interest are far below this value, but the reversible potential for hydrogen evolution will affect the rate of hydrogen evolution and will depend on the pH, which could change with time. Kinetic aspects might also change. The exchange current density reflects the catalytic properties of the surface. With time, the improved passivity might result in a decrease in the catalytic nature of the surface. If the exchange current density for the cathodic reaction were to decrease, or the cathodic Tafel slope were to increase, the OCP would tend to decrease, counter to the effects of passivity-induced ennoblement. Equally important is the development of new oxidizing cathodic reactions, as described above.

11.2.7 Localized Corrosion: Temperature Effects

[after Newman-Special Topic Report]

In the context of Yucca Mountain, conventional pitting is not to be expected, but crevice or underdeposit corrosion is much more likely and the applicable temperatures are much lower. Crevice corrosion occurs at lower temperatures, as well as potentials, compared with pitting. If care is taken to provide a repeatable crevice, the temperature dependence of crevice corrosion is also very steep, leading to the concept of a critical crevice corrosion temperature (CCT) as proposed by Brigham. Caution is necessary in using this quantity for predictive purposes, since it is so dependent on geometry. Good correlations with service performance have been reported. Specifically, for Alloy C-22, data are available that suggest a steep decline in crevice corrosion susceptibility below 90°C. Comparison with the well-studied Alloy 625 has been valuable in this work.

Localized corrosion of stainless steels and nickel base alloys shows a remarkable dependence on temperature. For pitting, a critical temperature exists (the critical pitting temperature or CPT) below which pitting vanishes at all potentials. For well-prepared surfaces of modern alloys the CPT can be reproduced to within 1°C, and does not depend on the chloride concentration, at least in the range 1 to 5M. The CPT does show some dependence on the surface finish, being up to ten degrees higher for polished than for rough-ground surfaces.

There has not been much progress in general testing philosophy for temperature effects since the pioneering work of Brigham in the 1970s. The main advance has been the recognition of the importance of specimen design and avoidance of crevice corrosion in CPT measurements. Alloy manufacturers have made many of the important refinements in this area, and given that

unwanted crevice corrosion can lower the CPT by 40 degrees, one can certainly understand their motivation for remaining at the forefront of this subject.

The deterministic nature of the CPT transition requires a deterministic explanation, and there is evidence that this lies in the anodic kinetics of the metal in the local pit environment. Passivation occurs below the CPT, even in the most aggressive local environment, preventing the attainment of the necessary current densities (ca. 10 A/cm²) for pit stabilization. Probably this passivation occurs beneath a freshly precipitated salt film. Metastable pitting occurs well below the CPT.

Pitting in inhibited solutions, for example chloride plus sulfate, tend to propagate under the metal surface. For certain solution compositions and potentials, this leads to enhanced pit stability and a lowering of the CPT, even though the pitting potential above the CPT is inhibited by sulfate in the normal way. This observation by Moayed requires further investigation in view of the anions present in the Yucca Mountain environment.

Above the CPT, the gradual variation of the pitting potential with temperature has been ascribed mainly to the enhanced dissolution kinetics of the metal (increase in corrosion current density in the pit environment). However in deep pits or crevices there will also be effects on the critical environmental conditions.

Crevice corrosion in a standard geometry also shows a critical temperature or CCT. This cannot be reproduced as well as the CPT; however it does have value especially for shallow crevices, where corrosion initiates by metastable pitting. In deep, tight crevices there may be a different initiation mechanism of the "Oldfield and Sutton" type, though this has yet to be demonstrated. The effects of surface deposits on the critical conditions for localized corrosion have not been studied in detail, but are likely to be as severe (at least) as those of conventional crevices.

Deleterious phase transformations or segregation effects can be quantified by CPT measurements according to the literature. It is not clear how conservative such evaluations are in view of the narrow regions that are subject to depletion in Cr or Mo. There is also a need for spatial mapping of the reduction in localized corrosion resistance due to such metallurgical effects.

11.2.8 Repassivation Potential as a Measure of Crevice Corrosion Susceptibility

[after Special Topic Reports by (a) Shibata and (b) Akashi]

The development of a laboratory test to measure crevice corrosion susceptibility of corrosion resistant metals is described in two Special Topic Reports [Shibata-Special Topic Report and Akashi-Special Topic Report].

Various electrochemical methods for evaluating the corrosion resistance of stainless steels have been developed and standardized in various industrial standards such as JIS, ASTM, ISO and others. Pitting potential is most popularly used for evaluating the pitting corrosion resistance of stainless steels and/or for evaluating the exact performance in the industrial applications. Tests for the potentials associated with crevice corrosion formation or repassivation have been not standardized because crevice corrosion depends not only on solution chemistry and alloy composition, but also on the crevice geometry. Various crevice electrode assemblies for the electrochemical tests have been proposed and polarization methods were used for identifying crevice generation and repassivation behavior. In Japan, Shiobara found a large decrease in the generation and repassivation potential for localized corrosion on creviced electrodes compared with nominally uncreviced titanium and stainless steel electrodes. Suzuki reported that crevice corrosion of stainless steels in the field could be effectively suppressed by maintaining the potential below a critical protection potential. In the 1970's, it was recognized that there are three

characteristic potentials relating to crevice corrosion of passive metals; generation, repassivation and protection potentials. In 1980, Tsujikawa reported that the protection potential could be evaluated by measuring a critical potential for stopping crevice growth under appropriate electrochemical and geometrical conditions. This critical potential was called repassivation potential for crevice corrosion, $E_{R,CREV}$.

Through the 80's and 90's, research committees organized by the Japanese Society of Corrosion Engineering (JSCE) published a series of progress reports, including case histories of field failures due to crevice corrosion, round robin tests, and a proposal for standardization of the measurement of $E_{R,CREV}$. Based on the accumulation of a sufficient database for the measurement of $E_{R,CREV}$, a JIS committee decided to standardize a method. "Method of determining the repassivation potential for crevice corrosion of stainless steels" will be published in 2002 (1).

The usefulness and reliability of this method proposed by Tsujikawa (2) has been discussed for years in Japan. Industrial engineers hesitate to standardize the Tsujikawa method, because they believe that $E_{R,CREV}$ determined by this method is too severe and conservative. It was claimed that $E_{R,CREV}$ of common stainless steels like Type 304 is sometimes less noble than the open circuit potential in ordinary environments in which the steel even could be utilized. This situation might be judged to be in the incubation stage. If stainless steel is used in this condition, we could expect the generation of a crevice after some incubation time. At present we have no definite model or reliable theory to predict the incubation time, and this material should be replaced one with higher $E_{R,CREV}$ if long time performance is required.

Because of its conservative nature, it is recommended that $E_{R,CREV}$ be determined and used to evaluate the long-term crevice corrosion behavior of candidate waste package materials. If $E_{R,CREV}$ of the candidate alloy is above the open circuit potential in the repository environment, confidence would be high to use the material for the WP for the long-term without crevice corrosion. Another important point which needs to be determined is how to assume the environmental condition for the candidate alloy in the repository site because $E_{R,CREV}$ depends on the environmental conditions.

1. S. Tsujikawa and T. Hisamatsu, *Boshoku Gijutsu(Corrosion Engineering)*, **29**, 37(1980).
2. Draft of the JIS on "Method of determining the repassivation potential for crevice corrosion of stainless steels," which will be published in 2002.

11.2.9 Formation of an Aqueous Environment from Condensation in Dust Layer

[after Frankenthal-Special Topic Report]

This report deals with the formation of the aqueous environment on waste package and drip shield surfaces. The source of water is condensation with no contribution from direct seepage or dripping. The typical environment while the repository is open and, in particular, during construction will contain all the components present in outdoor environments, such as gases derived from fossil fuel combustion processes, sulfur dioxide (SO_2) and nitrogen oxides (NO_x), particulate matter, and microbes. It will also contain components derived from indoor sources, such as outgassed vapors from paints, plastics, operational activities, smoking, office equipment, appliances, etc. The factors likely to affect the environment include, temperature, relative humidity, electric fields, air velocity, mechanical stresses, and thermal shock.

Particulates present in the environment are distinguished by a bimodal size distribution. Most of the particulate mass exists in the size range 0.1 to 15 μ m. Particles 2.5 to 15 μ m in size are

largely derived from natural materials and are largely mineralogical in composition. They typically form from the erosion of soils and rock due to wind and rain or are the result of human activity such as mechanical processes. Particles in the size range of 0.1 to 2.5 μm are mostly derived from anthropogenic sources such as fossil fuel combustion. Geological and volcanic activity may also contribute to their origin.

The corrosivity of dust particles is largely the result of the water-soluble ions they contain. The higher the fraction of these ions, the higher the corrosivity is likely to be. Coarse particles, due to their origin, tend to have a much lower water-soluble ion content than fine particles. As a result, coarse particles are generally much less corrosive than fine particles. The composition of the coarse particles at the Yucca Mountain site will be determined primarily by the composition of the local soils and rocks. Inside the repository, the origin of coarse particles will be the local rock formations and also external sources brought in with fresh air by ventilation processes. As shown by Sinclair and coworkers, fine particles contain principally ammonium (NH_4^+), sulfate (SO_4^{2+}), acid sulfate (HSO_4^-), and nitrate (NO_3^-) ions.

Deposition rates on surfaces depend on particle concentration and migration rates. Relevant factors affecting the migration rate include particle size, velocity, temperature, and surface configuration. Coarse particles are sufficiently large to deposit by gravitational settling. They most frequently deposit on top horizontal surfaces unless air velocities are very high and the surface is tacky. The sticking coefficient is almost always unity. The residence time of typical coarse particles suspended in air of an ordinary room is a maximum of a few minutes, i.e., these particles settle on surfaces rapidly. The migration of fine particles, on the other hand, is controlled by convective diffusion. They can remain in the air for hours and even days, depending on the ambient air exchange rate. They deposit with equal likelihood on all surface configurations and can penetrate narrow spaces and crevices more easily than coarse particles.

A most relevant factor determining deposition for the Yucca Mountain project is the thermophoretic effect. Particles are attracted to surfaces colder than the particles and are repelled from surface that are warmer. The thermophoretic force and velocity are both proportional to the thermal gradient, ∇T . The implication of this is that fine particles, i.e., the corrosive particles, are not likely to deposit on the containers until they cool to ambient temperature. By that time, presumably, all activities generating corrosive fine particles, i.e., combustion processes will have ceased for hundreds or thousand of years and the particles will have been deposited elsewhere.

In addition to the intrinsically corrosive dust, that is dust that absorbs moisture from the atmosphere to form an electrolyte solution, dust may be indirectly corrosive, absorbing moisture and corrosive agents from the atmosphere or being conductive and serving as a cathode, or it may be essentially harmless, but on occasion produce a geometry conducive to crevice corrosion. Fine particles contain a larger fraction of water-soluble ionic compounds, while coarse particles could form crevice geometries. Recommended experiments to gather greater understanding in this area include: sampling air for particulates, analysis of particulates and corrosion test of relevant alloys in presence of dust

11.2.10 Statistical and stochastic aspects of corrosion life prediction

[after Shibata-Special Topic Report]

Candidate materials for the waste package (WP) canisters are required to survive more than ten thousand years and reliable assessment of the canister design is required. For this assessment, corrosion life predictions have to be made. Two different approaches can be applied to predict

corrosion failure life. The first approach is deterministic and corrosion life can be estimated based on the exact corrosion rate measured by laboratory and/or field tests. A theoretical model to predict the failure life of a passive metal based on a deterministic approach was proposed by Macdonald [1] who developed the point defect model for the passive film breakdown. Reliable assessment of the long lifetime in the repository, however, should be based on the exact corrosion rate or be supported by complementary data from a natural analog.

The other approach [2,3], which is stochastic, describes corrosion life as the probability of occurrence. Corrosion failure statistics show that the major corrosion mode for passive alloys exposed to the repository environment, which is near-neutral and mildly oxidizing with aggressive halogen ions, is not general corrosion, but rather localized corrosion such as pitting, crevice corrosion and stress corrosion cracking. In the case of localized corrosion, the probability of occurrence plays a decisive role for deciding the corrosion failure life, as pointed out by Evans [4]. He stated that the knowledge of corrosion rate is less important than ascertainment of the statistical risk of localized corrosion initiation for predicting corrosion failure in actual field environments. Thus stochastic concepts and reliability assessment are necessary for the assessment of long-term corrosion life in the repository.

Various types of the probability distribution functions (pdf) have been observed for corrosion data. The normal distribution is most familiar, and data having an average and standard deviation can be properly analyzed by a normal probability distribution. In corrosion phenomena, however, extreme values including the largest or the smallest value are often more important than the average, so that extreme value distributions such as the Gumbel and Weibull distribution are useful for analyzing corrosion data. In this report, the important types of pdf's for reliability assessment are discussed for pitting corrosion, crevice corrosion and stress corrosion cracking. Life assessment based on reliability concept is also discussed.

The approaches to several localized corrosion applications were presented:

- Corrosion probability and Poisson type probability distribution
- Pit generation as a stochastic process
- Extreme value analysis to predict the maximum pit depth
- Statistical distribution of Stress corrosion cracking
- Quantitative assessment of SCC failure by the reliability concept

The parameters of the distribution have to be known and data accumulation on the probability distribution of failure life is required. Little data on the distribution of failure life exists compared to the corrosion rate data based on the deterministic approach.

Accumulation of the failure life distribution data for the candidate materials by an accelerated test or in the actual field is required for assessment of the reliability of the candidate materials.

1. D. M. Macdonald and M. Urquidi-Macdonald, *Electrochim. Acta.*, 31, 1079, 1986. *J. Electrochem. Soc.*, 134, 41, 1987.
2. T. Shibata and T. Takeyama, *Corrosion*, 33, 7, 243-251, 1977.
3. T. Shibata, *Corrosion Sci.*, 31, 413-423, 1990.
4. U. R. Evans, *Proc. Localized Corrosion*, Ed, by B. F. Brown, J. Kruger and R. W. Staehle, p.144, NACE, Houston, 1974.

11.2.11 Microbiologically Influenced Corrosion

[after Dexter-Special Topic Report]

The primary concern of research dealing with the microbiologically influenced corrosion (MIC) issue in the YM Project is to determine whether or not MIC will introduce a serious flaw into the design. Given the desired lifetime for the waste packages and the inherent adaptability of the microbial community over that time period, the question can never be fully answered. No matter how many experiments are done, it will never be possible to conclude that MIC poses no danger to waste package integrity.

Under the higher temperature mode (HTOM), it seems reasonable to conclude that organisms will be of no consequence to corrosion until after the temperature at the WP surface falls below the point mentioned above, and liquid water is present in the environment. Under the lower temperature mode (LTOM) scenario, it would be more prudent to assume that some microbes will be present, and potentially able to interact with corrosion at all times.

The sum available information is not sufficient to conclude whether or not there will be significant MIC on the waste package or drip shield surfaces during the YM confinement period. However, it does support the contention that MIC cannot be ruled out because of the harsh initial environment. The TMI experience also supports the contention expressed above that bulk liquid water needs to be avoided. Due to the tendency of the microbial community to change and adapt by mutations, especially under harsh conditions, it would seem to be a very difficult task to place any reliable, quantitative bounds on when microbes will exist, or under what conditions they will effect corrosion.

Overall Conclusions:

1. As a matter of first priority, the latest calculations for drainage of the drift need to be clarified. If it can be verified that even large quantities of bulk water can be drained sufficiently within two weeks that WP surfaces are not in contact with bulk liquid water, then the most damaging known MIC scenario can be dismissed. If that proves to be impossible, then the possibility of increasing the "dry-well" capacity of the drift, as has been suggested by Project personnel, should be considered.

It should be emphasized that the reliability of this conclusion is tied directly to the reliability with which one can determine that the WP surface, especially that portion containing a weld, will not encounter a bulk liquid water environment during the design confinement period.

2. Highest priority for Project resources should also be placed on accelerating the schedule for experiments to:
 - a) Clarify the initial findings of incipient pitting and dealloying of Alloy 22, and surface roughening of Ti Gr7.
 - b) Obtain microbial corrosion data under chemical, hydrodynamic, metallurgical and biological conditions more representative of those expected for the environment in the repository during the confinement period.

3. The MIC data measured so far are not suitable for use in modeling. Modeling of real benefit to the Project must await data from the measurements in more realistic environments. This work has started, and it should be accelerated.
4. The most vulnerable locations on waste package and drip shield surfaces are at welds and crevices.

Integrity of the welds, as specified in the YM Science and Engineering Report, 2001, Section 3.4.2., will be critical for resisting the effects of microorganisms.

5. The "rate enhancement factor" approach to modeling the effects of MIC is unsuitable in most cases because:
 - a) MIC often changes not only the rate, but also the mode of corrosion from uniform to localized, and
 - b) The living microbial community is adaptable by mutations, especially under the stressful conditions expected in the repository.
6. Accelerated testing will be very difficult to employ for the purpose of getting MIC data for modeling. The reason is that the organisms may not behave the same in short-term accelerated lab tests as in the real YM environment.
7. Experience with microorganisms in the radiation field at Three-Mile Island supports the contention that MIC cannot be ruled out for the YM Project because of the harsh initial environment. The TMI experience also supports the contention that bulk liquid water needs to be avoided during the YM confinement period.
8. MIC and other forms of corrosion may lead to deterioration of the rock faces of the drift, the carbon steel rock bolts and the carbon steel invert structure. Deterioration of these latter structures should be evaluated to see if this would pose a threat to WP integrity. If such corrosion would not compromise WP integrity, then it is recommended that these effects may be ignored.

11.2.12 Radiation Effects

[after Jones-Special Topic Report]

The waste canister and surrounding environment will be subjected to a flux of neutrons and gamma rays from the stored radioactive waste. These fluxes can cause the following damage: 1) neutrons will produce atomic displacement damage in the metal, 2) neutrons will produce atomic displacement damage and gamma rays will cause electron-hole pairs in the passive film and 3) gamma rays will cause radiolysis of the surrounding environment. The peak neutron flux has been calculated to be about 5×10^4 n/cm²-s. The total neutron fluence, taking the most conservative estimate with no nuclear decay of the waste, will be 1.5×10^{16} n/cm² in 10,000 years. The peak gamma flux is about 1000 rad/hr at the time of emplacement (DOE Report-Dose calculation); decreases to approximately 10 rad/hr after 200 years; and decreases to approximately 0.1 rad/hr after 400 years. Radiolysis from gamma radiation is only a factor in the environment on the waste package surfaces when the waste packages are wet.

There is no evidence to suggest that radiation damage to the waste canister will alter its mechanical properties; therefore, radiation damage studies of alloy 22 are not warranted. Also, there is no evidence that radiation damage of the passive film will alter its protective properties; although, this is based on studies by Saito et al. (1997) of Type 304 SS at 280°C. There are differences in the passive film formed on the iron based Type 304 SS at 280°C and the lower temperature (less than 170°C) film formed on the nickel based Alloy 22.

Results suggest that the production of H₂O₂ by radiolysis is the primary cause of a shift in the open circuit potential, but that this effect has not been sufficiently studied for Alloy 22 at gamma fluxes that will exist when condensed water is present.

11.2.13 High-Temperature Corrosion Related to Waste Package Corrosion

[after Rapp-Special Topic Report]

Certain aspects of the corrosion expected for nuclear waste burial canisters involve mechanisms, measurements and interpretations that have been well studied and understood in terms of high-temperature corrosion studies. In particular, the subjects of hot corrosion, scale growth and adherence, the role of interfacial metal/scale structure in vacancy annihilation, and the segregation of impurity solutes to interfaces are discussed here. The initial formation of a very thin, adherent chromia-rich air-formed film seems important and advantageous to the long-term stability of the protective layer. Optimization of the initial surface preparation is recommended, and traditional electrochemical studies of passivation are suggested to offer little relevance to the problem.

Based on certain YMP reports describing the proposed waste burial system at Yucca Mountain, discussions held at the July 2001 NWTRB Workshop on Long-Term Extrapolation of Passive Behavior, and especially the report of Gustavo Cragnolino to that Workshop, certain aspects of the corrosion of the waste containment vessels are worthy of critical consideration. First, the Alloy 22 containment vessels will begin their service in an essentially dry air atmosphere at a temperature as high as 250C. Depending on many factors, such as the manipulation of ventilation cooling, the intrusion/seepage of ground water, the effectiveness of the Ti drip shields, etc., the Alloy 22 canisters could remain dry, e.g. only experience the slow growth of a protective chromia-rich film for a relatively long period (one hundred years or more). Ultimately, after sufficient cooling resulting from the decomposition of the nuclear waste, the relative humidity in the vault could exceed that necessary for condensation of a water film on this surface. Otherwise, some water could be deposited on the surface directly via seepage, etc., if the Ti drip shields should fail. In any case, an extended period of protective chromia-rich scale growth would precede the presence of any surface water film. Thereafter, the corrosion problem would become a rather unusual case of "atmospheric corrosion" of a *prefilmed* surface.

Atmospheric Corrosion of Prefilmed Alloy 22 Surface: It seems clear that the oxidation rate in dry air in the range 200-300C (even following a parabolic rate law) can be considered absolutely negligible. Even iron and steels, the fastest oxidizing of all the practical alloy base metals, are estimated to suffer only about 15 microns of alloy recession with no breakaway kinetics after 1,000 years of oxidation in air at 250C. With respect to wet atmospheric conditions, properly designed experimentation studying the atmospheric corrosion of a preformed oxide film on Alloy 22 are likely to demonstrate very low attack rates: (a) the preexisting film should support all of the difference in oxidation state which otherwise drives atmospheric corrosion and (b) the expected inherent protective nature of chromate solute should prevent any contact of the

base alloy with the aqueous film in any case. There seems to be no apparent reason, except for the unlikely prospect of localized dissolution penetrating the air-formed film to reach the metal, that the formation or growth of a passive aqueous film would become relevant.

The distinction between passive corrosion of an alloy in a "deep" aqueous solution (especially a deaerated solution) and "atmospheric corrosion" caused by a thin aerated surface film is significant, and seems to be overlooked in the current corrosion studies of Alloy 22. This distinction and its ramifications should be pursued.

Role of the Metal-Scale Interface in Vacancy Annihilation; Effect of Surface Preparation:

In the estimation of life prediction for such an application, a principal unknown factor can be the occurrence of any "breakaway kinetics" resulting from the rupture, detachment or penetration of the protective film, whether it be a solid oxide or a hydrated passive film. One of the factors causing concern for the evaluation of the waste burial system is whether one can expect that vacancies active in supporting the diffusion of cations (or anions) through the protective film would experience a harmful coalescence (leading to local separation) at the metal/film interface, or whether vacancy annihilation at that interface would retain the attached film. As already mentioned, for the Waste Canister application, the uniform corrosion rate is not an issue, but the adherence of the barrier film could be important. From the available studies, and implications from the modern mechanistic models, an initial surface with minimal strain giving better scale adherence would be favored for an electropolished surface. I recommend the consideration and implementation of such surface preparation studies in the ongoing experimentation. For the extremely thin oxide films relevant to Alloy 22 oxidation and corrosion, with proper surface preparation, I do not foresee any problem with retention of an adherent protective oxide film for 10,000 years. I might also suggest that the electroplating solution contain some soluble cerium ions, as these have been shown to produce various advantageous effects in both reducing scaling kinetics and scale adherence for chromia films both at high temperatures¹⁴, and for aqueous corrosion.

Role of Interfacial Impurity Segregation

Some concern has been expressed that minor impurities in the alloy, e.g. sulfur and phosphorus, would segregate and concentrate at the metal/film interface, thereby degrading the film adherence and affecting its interactive role with vacancies. The problem of interfacial segregation has been carefully studied at high temperatures and the resulting conclusions should also be valid at much lower temperatures. The postulation is that sulfur in the alloy would accumulate/segregate (preferentially) at the alloy/film interface, leading to breakdown of the passive film and localized corrosion. Such a behavior for sulfur does not occur at *adherent* high-temperature metal/scale interfaces. To the extent that the preformed oxide film would protect the Alloy 22, and to the extent that any passive film would be crystalline, I would suggest that such a problem would not be expected for the Waste Canisters.

The author has attempted to introduce certain aspects of the body of knowledge of high-temperature corrosion to interpret the low-temperature corrosion problem for Alloy 22 nuclear waste canisters. Some of the suggestions made here may seem unusual to the aqueous community, e.g. the lack of relevance of traditional electrochemical corrosion methods, the importance of initial surface preparation, etc., and these points require some further discussion and resolution.

11.2.14 Interfacial Segregation in Nickel Base Alloys

[after Briant-Special Topic Report]

It is known that segregation to interfaces can enhance this corrosion. This study was undertaken to determine what segregants might be present on the metal interfaces that could lead to corrosive attack and whether or not segregation could increase during long-term storage. Some restrictions placed to focus the study. The temperature regime of interest, which is below 250°C, is much lower than the range where laboratory experiments have been generally performed. Thus one must try to extrapolate information obtained at higher temperatures to this low temperature regime. Much more work on segregation has been done on iron-base alloys than on nickel-base alloys. There does not appear to be any segregation data available for the Alloy 22; however, there are a few studies on C-276. It was assumed that radiation damage will not significantly affect the segregation.

In summary, one can show that some segregation is kinetically possible at the very long times considered in this Project. However, almost all segregation will take place during the thermal transient at the beginning of storage. The peak temperature and the rate of cooling will be important parameters in determining how much segregation will result.

For grain boundary segregation, it would appear that the primary impurity that would segregate would be phosphorus. Sulfur will be gettered in the matrix and there is little evidence that silicon is a strong segregant. Surface segregation could also occur if no metal oxide were present. In that case sulfur and phosphorus would be likely segregants. However, since it is assumed that an oxide will be present at all temperatures it seems unlikely based on all experimental evidence that segregation would occur. However, if internal voids were to form in some way, these elements could segregate to the surface of voids as a result of the thermal profile during the initial period of storage.

Grain Boundary Segregation: While there was no data available for Alloy 22, based on results for C-276 one would predict that phosphorus would be the primary segregant, since the chromium content of this material should eliminate sulfur segregation to grain boundaries. When the peak temperature is 250°C, segregation has reached equilibrium in approximately 100 years. However, at a peak temperature of 180°C several important differences can be noted. First, the total amount of segregation only reaches approximately 20% of the saturation value. Second, segregation continues through the first 200 years but then rapidly begins to die off. After 300 years the temperature has dropped enough so that there is little additional segregation. With a peak temperature of 85°C, the amount of segregation is extremely small. Another important question is how much segregation could occur in 10000 years at room temperature. It is found that even over this long time span the amount of segregation is negligible and is unlikely to have any effect on the material properties.

Segregation to Free Surface with No oxide: The main conclusions to be drawn from studies on both iron and nickel base alloys, is that sulfur is the primary segregant in that it will displace other elements from the surface if there is sufficient concentration in the matrix. Other elements such as O, N, P, Si, and C can also segregate; however, in most cases they can be displaced by sulfur. However, one must consider the fact that the surface is covered with an oxide. It appears that the metal-oxide bond may inhibit most segregation and that the results reported here for oxide-free surfaces are actually relevant for the case of internal voids.

Segregation to the Oxide-Metal Interface: For low temperature segregation effects in a nickel base alloy, it would appear that unless voids form at the metal-oxide interface, it is unlikely that segregation will occur there. Thus, if we assume that an oxide forms immediately on the metal at

room temperature, then it seems unlikely that there would be significant segregation to the free surface or the metal oxide interface at the temperatures under consideration here.

11.2.15 Effect of Grain Boundary Precipitates

[after Floreen.-Special Topic Report]

The Project staff has taken the approach that precipitation only becomes detrimental when 100 per cent of the grain boundaries are covered. This is too optimistic. Detrimental effects from second phases can result with very small amounts and with only a small fraction of the boundaries containing precipitates. If precipitates cause trouble, a little bit can go a long way. The author suggests that if precipitates are damaging, the effect may be observed an order of magnitude in time before 100 per cent coverage.

Detrimental effects of precipitation are likely to be most prevalent in the weld metal. Depending upon the welding details detrimental phases may be present from the start. Precipitation will occur faster than in base plate because of segregation in the cast structures of the weld. The rate of precipitation will increase with temperature of course, which is a penalty for higher temperature operation.

11.2.16 Effect of Stress Relaxation

[after Special Topic Reports: (a) Jones (b) Floreen]

The effect of long-term stress relaxation on residual stresses in waste packages should be determined. Stress relaxation refers to the decay in applied or residual stresses during elevated temperature exposure through a combination of small-scale creep and annealing processes. The classic case is a bolt holding two pieces together. With thermal exposures the bolt force will drop and eventually fully relax. The relevance to waste package performance is the effects of stress relaxation on beneficial stresses, e.g. post-weld laser treatment for creating residual compressive stresses in the welds and detrimental stresses, e.g. the residual tensile stresses from the initial welding. Clearly, the importance of the stress mitigation process to alleviating stress corrosion cracking and the fact that low temperature stress relaxation occurs in metals suggests that stress relaxation measurements be made of the compressive residual stresses in alloy 22 following both induction heating and quenching and laser peening.

11.2.17 Corrosion of Nickel Base Alloys in Flue Gas Desulfurization Systems

[after Beavers-Special Topic Report]

Emissions of sulfur dioxide (SO₂) result from burning coal for electric power generation. Flue gas desulfurization (FGD) minimizes emissions by scrubbing the flue gas generated by the combustion of high-sulfur. Counter current spraying with aqueous slurry of lime or limestone removes the SO₂ present in the flue gas. The slurry becomes very corrosive as a result of the absorption of the acid gases in the flue gas, including SO₂, HF, and HCl. The environment is highly corrosive: highly acidic (less than pH 2), high chlorides, oxidizing and mixed ionic species.

Field experience and laboratory testing of stainless steels and nickel base alloys for FGD applications demonstrate that Alloy 22 and other nickel base alloys of similar composition, such as Alloy C-276 and Alloy C-4, are highly resistant to localized corrosion in aggressive FGD

environments. While providing good overall performance, these alloys are not immune to corrosion attack and have experienced incipient pitting and crevice corrosion. In several cases, the corrosion was associated with thicker oxide (heat tint) patches on the surface.

The most corrosive conditions were found in the pre-scrubbers, the ducts upstream of the re-heaters, and in the re-heaters. It was found that pitting and crevice corrosion of stainless steels and, to a lesser degree, nickel base alloys commonly occurred in these components. Stress corrosion cracking failures of stainless steels were found in the pre-scrubbers and in the re-heaters for these systems where higher temperatures and more acidic conditions were encountered. In most cases, the localized corrosion and SCC problems with metallic materials could be prevented by the application of higher alloyed materials.

Thompson and Syrett (1992) used a statistical experimental design and electrochemical tests to investigate the localized corrosion behavior of several alloys in the complex environments comprised of a range of multiple ionic species and pH. Samples were tested in simulated FGD solutions using a standard cyclic potentiodynamic polarization procedure (ASTM G-61), a potentiostatic polarization procedure, and a modified version of the ASTM F-764 procedure. In the latter, specimens were potentiostated above the pitting potential for various times to produce pitting and then shifted to more negative values. The process was repeated over a range of pitting times and final potentials until a potential was established above which pitting would continue and below which passivation would occur. The approach was highly successful and the single and mixed-ion contributions to corrosion were determined. The range of corrosion-resistant service for each of the alloys was determined.

N. G. Thompson and B. C. Syrett, "Relationship Between Conventional Pitting and Protection Potentials and a New, Unique Pitting Potential," *Corrosion*, Vol. 48, No. 8, 1992, p. 649.

11.2.18 Atmospheric Corrosion of Nickel Base Alloys

[after Beavers-Special Topic Report]

Conventional ferritic and austenitic stainless steels are used extensively in atmospheric applications including marine atmospheres. Nickel base alloys have excellent resistance to atmospheric corrosion even in marine environments. Hastelloy Alloy C was bright and shiny, with no evidence of localized or general attack following 50 years marine exposure at the Kure Beach atmospheric corrosion test site. Stress corrosion cracking and hydrogen embrittlement are common problems for stainless steels in marine environments, primarily those alloys with high strength levels or a sensitized microstructure. For 5-year exposures of U-bends of a number of stainless steels and a few nickel base alloys at the Kure Beach test site, none of the annealed, cold worked, or welded specimens failed by SCC but a high proportion of the stainless steel specimens that were sensitized underwent cracking. Incoloy Alloys 800 and 825, Inconel Alloy 600, and Alloy 20-CB-3 were resistant to cracking, even in the sensitized condition.

A few studies have been conducted in which the effect of sheltered versus exposed atmospheric conditions was evaluated. The kinetics of corrosion of copper, zinc, steel, and aluminum were fitted to power laws for exposure periods of up to 8 years. For steel and aluminum, the corrosion rates initially were higher for the fully exposed condition but the slopes for the power laws were higher for the sheltered exposure, such that the corrosion rates at the end of the eight-year period were higher for the sheltered exposure. The behavior was attributed to the accumulation of corrosive deposits and non-protective corrosion products on the sheltered metal surfaces.

These results show that corrosion processes can occur in sheltered (no direct impingement of rain water or dripping) conditions. In addition, stress corrosion cracking of susceptible metals, e.g. sensitized stainless steels, occurs in marine open marine atmospheres. More corrosion resistant metals did not exhibit stress corrosion cracking. Based on these results, any substitution of metals with less corrosion than Alloy 22 for waste packages is not recommended. Clearly, 304/316 would fail under much more benign conditions. It is prudent to go with the best unless there is strong evidence that less resistant metals will work. There will be a strong economic incentive to use less expensive alloys. This should be evaluated carefully and materials substitutions allowed only with strong technical evidence to support long-term performance.

11.2.19 Corrosion Of Stainless Alloys And Titanium In Peroxide Solutions

[after Newman-Special Topic Report]

Generation of aqueous peroxide by radiolysis can be expected at the surface of Yucca Mountain waste containers, and also on the drip shield, provided the conditions are such as to promote the retention of an aqueous phase. One can argue about the stability of peroxide under the repository conditions, but there are some factors, such as the presence of fluoride, that might lead to its stabilization. The purpose of the review is to consider the possible corrosion processes that might occur in the more extreme circumstances that could be envisaged. A full list of these would include crevice corrosion, transpassive corrosion and HO_2^- complexation. The review focused only on the latter two possibilities, which are essentially uniform modes of corrosion.

Peroxide can cause uniform corrosion in a variety of pitting-resistant materials, but two completely different mechanisms are involved: transpassive dissolution, and HO_2^- complexation. These two topics are now reviewed, as they may be relevant to the condensed environment in Yucca Mountain where radiolytic formation of peroxide cannot be ruled out.

Transpassive corrosion of FeCr or NiCr based alloys can occur in highly oxidizing aqueous environments. In bleaching processes, such corrosion has been encountered with a variety of oxidants, especially chlorine dioxide, but also hydrogen peroxide. It may occur with hypochlorite, but only at concentrations higher than those usually used in pulp bleaching.

Transpassive corrosion in bleaching processes was discovered in nickel-base alloys, with stainless steels appearing immune. The reason for this is that iron (III) oxide or oxyhydroxide provides an adequately protective film in mildly alkaline environments, provided the conditions are not such as to promote pitting (i.e. the temperature is lower than the critical pitting temperature), and provided that there are no complexants of Fe(III) present. Nickel base alloys such as C-276 and C-22 have low iron contents and are prime candidates for transpassive corrosion. It is likely that an alloy could be engineered to provide optimum resistance to transpassive corrosion by including a critical content of iron and/or other elements that do not dissolve at the relevant potentials. It is not clear why NiO is so vulnerable to destruction of its passivating properties compared with Fe_2O_3 or FeOOH , but one can speculate that this involves the very thin, crystalline, well-defined nature of the NiO film, compared with the more flexible nature of the range of products, including hydrated networks, that can form on iron.

Transpassive corrosion, or rather discoloration, has been observed in stainless steels when phosphonates are present, as these are complexants of Fe(III) and enable continuous dissolution of Cr(VI) to occur. This was essentially a cosmetic problem, but there are also some anecdotal cases of serious transpassive corrosion loss in stainless steels. Such problems may be due to

extreme oxidant concentrations, presence of high levels of complexants such as EDTA, low water activity or perhaps particular values of pH where iron cannot provide a protective film. At one time it was thought (e.g. by the author) that molybdenum dissolution was the main transpassive process occurring in this kind of corrosion, with Cr transpassivity being a subsidiary aspect. Now it appears that Cr transpassivity is both necessary and sufficient, although Mo definitely assists the process. There are various possibilities to inhibit this kind of corrosion, such as the use of silicates.

Titanium corrodes in alkaline peroxide solutions because the HO_2^- anion is a complexant for Ti(IV) as well as an oxidant. The corrosion has a fairly simple mechanism and appears to be well understood. The corrosion rate can be high, more than 10 mm/year in the worst cases. Low levels of calcium ions may act as effective inhibitors, as well as other species including magnesium, silicate and phosphate. Published corrosion-rate data may be unreliable because of very short test durations such as 1 hour. There are few data on the corrosion of titanium alloys in such media, but the rates and mechanism are probably similar to those of pure titanium. It is unlikely that low levels of elements such as Pd will block the corrosion significantly, but some experimentation may be worthwhile. It is possible that long-term corrosion rates will be higher with Pd or other electrocatalytic alloying elements, as these will catalyze the cathodic reaction.

APPENDICES

Appendix A: Peer Review Panel for the Waste Package Materials Performance Peer Review

Dr. Joe H. Payer	-	Chairperson
Professor, Department of Materials Science and Engineering		University
Case Western Reserve		Avenue
10900 Euclid		
Cleveland, Ohio 44106-7204; Phone: (216) 368-4218; Fax: (216) 368-2981; e-mail: jhp@po.cwru.edu		

Dr. John A. Beavers
Executive Vice President
CC Technologies
6141 Avery Road
Dublin, Ohio 43016-8761
Phone: (614) 761-1214; Fax: (614) 761-1633; e-mail: jbeavers@cctlabs.com

Dr. Thomas M. Devine, Jr.
Chairman, Department of Materials Science and Engineering
University of California, Berkeley
11 Teodora Court
Moraga, California 94720-1760
Phone: (510) 642-3801; Fax: (510) 642-3803; e-mail: devine@socrates.berkeley.edu

Dr. Gerald S. Frankel
Professor, Department of Materials Science and Engineering
The Ohio State University
477 Watts Hall, 2041 College Road
Columbus, Ohio 43210
Phone: (614) 688-4128; Fax: (614) 292-9857; e-mail: frankel.10@osu.edu

Dr. Russell H. Jones
Senior Staff Scientist and Technical Group Manager
Battelle-Northwest

Phone: (509) 376-4276; Fax: (509) 376-0418; e-mail: rh.jones@pnl.gov

Dr. Robert G. Kelly
Associate Professor, Department of Materials Science and Engineering
University of Virginia
Charlottesville, VA

Phone: (804) 982-5783; Fax: (804) 982-5799; e-mail: rgkelly@virginia.edu

Dr. Ronald M. Latanision
Professor, Department of Materials Science and Engineering
Professor, Department of Nuclear Engineering
Massachusetts Institute of Technology
77 Massachusetts Avenue – Room 8-202
Cambridge, Massachusetts 02139-4307

Phone: (617) 253-4697; Fax: (617)253-8745; e-mail: lats@mit.edu

Appendix B: Biographical Sketches of Waste Package Materials Performance Peer Review Panel Members

Dr. Joe H. Payer, Panel Chairperson, Professor of Materials Science and Engineering, Case Western Reserve University.

Dr. Payer is Director of the Yeager Center for Electrochemical Sciences at CWRU. Specialties include materials performance and reliability, failure analysis, development and verification of corrosion control methods, advances to test methods and monitoring systems and determination of degradation mechanisms. He is a Fellow of ASM International, a Fellow and past president of NACE International and recipient of the ASTM Sam Tour Award for Contributions to Corrosion Test Methods.

Dr. John A. Beavers, Executive Vice President of CC Technologies Laboratories, Inc., Dublin, Ohio.

Dr. Beavers directs programs in corrosion control, reliability and life prediction. He has utilized state-of-the-art electrochemical, surface analytical, and mechanical techniques for evaluation of materials performance for different forms of corrosion. A major emphasis his research has been the mechanistic and practical aspects of corrosion and stress corrosion cracking (SCC) on underground structures.

Dr. Thomas M. Devine, Jr., Chairman and Professor, Department of Materials Science and Engineering, University of California, Berkeley.

Dr. Devine conducts research on the role of surface films in corrosion phenomena and the mechanism of passivity. He has been a leader in the application of surface analytical methods to corrosion studies. He is recipient of the Exxon Education Foundation Award, Research Award from the Jacob Wallenberg Foundation and the Royal Swedish Academy of Engineering Sciences, and the Alfred H. Geisler Memorial Award of the American Society for Metals.

Dr. Gerald S. Frankel, Professor of Materials Science and Engineering, Ohio State University.

Dr. Frankel is Director of the Fontana Corrosion Center at OSU. Specialties include passivity of metals, initiation and propagation of localized corrosion, effects of microstructure on corrosion of Al alloys,

novel techniques for the study of corrosion, including AFM-based methods, corrosion of microelectronic and magnetic devices. He is the recipient of 2000 H.H. Uhlig Young Educator award of NACE International and an IBM Outstanding Technical Achievement Award.

Dr. Russell H. Jones, Senior Staff Scientist and Technical Group Manager, Structural Materials Research, Battelle-Northwest, Richland, WA.

Dr. Jones and his colleagues at Battelle have made significant contributions to understanding the relationships between grain boundary chemistry and environmental interactions. His research determines the structure-property relationships of stress corrosion cracking and hydrogen embrittlement through the use of modern analytical tools. He is a Fellow of ASM International and a Fellow of the Russian Academy of Engineering Sciences.

Dr. Robert G. Kelly, Associate Professor of Materials Science and Engineering, University of Virginia.

Dr. Kelly's specialties include developing fundamental understanding of localized corrosion and electrochemistry of metals and alloys with particular emphasis on ferrous, aluminum and nickel-based alloys in both aqueous and non-aqueous solutions. He was selected as the recipient of the 1997 A. B. Campbell for the best paper by an author 35 years old or younger, and the 1999 H. H. Uhlig Award for young corrosion educators, both awards from the National Association of Corrosion Engineers.

Dr. Ronald M. Latanision, Professor, Department of Materials Science and Engineering and Department of Nuclear Engineering, Massachusetts Institute of Technology.

Dr. Latanision is also Director of H. H. Uhlig Corrosion Laboratory. His specialties include: hydrogen embrittlement of nickel- and titanium-base alloys and intermetallics; behavior of nickel-base alloys in light water reactor and supercritical water systems; aqueous corrosion resistance of composites, metastable alloys, and surface-modified solids; and photoelectrochemical studies of the electronic properties of passive films on metal substrates. He is a member of the National Academy of Engineering and a Fellow of the ASM International, NACE International, and the American Academy of Arts and Sciences.

Appendix C: Objective Sub-issues and Pre-defined Questions for the Peer Review

Assessment of potential degradation modes

Long term failure modes, consider any "fatal flaws", long-term metallurgical behavior

Long term performance of passive metals

Long term behavior of passive films, growth of film, remnants of film growth, basis for penetration rate of metal, relevant information from the chemical process and other industries, geological and archaeological analogues, technical rationale for long-term projections

Composition of waters in contact with waste package materials

Basis for identification of likely and extreme environmental conditions, changes in solution near and on waste package surface, technical rationale for long-term projections

Understanding and control of crevice corrosion and pitting

Conditions and basis under which process initiates, propagates, arrests, and reinitiates, basis for environmental limits for a given metal, critical temperature treatment, propagation in unsaturated media, potential penetration distribution and morphology, technical rationale for long-term projections

Understanding and control of stress corrosion cracking

Conditions and basis under which process initiates, propagates, arrests, and reinitiates, basis for performance of given metal, means to control, potential penetration distribution and morphology, technical rationale for long-term projections

From: *Appendix A, Peer Review Plan for the Waste Package Materials Performance Peer Review, Revision 01, June 6, 2001*

Appendix D: Roster of Subject Matter Experts

The following Subject Matter Experts provided advice and information and prepared helpful background reports to assist the Panel in its deliberations.

Name	Location	Technical Area
United States		
Craig M. Bethke	University of Illinois	Hydrogeology
Clyde L. Briant	Brown University	Metallurgy
Stephen C. Dexter	University of Delaware	Corrosion-MIC
Stephen Floreen	Schenectady, New York	Metallurgy
Robert P. Frankenthal	Red Bank, New Jersey	Corrosion-passivity
Carl E. Jaske	CC Technologies, Columbus, Ohio	Fracture mechanics-life prediction
John C. Lippold	Ohio State University	Welding
Kathryn L. Nagy	University of Colorado	Geochemistry

Robert A. Rapp	Ohio State University	Oxidation
International		
Roger C. Newman	UMIST; Manchester, UK	Corrosion-passivity
Alan Turnbull	National Physics Lab; Teddington, UK	Corrosion
Toshio Shibata	Fukui University of Technology; Osaka, Japan	Corrosion-passivity
Masatsune Akashi	Ishikawajima-Harima Heavy Industries Co., (IHI), Tokyo, Japan	Life prediction-corrosion
Hannu Hanninen	Helsinki University of Technology; Finland	Metallurgy-Corrosion
Bo Rosborg	Rosborg Consulting, Sweden	Corrosion-SCC

Appendix E: Special Topic Reports

Design And Fabrication Factors:

- **Fabrication Processes and Metallurgy: Sub-Panel Meeting;** Special Topic Report, F. Wong
- **Development of Weld Procedures;** Special Topic Report, J. Lippold
- **Composition Effects within the Chemical Specification for Alloy 22;** Special Topic Report, S. Floreen
- **Residual Stress in Stainless Steel Cylinders from Quenching;** Special Topic Report, C. Jaske
- **Corrosion Product Passive Films: Effect of Surface Finish;** Special Topic Report, R. Rapp

Corrosion, Chemistry and Metallurgy Factors:

- **Localized Corrosion: Phenomenology and Controlling Parameters;** Special Topic Report, G. S. Frankel
- **Water Composition within Yucca Mountain;** Special Topic Report, K. Nagy
- **Localized Corrosion: Chemistry and Radiolysis Effects;** Special Topic Report, A. Turnbull

- **Passive Films and the Long-Term Uniform Corrosion Resistance of Alloy 22;** Special Topic Report, T. Devine
- **Inhibition of Localized Corrosion by Non-Halide Anions;** Special Topic Report, R. Newman
- **Passivity-Induced Ennoblement;** Special Topic Report, G. S. Frankel
- **Localized Corrosion: Temperature Effects;** Special Topic Report, R. Newman
- **Development in the Concept of Repassivation Potential as a Measure of Crevice Corrosion Susceptibility;** Special Topic Report, T. Shibata
- **The Critical Potential for Localized Corrosion;** Special Topic Report, M. Akashi
- **Formation of an Aqueous Environment from Condensation in Dust Layer;** Special Topic Report, R. Frankenthal
- **Statistical and stochastic aspects of corrosion life prediction;** Special Topic Report, T. Shibata
- **Microbiologically Influenced Corrosion;** Special Topic Report, S. Dexter
- **Radiation Effects;** Special Topic Report, R. Jones
- **High-Temperature Corrosion Related to Waste Package Corrosion;** Special Topic Report, R. Rapp
- **Interfacial Segregation in Nickel Base Alloys;** Special Topic Report; C. Briant
- **Comments on Metallurgy and Fabrication of Alloy 22 Waste Packages;** Special Topic Report, S. Floreen
- **Effects of Stress Relaxation on Stress Mitigation;** Special Topic Report, R. Jones
- **Corrosion of Nickel Base Alloys in Flue Gas Desulfurization Systems;** Special Topic Report, J. Beavers
- **Atmospheric Corrosion of Nickel Base Alloys;** Special Topic Report, J. Beavers
- **Corrosion Of Stainless Alloys And Titanium In Peroxide Solutions;** Special Topic Report, R. Newman

Reports prepared for the Waste Package Materials Performance Peer Review.

A "Compilation of Special Topic Reports", will be released in March 2002.

Figure 1: The chemical divides concept applied to natural waters (Drever, 1997).

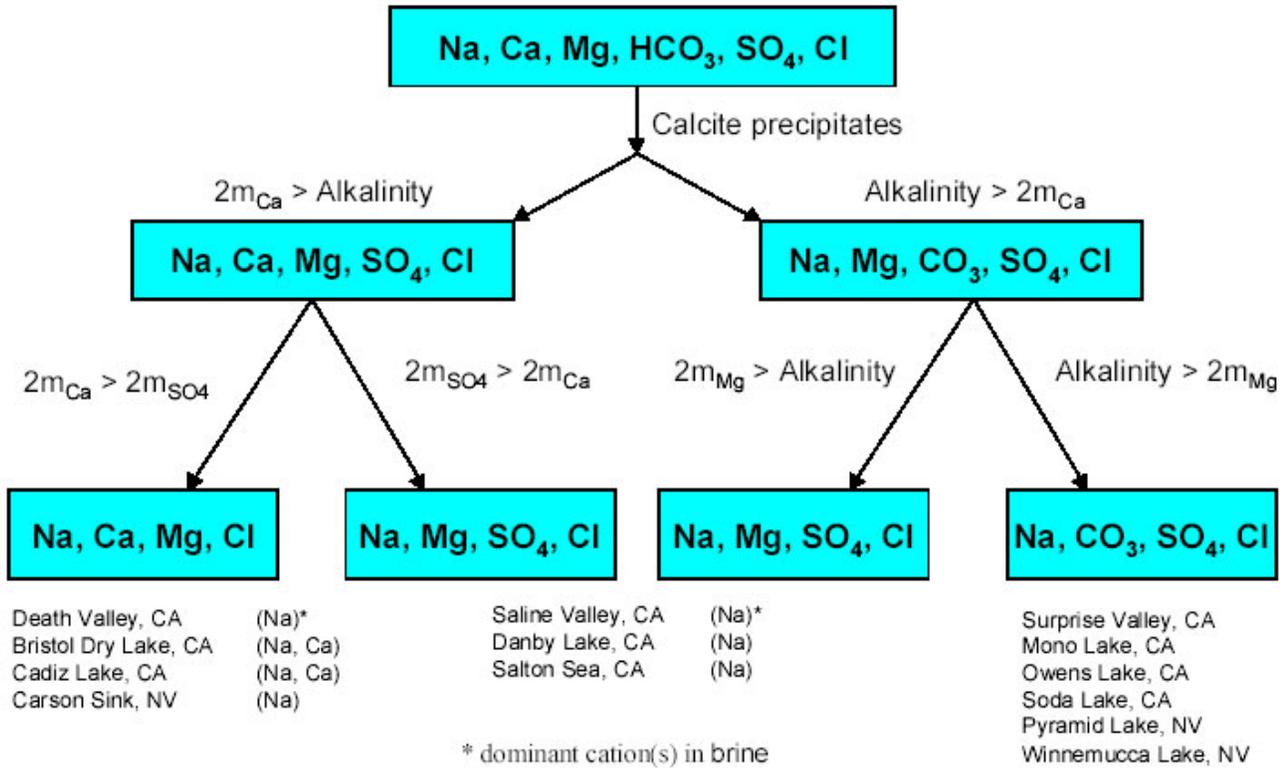


Figure 1: The chemical divides concept applied to natural waters (Drever, 1997).

Figure 1. Predicted crack velocity for Alloy 22 based on slip dissolution model as a function of stress intensity factor and assumed value of n.

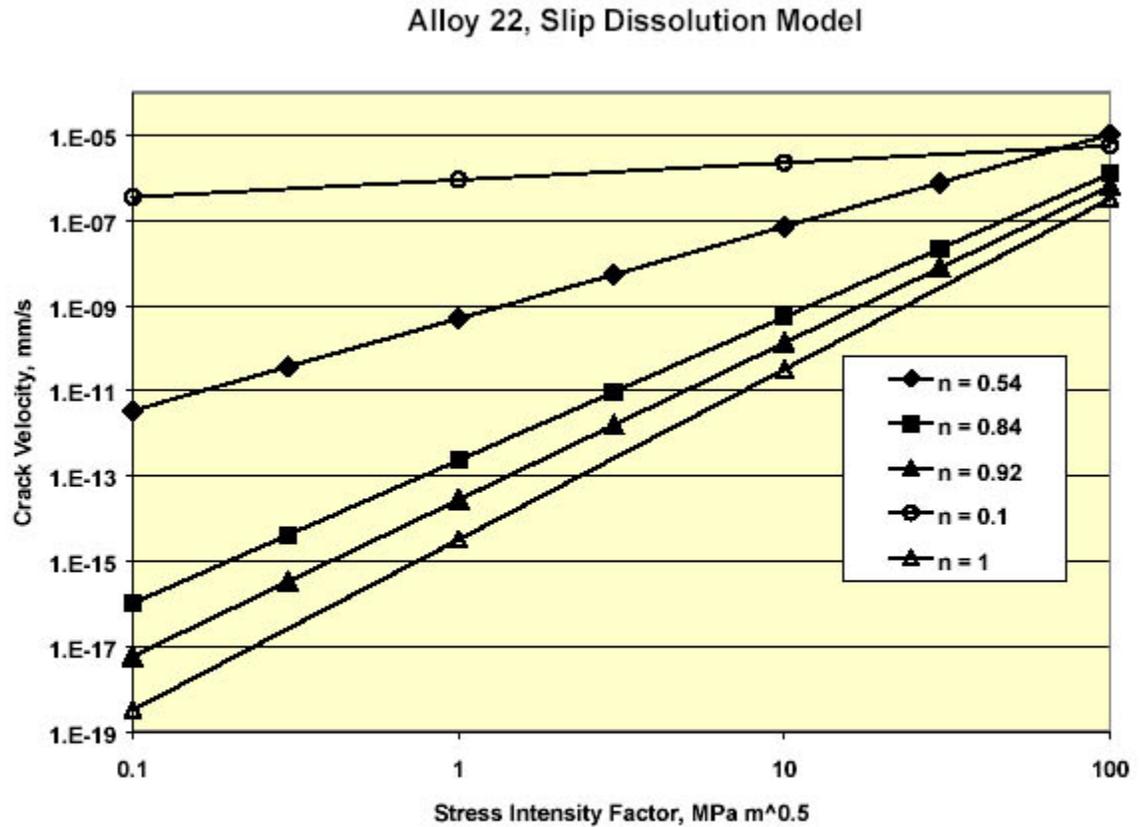


Figure 1. Predicted crack velocity for Alloy 22 based on slip dissolution model as a function of stress intensity factor and assumed value of n.

Figure 2. Predicted life for an Alloy 22 canister based on slip dissolution model as a function of stress intensity factor and assumed value of n.

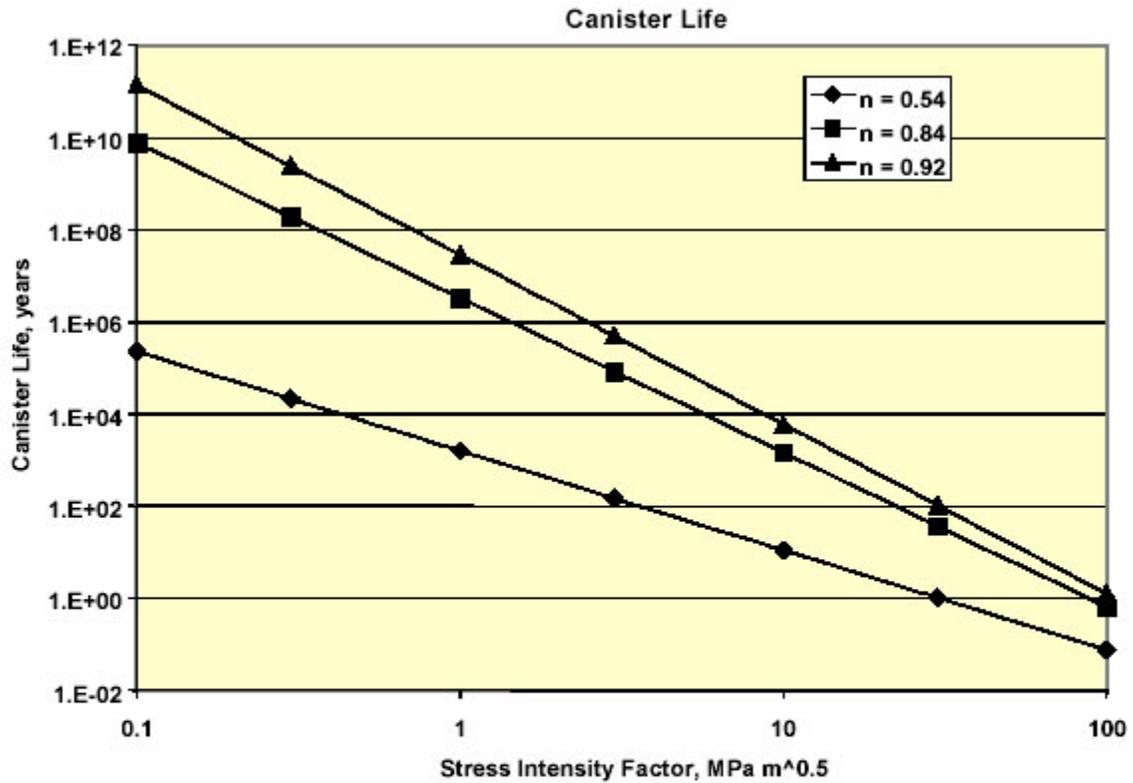


Figure 2. Predicted life for an Alloy 22 canister based on slip dissolution model as a function of stress intensity factor and assumed value of n.

Table 1: Composition of J-13 Well Water and Pore Water from the Unsaturated Zone of Yucca Mountain
(Rosenberg, *et al.*, 2001).

	J13 Well Water (mg/L)	UZ Pore Water (mg/L)
Na ⁺	45.8	9.0
K ⁺	5.04	0.01
Mg ²⁺	2.01	12
Ca ²⁺	13	65
SiO ₂	61	46
HCO ₃ ⁻	128.9	66
SO ₄ ²⁻	18.4	79
Cl ⁻	7.14	77
NO ₃ ⁻	8.78	12
F ⁻	2.18	
pH	7.41	5.6

Table 2: Test solutions used by Project for corrosion testing based on J-13 Well Water Analyses.
SDW: Simulated Dilute Water, SCW: Simulated Concentrated Water, SAW: Simulated Acidified Water, SSW: Simulated Saturated Water.

Ion	SDW	SCW	SAW	SSW
	(mg liter⁻¹)	(mg liter⁻¹)	(mg liter⁻¹)	(mg liter⁻¹)
K ⁺¹	34	3,400	3,400	141,600
Na ⁺¹	409	40,900	40,900	48,700
Mg ⁺²	1	1	1,000	0
Ca ⁺²	0.5	1	1,000	0
F ⁻¹	14	1,400	0	0
Cl ⁻¹	67	6,700	6,700	128,400
NO ₃ ⁻¹	64	6,400	6,400	1,310,000
SO ₄ ⁻²	167	16,700	16,700	0
HCO ₃ ⁻¹	947	70,000	0	0
Si	27 (60°C), 49 (90°C)	27 (60°C), 49 (90°C)	27 (60°C), 49 (90°C)	0
pH	8.1	8.1	2.7	7.0

Table 7.2 - II
Characterization of the Passive Films of Alloy 22 as a Function of Time of Immersion in 90°C
 SAW.

XPS and AES Depth Profiling					
Sample	Solution	Ecorr (vs Ag/AgCl)	Time	Film Thickness	Film Structure
22	SAW/LTCTF	+390 mV	4.5 yrs.	2000Å	Fe strong Ni depletion Cr/Ni>>1
22	SAW	-120 mV	10 days	100Å	No Fe
22	SAW/LTCTF	+50 mV	4.5 yrs.	400Å	Silicate Ni depletion Cr/Ni>>1

Table 7.2.3-I

Values of Key Electrochemical Parameters of Alloy 22 Immersed in SAW at 90°C for 24h

State of Aeration	Corrosion Potential Vs. Ag/AgCl	Passive Corrosion Rate at 500 mV vs. Ag/AgCl	Transpassive Potential
Aerated	-26 mV	3.9×10^{-6} A/cm ²	+672 mV
Unaerated	-98 mV	4.5×10^{-6} A/cm ²	+665 mV
Deaerated	-301 mV	14.3×10^{-6} A/cm ²	+647 mV

**Table 7.2.2-I
Measurements of Corrosion Rate of Alloy 22**

Test	Corrosion Rate	Reference
Wt. Loss in LTCTF	Mean of the time-average corrosion rate Of 144 samples over 2 yr. = 113 nm/y = 1.13 mm/10 ⁴ y	1*
	Maximum of the time-average corrosion Rate of 144 samples over 2 yr. = 794 nm/y = 7.94 mm/10 ⁴ y	1*
LPR in 10xJ-13 At 25°C for 5 mos.	11 nm/y = 0.11mm/10 ⁴ y	2*
Potentiostatic polarization 100 mV above corrosion potential for 300 hrs. in 0.028M NaCl at 95°C	80 nm/y = 0.80mm/10 ⁴ y	3*
Potentiostatic polarization 100 mV above corrosion potential for 300 hrs. in SCW at 90°C	8 μm/y = 14 mm/10 ⁴ y	3*
1M NaCl + 0.1M H ₂ SO ₄ 200 mV/48 hrs. at 75°C	19x10 ⁻⁹ A/cm ² = 1.33 mm/10 ⁴ y	Lloyd
500 mV/48 hrs. at 75°C	2x10 ⁻⁷ A/cm ² = 14 mm/10 ⁴ y	Lloyd
SAW at 90°C, 167 hrs. 400 mV vs Ag/AgCl	4x10 ⁻⁸ A/cm ² = 2.8 mm/10 ⁴ y	Lian
1* AMRGeneral Corrosion Localized Corrosion Waste Package Outer Barrier(Jan. 2000)		
2* Waste Package Degradation Process Model Report (Dec. 2000)		
3* "Summary of Recent information Relevant to Waste Package and Drip Shield Degradation Process Model," p.E-19, Nov. 2001.		