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**Civilian Radioactive Waste Management System
Management and Operating Contractor**

**Waste Package Degradation Expert Elicitation Project
Revision 0**

August 1997

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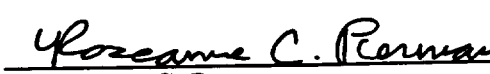
**Under Contract Number
DE-AC01-91RW00134**

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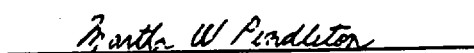
**Final Report
Waste Package Degradation Expert Elicitation Project
August 15, 1997**

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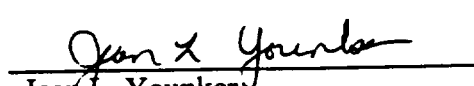
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1.0 INTRODUCTION

1.1 OBJECTIVES

This report presents results of the Waste Package Degradation Expert Elicitation (WPDEE) study for the Yucca Mountain, Nevada project. This project was sponsored by the U.S. Department of Energy (DOE) and managed by Geomatrix Consultants, Inc. (Geomatrix), for TRW Environmental Safety Systems, Inc. The WPDEE project is one of several that involve the elicitation of experts to characterize the knowledge and uncertainties in key inputs to the Yucca Mountain Total System Performance Assessment (TSPA). The DOE is characterizing a site at Yucca Mountain, Nevada, as part of the Yucca Mountain Site Characterization Project (referred to as the YMP). The YMP is intended to evaluate the suitability of the site for construction of a mined geologic repository for the permanent disposal of spent nuclear fuel and high-level radioactive waste. The objective of the current project was to characterize the spatial and temporal distribution of degradation of the waste packages, including uncertainties. An understanding of waste package degradation processes is critical to evaluating the performance of the potential high-level nuclear waste repository at Yucca Mountain.

A major goal of the project was to capture the uncertainties involved in assessing waste package degradation processes, including uncertainty in both the *models* used to represent physical controls on corrosion processes and the *parameter values* used in the models. To ensure that the analysis included a range of perspectives, multiple individual judgments were elicited from members of an expert panel. The panel members, who were experts from within and outside the Yucca Mountain project, represented a range of experience and expertise. A deliberate process was followed in facilitating interactions among the experts, in training them to express uncertainties, and in eliciting their interpretations. The resulting assessments and probability distributions, therefore, provide a reasonable aggregate representation of the knowledge and uncertainties about key issues regarding waste package degradation.

1.2 RELATIONSHIP OF WPDEE PROJECT TO STUDIES OF WASTE PACKAGE DEGRADATION AT YUCCA MOUNTAIN

The WPDEE study has two principal purposes: (1) to characterize uncertainties associated with certain key issues that provide input to the TSPA; and (2) to provide a perspective on modeling and data collection activities that may help to characterize and reduce uncertainties. In addition, certain aspects of the present design considerations were evaluated during the elicitations. The next iteration of the TSPA will be conducted for the Viability Assessment (VA) for Yucca Mountain. The TSPA-VA provides a probabilistic assessment of the performance of the potential repository system based on the information developed as part of site characterization and repository design. The technical components of the TSPA are intended to incorporate a range of knowledge and to characterize uncertainties. As such, the expert panel's assessment of key technical issues related to waste package degradation—including the expressions of uncertainty—will be directly applicable to the TSPA-VA. For example, an important issue addressed by the experts is the corrosion modes for the carbon steel outer barrier of the waste package as a function of temperature, relative humidity, and pH. The experts provided their assessments of the behavior of corrosion processes as a function of these conditions and, for example, expressed their interpretation and uncertainties regarding the relative humidity thresholds at which the package would undergo dry oxidation, humid air corrosion, and aqueous corrosion. These assessments, and their associated uncertainties across the panel, now can be incorporated into the waste package degradation modeling for the TSPA-VA.

If the Yucca Mountain site is deemed suitable for repository development, the repository would be constructed in the unsaturated zone in welded tuff at a depth of about 250 meters below land surface and a distance of about 250 meters above the regional water table. About 11,000 waste packages containing spent nuclear fuel and high-level waste associated with defense activities will be emplaced in a series of horizontal drifts, the spacing of which will produce significant heating of the rock mass for thousands of years following emplacement. The canister design includes a two-barrier wall consisting of a 10-cm-thick corrosion-allowance material (CAM) and a 2-cm-thick corrosion-resistant material (CRM). Candidate alloys for the CAM are carbon steel (current reference) and Monel 400, and for the CRM are Alloy 625 (current reference) and C-22. During the elicitation, the experts considered the

corrosion behavior of the assumed design under assumed environmental conditions (discussed in Section 3).

The WPDEE study is intended to complement the ongoing modeling, testing, and data collection programs (conducted principally by Lawrence Livermore National Laboratory [LLNL]) while contributing to the performance assessment (conducted by the M&O). The WPDEE experts were given detailed summaries and presentations of the progress being made in various components of the modeling and testing program, available data, and models. Although the present testing program is focused on *reducing* the uncertainties associated with corrosion processes during the long-term testing program, the focus of the WPDEE project was on *characterizing* and, where possible, quantifying the uncertainties that currently are associated with the various models, parameters, and components of waste package degradation, as well as providing an independent perspective on the approaches taken in the modeling efforts. As such, the WPDEE project is an interim step in the waste package degradation program for the Yucca Mountain project and provides a "snap-shot" of the present knowledge and uncertainties.

The Viability Assessment will rely largely on the next round of performance assessment (TSPA-VA). The TSPA-VA will be an assessment at a particular point in time of the level of knowledge and uncertainties regarding the site characteristics and engineered systems that affect performance of the potential repository system. As such, the performance assessment requires a reasonably complete description of all key processes affecting performance, including waste package degradation. Further, the TSPA, as a probabilistic analysis, will include an appropriate expression of uncertainties. The quantification of uncertainties at any given time does not imply that issues have been resolved, that additional data should not be gathered, or that the issues will not be revisited during subsequent evaluations (e.g., licensing). A goal of the WPDEE project is to support the TSPA-VA by providing an expression of uncertainties regarding key issues for waste package degradation. This expression has been developed by experts from both within and outside the YMP. As such, results of the WPDEE study are realistic and defensible assessments at this point in the characterization program for Yucca Mountain. In addition to providing inputs to the TSPA-VA, the results of the study can also provide a focus for subsequent data collection activities aimed at reducing key uncertainties.

1.3 ORGANIZATION

The WPDEE project was organized into four groups: the WPDEE contractor, the methodology development team (MDT), the expert panel, and the technical specialists. The principal responsibilities of each group are described here; the technical roles of each group are described in detail in Section 2.2 of this report.

WPDEE Contractor: Under contract with TRW, Geomatrix served as the WPDEE contractor responsible for conducting all aspects of the project and for delivering this report describing the methodology and the results. WPDEE contractor personnel also were members of the MDT.

Methodology Development Team (MDT): As a group, the MDT served both to carry out the project and to review the progress of the project. The participation role included developing a project plan, facilitating workshops, eliciting members of the expert panel, performing calculations and related analyses, and documenting methodology and results. The review role included reviewing the progress of the study and recommending mid-course adjustments to ensure that the study met its objectives. The members of the MDT and their responsibilities for the WPDEE project are summarized in Table 1-1.

Expert Panel: The six widely recognized engineers and scientists on the expert panel were responsible for providing and documenting their judgments regarding models, parameters, and uncertainties about waste package degradation. These subject-matter experts were responsible for developing the interpretations that form the technical substance of the WPDEE project. Table 1-2 lists the experts on the panel and their affiliations. Brief biographies for members of the expert panel are provided in Appendix A.

Technical Specialists: Numerous technical specialists participated in the project by providing the experts with specialized data, interpretations, or training through workshops and a field trip. A list of the technical specialists and their affiliations is given in Table 1-3. Members of both the MDT and the expert panel sometimes also acted as technical specialists.

1.4 PRODUCTS OF STUDY AND STRUCTURE OF REPORT

The WPDEE study was conducted throughout approximately six months. The project began with developing a plan for the study and identifying the goals to be accomplished and methodologies to be implemented in meeting these goals. Next, the MDT developed and implemented a process for selecting the members of the expert panel, resulting in the selection of six experts. The bulk of the study was centered around three workshops and one field trip. These activities were designed to facilitate interaction among the experts, provide all data needed for their assessments, and provide a forum for discussing a range of technical interpretations. Following the third workshop, the interpretations of each expert were elicited in individual interviews and documented in elicitation summaries. After reviewing the elicitation summaries of all members of the expert panel, the experts finalized their assessments.

This report contains the products of the WPDEE project outlined above. Section 2 describes in detail the process followed in eliciting the expert interpretations. Appendices B and C provide summaries of the references and reports provided to the experts and of the three workshops. This information provides written documentation of the technical data discussed by the panel, the formats and content of interpretations presented by outside technical specialists, and the expert panel's preliminary interpretations.

Section 3 of this report presents in detail the final interpretations provided by the expert panel and the results of the study. Both the results for each of the six individual experts and the aggregated results are discussed. The conclusions of the study are summarized in Section 4. Key products of the study are the written elicitation summaries prepared by each expert, which are provided in Appendix D. The experts expended considerable effort to ensure that their summaries provide a reasonably complete record of the deliberations they followed in arriving at their interpretations. Information related to quality assurance is provided in Appendix E.

TABLE 1-1
METHODOLOGY DEVELOPMENT TEAM MEMBERS AND THEIR
PRINCIPAL RESPONSIBILITIES

NAME	AFFILIATION	RESPONSIBILITIES
Kevin J. Coppersmith	Geomatrix Consultants, Inc.	Project management and planning; methodology development; facilitating workshops; expert elicitation; documentation
Roseanne C. Perman	Geomatrix Consultants, Inc.	Project planning and methodology development; organizing workshops and field trip; elicitation documentation
Robert R. Youngs	Geomatrix Consultants, Inc.	Project planning and methodology development; documentation of results
Peter A. Morris	Applied Decision Analysis, Inc.	Project planning and methodology development; peer review of project direction; expert elicitation methodologies
David Haught	U.S. Department of Energy	Project planning and oversight; review of project direction
Joon H. Lee	M&O/INTERA	Project planning and methodology development; workshop planning; expert elicitation; documentation
Martha Pendleton	M&O/Woodward-Clyde Federal Services	Project planning and oversight; expert selection process; review of project direction
David Stahl	M&O/Framatone Cogema Fuels	Project planning and methodology development; workshop planning; expert elicitation; documentation

**TABLE 1-2
EXPERT PANEL MEMBERS**

EXPERT	AFFILIATION
Peter L. Andresen	GE Corporate Research & Development
Joseph C. Farmer	Lawrence Livermore National Laboratory
Brenda J. Little	Stena Space Laboratory, U.S. Navy
R. Daniel McCright	Lawrence Livermore National Laboratory
John R. Scully	University of Virginia
David W. Shoesmith	Atomic Energy of Canada Limited

**TABLE 1-3
TECHNICAL SPECIALISTS PARTICIPATING IN
WPDEE WORKSHOPS AND FIELD TRIP***

WORKSHOP 1 - SIGNIFICANT ISSUES AND AVAILABLE DATA	
Joel Atkins	M&O/INTERA
Greg Gdowski	Lawrence Livermore National Laboratory
Joanne Horn	M&O/Lawrence Livermore National Laboratory
Denny Jones	M&O/University of Nevada, Reno
D.G. McKenzie, III	M&O/MK
Jerry McNeish	M&O/INTERA
Ajid Roy	M&O/FCF/Lawrence Livermore National Laboratory
Narasi Sridhar	Center for Nuclear Waste Regulatory Analyses
WORKSHOP 2 - ALTERNATIVE MODELS AND INTERPRETATIONS	
Joe Payer	Case Western University
Alberto Sagues	University of South Florida
David Sassani	M&O/INTERA
Narasi Sridhar	Center for Nuclear Waste Regulatory Analyses
Simcha Stroes-Gascoyne	Atomic Energy of Canada Limited

* Note that members of the MDT and the expert panel also acted as Technical Specialists at the workshops.

2.0 PROCESS FOR ELICITING EXPERT JUDGMENTS

2.1 INTRODUCTION

This section summarizes the methodology that was followed in carrying out the WPDEE project. It is our belief that to be credible and useful, a technical analysis such as the WPDEE must: (1) be based on sound technical information and interpretations, (2) follow a process that considers available data, and (3) incorporate uncertainties into the assessments. A key mechanism for quantifying uncertainties in the WPDEE is the use of multiple expert judgments. The *process* used to select the experts, facilitate their interaction and mutual education, and elicit their judgments is as important as the technical content of their interpretations.

Because of the importance of the entire process, a methodology development team (MDT) was established at the outset. MDT members have experience in developing guidance for and implementing multi-expert studies, understanding technical aspects of waste package degradation processes, and performing Total System Performance Assessments (TSPAs). For example, Drs. Coppersmith and Morris were members of the Senior Seismic Hazard Analysis Committee (SSHAC, described below). Several members of the MDT (Drs. Coppersmith, Youngs, Perman, and Morris) also participated in the Probabilistic Volcanic Hazard Assessment for Yucca Mountain (U.S. DOE, 1996), which employed a multi-expert approach. Several members (K. Coppersmith, R. Perman, M. Pendleton, R. Youngs, and P. Morris) have conducted recent and ongoing expert elicitations related to unsaturated zone flow (UZFMEE in M&O, 1997) and saturated zone flow and transport at Yucca Mountain. Importantly, the MDT included representatives from performance assessment (Dr. J. Lee) and waste package materials programs (Dr. D. Stahl) for the Yucca Mountain project. The waste package materials program is conducting and interpreting the laboratory tests and surveying the literature to provide the data necessary for the development of waste package degradation models. The waste package materials program and performance assessment organizations are developing detailed mechanistic and stochastic degradation models for use in waste package degradation analyses. The performance assessment organization is applying these models in evaluation of system and subsystem repository performance.

2.1.1 Pertinent Guidance Regarding Expert Judgment

In the study of any complex technical problem—such as the degradation of waste packages over long periods of time—expert judgment is used. The data themselves do not provide an interpretation of the processes and outputs needed for subsequent analyses. For example, corrosion tests can provide information on the modes and penetration depths of pits as a function of environmental conditions (e.g., temperature, pH, Cl^- , O_2). These data must be interpreted to assess rates of pit growth and modes of corrosion for a given alloy and environmental conditions. Various conceptual models must be combined with observed data to extrapolate test results to other alloys or environmental conditions, or to extend the short-term test results to much longer periods. Through the scientific process, experts integrate and evaluate data to arrive at conclusions that are meaningful to assessments of waste package degradation, including quantitative and qualitative expressions of the uncertainties. This process is the same regardless of the abundance or scarcity of data. In this sense, expert judgment is not a substitute for data; it is the process by which data are evaluated and interpreted. If data are scarce and uncertainties large, the uncertainties expressed by each expert and the range of judgments across multiple experts should reflect this high degree of uncertainty.

The procedures and approaches for eliciting expert judgments, developed through conducting many studies, have been formalized in guidance documents, which were followed in the WPDEE project. DOE recently developed guidance for the formal use of expert judgment by the Yucca Mountain project (DOE, 1995), and the Nuclear Regulatory Commission (NRC) staff issued a Branch Technical Position (BTP) on use of expert elicitation in the high-level waste program (Kotra et al., 1996). Comprehensive guidance on eliciting expert judgment for seismic hazards recently was set forth in a study sponsored by the DOE, the EPRI, and the NRC (SSHAC, 1995).

SSHAC (1995) defines the expert roles of *proponent*, *evaluator*, and *integrator*. A proponent advocates a particular technical view or interpretation; an evaluator weighs the relative merits of alternative views; and an integrator combines the alternative views into a composite distribution that includes uncertainties. The WPDEE members were informed of their roles as evaluators and of the need to forsake the role of proponents in making their assessments and evaluating uncertainties. Expert interactions are deemed very important in the SSHAC

2.2.3 Review of Technical Issues/Expert Interaction

Technical issues related to the WPDEE project were identified in the first workshop and reviewed throughout the project. The workshops and field trip provided an opportunity for technical discussion and interaction, with an objective of ensuring a common understanding of the issues to be assessed and the data available to provide the technical basis for assessment. Literature and data sets pertaining to waste package degradation were sent to members of the expert panel throughout the project. A list of the references distributed is provided in Appendix B.

The following sections summarize the activities (workshops and field trip) conducted during the project. These are summarized under the topic of Review of Technical Issues/Expert Interaction because the workshops and field trip were the primary vehicle for accomplishing this interaction. Summaries of the workshops and field trip are included in Appendix C.

2.2.3.1 Workshop on Significant Issues and Available Data

The first of the three workshops conducted for the WPDEE project was the Workshop on Significant Issues and Available Data. The goals of this workshop were to introduce the panel to the Yucca Mountain project, identify significant issues related to both waste package degradation and the Total System Performance Assessment, and to present the various data sets related to the significant issues. A number of technical specialists presented and discussed the data sets and modeling studies conducted during the past few years.

2.2.3.2 Workshop on Alternative Models and Interpretations

This second workshop conducted for the WPDEE project was designed to present and discuss alternative methods and conceptual models for evaluating key waste package degradation issues. The issues discussed included microbiologically influenced corrosion, pitting and crevice corrosion modeling, stress corrosion cracking, galvanic protection, and electrochemical modeling. The specific subjects to be addressed in the expert elicitations also were discussed.

2.2.3.3 Workshop on Preliminary Interpretations

The Workshop on Preliminary Interpretations, the third and final project workshop, was conducted prior to the elicitation interviews. This workshop provided an opportunity for the

experts to present and discuss their preliminary interpretations and uncertainties regarding key issues in waste package degradation processes. The experts presented their interpretations of each of seven issues: pitting factors for CAM, alternative CAM materials, pitting and crevice corrosion of CRM, microbiologically influenced corrosion, variability and uncertainty, welds, and ceramic coatings.

2.2.3.4 Field Trip

The MDT organized a half-day field trip to Yucca Mountain at the request of the expert panel members, who wanted to observe first-hand the general setting of the site. The field trip, which was led by engineers from the M&O, focused on the Exploratory Studies Facility (ESF). The field trip gave the experts an opportunity to observe the ESF and to discuss the ambient environmental conditions and the environmental conditions that might develop during operation of the repository.

2.2.4 Elicitation of Experts

Through the elicitation process the experts' interpretations of waste package degradation processes were obtained. The elicitations involved a series of activities, which can be grouped into three steps: (1) preparation for the elicitation, (2) the elicitation interview, and (3) documentation and review.

2.2.4.1 Preparation for the Elicitation

Peter A. Morris of the MDT provided elicitation training at the third workshop. The objectives of the training were to demonstrate how to quantify uncertainties using probabilities, to recognize common cognitive biases and compensate for them, and to present examples of the types of assessments that would be made at the elicitation (e.g., continuous variables, discrete hypotheses, and associated weights). The training was designed to allow the experts to be comfortable with the *process* of eliciting their judgments, so that the elicitation interview could be focused on the *technical issues* of importance to the WPDEE.

A list of questions to be addressed in the project was provided to the experts to assist them in preparing for the elicitation interview. This list was discussed at the second workshop and provided prior to the third workshop. This list is given in Table 2-1. The list of questions was intended to help the experts prepare for their interviews, to focus their data review on the

issues of most significance, and to ensure that all important topics were addressed by all experts.

2.2.4.2 The Elicitation Interview

The elicitations of the expert panel members took place in individual one-day interviews in the San Francisco office of Geomatrix. The interviews were conducted by members of the MDT: K. Coppersmith, D. Stahl, J. Lee, and R. Perman. In addition, P. Morris, the normative expert for the project, attended the first elicitation interview and discussed the process of elicitation with the MDT members.

All data sets provided or made available to the experts during the project were present during the elicitations. The elicitation interview followed a logical sequence based on the time-history of the repository system, ranging from elevated to ambient temperatures. Alternative models, approaches, and hypotheses were discussed and probability distributions were developed. The elicitation team took written notes of all assessments during the interviews.

During the interview, all of the questions given in Table 2-1 were reviewed. In some cases, the issues were tangential to or outside the expertise of a particular expert. In these cases, the expert either provided a limited response or deferred entirely on that component of the elicitation. For example, Dr. Brenda Little, who is an acknowledged expert in the specialized field of microbiologically influenced corrosion (MIC), deferred on many of the issues related to corrosion of the inner and outer barriers because of a lack of expertise in these areas. She did, however, provide a detailed response to questions concerning MIC. Most of the other experts, in turn, provided only limited assessments of MIC issues.

2.2.4.3 Documentation and Review

Documentation of the expert elicitations began with notes taken by the elicitation team during the interviews. Experience on several other expert assessment projects has shown this approach to be preferable to other documentation methods (e.g., written questionnaires, experts writing their interpretations following the interview). During the one-day interview, each WPDEE expert was asked to make many assessments, to quantify his/her uncertainties, and, most importantly, to provide the technical basis for interpretations. By having the elicitation team take notes, the experts were free to focus on thinking through their answers

and thoroughly expressing their interpretations. The elicitation team was able to be flexible in the elicitation sequence (i.e., following the logic comfortable to the expert) while ensuring that all elements were covered.

Following the interviews, the elicitation team provided each expert with written documentation of the interview, organized by model component. The experts were instructed to review, revise, and expand their preliminary assessments in this "First Draft" documentation summary so that it fully reflected their interpretations. The summaries revised by each expert became the "Second Draft" document. The "Second Draft" summaries from each expert were then distributed to all members of the panel as part of the feedback package so that each expert could review the judgments of others and the technical basis for each judgment. After reviewing the feedback package, the experts made additional revisions to their elicitation summaries to reflect any resulting changes in their judgments. These revised summaries became the final elicitation summaries, which are provided in Appendix D.

2.2.4.4 Feedback and Sensitivity

Feedback to the experts occurred throughout the WPDEE project, primarily through interaction among experts. By presenting their ideas on models and interpretations at workshops and in general discussions, the experts both provided and received feedback from their peers on the panel, as well as from others participating in the workshops.

More formally, feedback was provided to the experts in several other ways.

- At Workshop 3, the experts presented to the panel their interpretations of key issues. Discussions included the technical bases for the interpretations.
- Written elicitation summaries were provided to all panel members for their review.
- The MDT reviewed the first draft written elicitation summaries for adequacy and completeness of documentation of the technical basis for judgments.

The feedback-revision process required the experts to defend/revise their assessments and to provide appropriate documentation. In all cases, the experts on the panel responded positively to technical criticisms of their interpretations and to reviews of their

documentation. The resulting assessments and finalized elicitation summaries reflect the significant effort expended by each member of the expert panel.

2.3.4.5 Aggregation of Expert Assessments

The approach taken to combine, or aggregate, the expert assessments is equal weighting. Importantly, this approach was not a "default" but a goal throughout the project. Accordingly, the proper conditions were created throughout the project to ensure that a deliberate, defensible decision could be made to use equal weights (after SSHAC, 1995). The actions that were taken to create these conditions included:

- carefully selecting highly qualified experts who represented diverse views and experience;
- establishing the commitment of each expert to provide the required effort throughout the project;
- identifying a comprehensive data base and disseminating it to all experts;
- educating the experts in issues important to WPDEE and training the experts in elicitation methodologies and the role of experts as evaluators;
- facilitating interaction of the experts in workshops and field trips to foster a free exchange of data and interpretations and scientific debate of all hypotheses;
- providing feedback to the experts; and
- providing an opportunity for experts to revise their assessments in light of feedback.

It should be noted that, in accordance with the guidance provided by the SSHAC study (1995), conditions could have been such that differential weights would have been necessary. For example, if a member of the expert panel had been unwilling to forsake the role of a *proponent* who advocates a singular viewpoint, for that of an *evaluator* who is able to consider multiple viewpoints, that expert may have been given less weight or removed from the panel entirely.

TABLE 2-1
QUESTIONS TO BE ADDRESSED IN THE
WASTE PACKAGE DEGRADATION EXPERT ELICITATION

In their elicitation following the third workshop, the experts will address (1) primary issues, and (2) secondary issues. The primary issues are of utmost importance to the TSPA and should be the primary focus of the experts' assessments. The secondary issues, although potentially important, should be given less focus.

Note that the context of the questions will be the "reference conditions" assumed for the waste package environmental and design conditions.

A. PRIMARY ISSUES

I. CORROSION OF CARBON STEEL

- I-1) What is the temperature threshold for corrosion initiation of the carbon steel outer barrier?**

A temperature threshold of 100°C was assumed in TSPA-95.

- I-2) What is the threshold for humid-air corrosion initiation of the carbon steel outer barrier?**

RH between 65% and 75% (uniformly distributed) was assumed in TSPA-95.

- I-3) What is the threshold for aqueous corrosion initiation of the carbon steel outer barrier?**

RH between 85% and 95% (uniformly distributed) was assumed in TSPA-95.

- I-4) What is the pit density for the carbon steel outer barrier and corrosion-resistant inner barrier?**

A pit density of 10 pits/cm² was assumed for both the outer and inner barriers in TSPA-95.

- I-5) What are the effects of water drips on the corrosion rate of the carbon steel outer barrier?**

II. PITTING FACTOR OF CARBON STEEL

The "pitting factor" describing the corrosion of the carbon steel outer barrier could be an important issue for long-term waste package degradation. The pitting factor is defined as the ratio of the localized corrosion depth (or "pit" depth) to the general corrosion depth.

II-1) Is the "pitting factor" an acceptable approach to represent localized variations of carbon steel outer barrier corrosion?

II-2) If the pitting factor is an acceptable approach, what type of distribution is most representative of the pitting factor?

In TSPA-1995, it was assumed that the pitting factor has a normal distribution with a mean of 4 and a standard deviation of 1. Some literature data indicate that it seems to mimic an exponential distribution skewed to the right.

II-3) How does the pitting factor evolve as a function of the general corrosion depth?

Some literature data suggest that the pitting factor decreases with the general corrosion depth.

III. ALTERNATIVE CORROSION-ALLOWANCE MATERIAL

There is a serious consideration of replacing the carbon steel outer barrier with Monel 400 (Ni [about 70 wt. %]-Cu[about 30 wt. %] alloy).

III-1) What are the dominant corrosion modes of Monel 400? What are the corrosion rates and their distribution of Monel 400?

III-2) What are the effects of water drips on the corrosion rate of the alternative corrosion-allowance outer barrier material?

IV. PITTING AND CREVICE CORROSION OF CORROSION-RESISTANT MATERIALS (CRM)

IV-1) How would the probability of pit generation in the CRM vary with time or environmental condition? What is the probability of stifling of pits with depth (or time)? What other factors would influence this probability?

IV-2) What is the rate of pitting/crevice corrosion of the candidate corrosion-resistant inner barrier materials, as a function of various factors?

The elicited model(s) may be expressed as a function of temperature, pit depth, chloride concentration of the contacting solution, relative humidity, and other important factors. The elicited model(s) should include associated uncertainties and/or bounding uncertainties.

IV-3) What are the pit spatial density and pit size developed in the candidate corrosion-resistant inner barrier materials, as a function of various factors?

The elicited model(s) may be expressed as a function of degree of pitting degradation, exposure conditions, and other important factors. The elicited model(s) should include associated uncertainties and/or bounding uncertainties.

- IV-4) What is the rate of pitting/crevice corrosion of the candidate corrosion-resistant inner barrier materials (CRM) in the presence of galvanic coupling with the carbon steel outer barrier, as a function of various factors?

The elicited model(s) may be expressed as a function of temperature, pit depth, chloride concentration of the contacting solution, relative humidity, degree of the outer barrier degradation, and other important factors. The elicited model(s) should include associated uncertainties and/or bounding uncertainties.

- IV-5) What are the effects of water drips on the rate of pitting and crevice corrosion of the candidate corrosion-resistant inner barrier materials (CRM)?

V. MICROBIOLOGICALLY INFLUENCED CORROSION (MIC)

- V-1) What is the probability of microbe (bacteria and/or fungi) colony population on the carbon steel outer barrier? What is the spatial distribution of the microbe colonies on the waste package? What is the corrosion rate and its distribution under the microbe colony?

The elicited model(s) may be expressed as a function of the exposure conditions such as temperature, relative humidity, nutrient availability, "liquid" water availability, and other important factors. The elicited model(s) should include associated uncertainties and/or bounding uncertainties.

- V-2) What is the probability of a microbe (bacteria and/or fungi) colony population on the corrosion-resistant inner barrier? What is the spatial distribution of the microbe colonies on the waste package? What is the pitting/crevice corrosion rate and its distribution under the microbe colony?

The elicited model(s) may be expressed as a function of the exposure conditions such as temperature, relative humidity, nutrient availability, "liquid" water availability, presence of carbon steel and its corrosion products, and other important factors. The elicited model(s) should include associated uncertainties and/or bounding uncertainties.

VI. REPRESENTATION OF VARIABILITY AND UNCERTAINTY IN STOCHASTIC WASTE PACKAGE DEGRADATION MODELING

There are about 12,000 waste packages across the repository. There will be considerable variability in exposure conditions (T, RH, water dripping, water chemistry, microbial activity) across the repository (termed the WP-to-WP variability in TSPA-1995). There will also be variability in exposure conditions (T, RH, water dripping, water chemistry, microbial activity) within a single waste package (termed the pit-to-pit variability in TSPA-1995). There is also uncertainty in the waste package degradation conceptual model and individual corrosion models.

- VI-1) Can we stochastically represent variability and uncertainty in waste package degradation using the uncertainties in individual corrosion models?

In TSPA-1995, the WP-to-WP variability and the pit-to-pit variability were represented stochastically by equally splitting the uncertainties and variabilities in the individual corrosion models. Does this appear to be an acceptable approach? If it is not, what is an acceptable approach to represent the WP-to-WP variability and the pit-to-pit variability?

B. SECONDARY ISSUES

VII. WELDS

It is generally accepted that welds are preferential sites for corrosion.

- VII-1) What are the corrosion rates and their distribution on welds on the carbon steel outer barrier?
- VII-2) What are the corrosion rates and their distribution on welds on the nickel-based inner barrier?

VIII. CERAMIC COATING

Currently, if it is decided to use a coating, the most probable candidate materials for coating the carbon steel outer barrier surface are alumina (Al_2O_3) and rutile (TiO_2). The ceramic coatings will be applied by plasma spray technique and with several layers of the chosen ceramic, i.e., repeated coatings to a specified thickness. The carbon steel surface will be coated prior to waste loading. The weld area will be coated after the waste package is loaded with the waste and sealed. After loading, the waste package would weigh about 45 to 50 tons, and have a length of about 5.3 m and a diameter of 1.8 m. The main purpose of the ceramic coating is to avoid the contact of the carbon steel with dripping water for an extended period of time. Following are specific issues related to the ceramic coating.

- VIII-1) How long could the ceramic coating last without cracks to effectively prevent the carbon steel barrier from contacting water (including water vapor)?**

This issue should be considered by taking into account: (1) potential difficulties associated with the transportation and handling of the waste packages in the repository; (2) potential stresses to the coating induced from differential thermal expansions of the carbon steel barrier and the coating material during the thermal perturbation period; (3) potential effects of long-term exposure (or aging) of the coating material to the repository environment; and (4) potential effects of rockfalls on the "aging" ceramic coatings.

- VIII-2) What are the dominant corrosion modes of carbon steel underneath the cracks—general and/or narrow, deep localized corrosion?**

- VIII-3) Will the carbon steel corrosion stop due to limited supply of oxygen to the corroding surface?**

- VIII-4) Will the carbon steel corrosion continue because of potential "debonding" of the coating due to volume expansions generated by the formation of carbon steel corrosion products?**

Debonding is likely to create deep crevices between the carbon steel surface and debonded ceramic coatings.

- VIII-5) If debonding of the coatings occurs, what are the consequences of extensive debonding to carbon steel corrosion underneath the debonded coating?**

3.0 ASSESSMENT OF KEY ISSUES

3.1 INTRODUCTION

The experts involved in the Waste Package Degradation Expert Elicitation (WPDEE) addressed a variety of technical issues related to waste package degradation for the potential repository at Yucca Mountain. Included were issues important to the Total System Performance Assessment (TSPA; e.g., relative humidity thresholds for CAM corrosion, corrosion modes and spatial distribution of corrosion processes on the waste package, CAM and CRM corrosion rates). In addition, the experts were asked to provide their perspectives on issues related to materials and design (e.g., alternative CAM materials, galvanic protection of the CRM, ceramic coating) and on additional data collection or analyses that could serve to reduce the uncertainties in the assessments of waste package degradation. The experts' evaluations are given in their elicitation summaries (Appendix D) and summarized in this chapter.

It is important to remember the context of the experts' evaluations. First, the goal of this expert elicitation was to quantify the *uncertainties* associated with various aspects of the waste package degradation models so that the TSPA-VA can incorporate a range of uncertainty when modeling important processes. As a result, the experts focused considerable attention on *what is not known*, and the reasons for that lack of knowledge. The reasons could include data gaps, limited experience with certain materials, nonpertinent data, or multiple models consistent with the data. Rather than merely identifying and acknowledging the uncertainties, the experts were required to provide—to the extent possible—their quantification of the uncertainties for certain key issues with reference to the technical literature when applicable. For example, the experts identified possible corrosion modes for the carbon steel CAM, which could be dependent on the exposure conditions (RH, temperature, water dripping, and pH of the drips) and the corrosion rates for these modes. Likewise, the experts characterized their knowledge and uncertainty regarding the mechanisms for initiating corrosion of the corrosion-resistant inner barrier and, given initiation, the rates of corrosion. For many of the candidate CRM materials (e.g., Alloy C-22), there are very few data on which to make these assessments; as a result, the expert evaluations reflect a large degree of uncertainty.

It is also important to note that the experts' evaluations are, to a large extent, an expression of the professional judgment of each expert and are not based on extensive modeling or calculations carried out for this study. These judgments are derived not only from a consideration of Yucca Mountain data, but also data and observations from previous experience. Members of the panel were given a limited time in which to review Yucca Mountain data sets, test results, and models. Further, the experts were unable within the time-frame of the project to conduct their own analyses and calculations. In many cases, the experts relied on the results of analyses presented in workshops by the Yucca Mountain researchers, their colleagues on the panel, or other researchers.

The results of the WPDEE expert assessments have potential application in both the upcoming TSPA for the Viability Assessment (TSPA-VA), the ongoing corrosion testing program, and waste package design activities. The TSPA is a probabilistic analysis that is capable of incorporating uncertainties, including those expressed by the WPDEE expert panel. The panel members reviewed the waste package modeling carried out for the previous iteration (TSPA-95). By focusing on the issues of most importance to the degradation modeling, their evaluations will improve the models to make them more realistic and to better characterize the uncertainties. Several members of the panel have considerable experience in designing and conducting corrosion testing programs and provided advice regarding focused experiments that, they believe, could reduce significantly the present level of uncertainty. The waste package design, including selection of materials, is an ongoing and iterative process. The WPDEE panel provided their views of certain aspects of the present conceptual design (e.g., two-barrier system with shrink fit to enable metallic coupling, CRM consisting of Ni-Cr-Mo alloys). These perspectives will be useful in further revisions and refinements of the waste package design.

3.2 ASSUMED ENVIRONMENTAL AND DESIGN CONDITIONS

In order for the experts to address the key issues related to waste package performance over the lifetime of the potential repository, two important aspects must be defined: (1) the environmental conditions expected during the potential repository's lifetime, and (2) the conceptual design conditions that describe the basic waste package system. The environmental conditions to which the waste packages will be submitted is time-varying and, because of the long periods involved, is uncertain. Further, the important environmental conditions

(temperature, relative humidity, water dripping, chemistry of the drips, oxygen partial pressure, etc.) have not yet been firmly established. For example, thermohydrologists presently are measuring and modeling the nature of the hydrologic regime beneath Yucca Mountain under ambient conditions and under the thermally perturbed conditions that will exist after emplacement of waste packages. They are focusing on the time-varying nature of moisture movement through the rock and fractures, the nature of the boiling front that will develop around the drifts, geochemistry of the waters that may pass through the fractures, the potential for drips into the emplacement drifts, the chemistry of water that may pass through degrading concrete liners of the drifts, and the constituents of water, vapor, and gases that will exist within the drifts. All of these aspects are expected to be spatially and temporally variable as well as uncertain. As will be shown later in discussing the WPDEE evaluations, many of these characteristics are quite important to the processes and rates of degradation of the waste packages.

To enable waste package performance to be assessed before the hydrologists finalize their interpretations, we made a concerted attempt to summarize the current best estimates and range of environmental conditions expected in the potential repository throughout its lifetime. These assessments were summarized by the technical principal investigators at the workshops and were provided to the experts in the form of a summary, given in Table 3-1. Conditions are described in terms of bulk environmental conditions as a function of time that are expected on the waste package surfaces, including temperature, relative humidity, water seepage flux, and water chemistry. These conditions, which are subject to revision as the hydrologists continue their work, provide the basic assumed conditions the WPDEE experts used in developing their interpretations.

The second set of assumptions is the design conditions for the waste package system, which also are given in Table 3-1 and were provided to the experts. The design conditions are described in terms of the basic elements of the waste package (e.g., two-wall design, wall thicknesses), the candidate materials being considered for the inner and outer barriers, mechanical loads, the fabrication and assembly methods planned, and the anticipated radiation/waste package shielding.

3.3 SUMMARY OF EXPERT INTERPRETATIONS

This section summarizes the interpretations made by members of the WPDEE panel regarding certain key issues related to waste package degradation. The intent is to provide the reader with a perspective on the evaluations made by the experts, the manner in which each issue was addressed, an overview of the technical bases for the interpretations, the uncertainties identified by the experts, and the degree of convergence or divergence in the aggregate range of interpretations across the panel. For a more complete exposition of the interpretations made by the experts, the reader is directed to the elicitation summaries given in Appendix D.

Each of the key issues shown in Table 3-2 is discussed below.

3.3.1 Corrosion of Carbon Steel CAM

In the two-barrier design, the outer corrosion allowance material (CAM) is a 10-cm-thick barrier of carbon steel. An alternative CAM material is Monel 400, which is discussed below. The experts addressed the issue of corrosion of the carbon steel as a function of the temperature, relative humidity, and localized dripping within the repository. The relatively short period during which the waste packages are emplaced in the repository and the time to raise the temperature of the drifts is ignored.

Oxidation of the CAM. The first assessment is the nature of oxidation of the carbon steel CAM during the initial period when the repository experiences its hottest conditions and relative humidities are lowest. It is assumed that because temperatures are above the boiling point, there will be essentially no drips onto the packages. Also, boiling may reduce the availability of oxygen during at least part of this time. The experts generally agreed that the dominant process during this period would be dry oxidation of the carbon steel and consequent very slow corrosion. Dr. Andresen postulated that because of the high temperatures, boiling would lead to atmospheric gas exclusion (including O_2 and CO_2) such that oxidation would be delayed until oxygen partial pressures were increased. Drs. McCright, Farmer, and Shoesmith acknowledged that oxygen may be depleted but nevertheless would expect oxidation to occur, perhaps to lower oxidation states.

There were differences of opinion regarding the nature and thickness of the oxide film that would develop on the waste package during this period, and the potential for spalling of the oxide layer. Spalling of the oxide layer is a potentially important issue in that, most experts believed, locations of significant spalling during the dry, hot period could be the locations of potentially enhanced corrosion after relative humidities rise. Drs. Shoesmith and McCright concluded that, because the temperatures are relatively low (relative to 500°C where significant carbon steel oxidation has been observed), a thin oxide layer would develop that is not flaky or prone to spalling. Dr. Scully, however, would expect a layer that is flaky and susceptible to spalling. Drs. Farmer and Andresen believe that, initially, the layer formed during oxidation would be adherent, compact, and protective, but eventually it would become thick, nonadherent, flaky, and porous. They also believe that it will become prone to spalling.

Temperature Threshold for Corrosion of CAM. As the temperature of the repository cools, there will be a threshold temperature below which dry oxidation of the carbon steel is replaced by corrosion under water layers (i.e., humid-air corrosion or aqueous corrosion). All of the experts concluded that the threshold temperature was essentially the boiling point of water that contacts the waste package surface. Dr. Shoesmith allowed for a slightly elevated boiling point due to the possibility of salts that may exist on the packages from evaporated drips, and Dr. Farmer concluded that the presence of salts may lead to significant elevation of the temperature threshold.

Importance of Drips to CAM Corrosion. A persistent theme across the panel was that drips are very important to the corrosion processes and rates of corrosion of the CAM (as well as the CRM). Important aspects are the spatial distribution, persistence through time, and frequency of drips. All experts noted that drips during the time that the waste packages are relatively hot will evaporate and leave behind hydrated salt deposits, the constituents of which would include concentrated J-13 water as well as contributions from the concrete liner. Persistent drips onto these salt deposits could lead to saturated chemistries. Dr. McCright noted that dust and concrete debris also will contribute to these chemistries, and Dr. Scully concluded that salt caking at relative humidities (RH) >95 percent would maintain aqueous conditions for longer periods. Importantly, the presence or absence of drips is also judged to control to a large extent the pH of water on the package surface, which, in turn, controls the mode of corrosion of the carbon steel, discussed further below.

Relative Humidity Threshold for Onset of Humid Air Corrosion. In addition to temperature, corrosion of the carbon steel is controlled by the relative humidity (RH) on the surface of the waste packages. In general, the experts believe that the RH threshold at which humid air corrosion (HAC) processes become operative is a function of the nature of the surface that exists at the time that relative humidities rise. In general, assessments of the RH threshold ranges from about RH 60 to 80 percent across the panel, depending on the nature of the surface. Dr. Scully noted that if the oxide surface has spalled and drips are present, the threshold is lower than if there is no spalling and no drips. Likewise, Dr. McCright concluded that a surface holding oxides, salts, and dust will have a lower RH threshold for humid air corrosion than a carbon steel surface holding dust only.

Relative Humidity Threshold for Onset of Aqueous Corrosion. The experts generally define "aqueous" conditions as being equivalent to "immersion" or "bulk water" conditions on the waste package. As such, they concluded that dripping conditions are required to achieve such a thick water film thickness. Therefore, the RH threshold is generally in the range of 85 to 100 percent and drips or pooled water are required to achieve aqueous corrosion conditions. Dr. McCright noted that the RH threshold for aqueous conditions is lower when salts have been deposited on the package surface (which, in turn, is also directly related to the presence of drips).

Corrosion Modes for CAM. Assuming the onset of corrosion, the mode of corrosion of the carbon steel CAM is assessed. It generally was concluded across the panel that the corrosion mode is governed by the pH of the water contacting the surface. The assumed pH conditions provided to the panel call for water that has passed through the degrading concrete liner and drips onto the waste package, producing alkaline conditions (pH greater than 10). After the liner degrades, the waters will return to neutral ambient levels. The experts concluded that the expected corrosion mode of the carbon steel in the case of no drips and neutral pH is uniform or general corrosion, and in the case of high pH drips is high-aspect-ratio pitting. Drs. Shoesmith and Scully noted that under neutral conditions, hemispherical "pits" would form in the carbon steel, which, with time, would coalesce to form a rough corrosion front. Dr. McCright expected this rough front to become more uniform with depth and time; Dr.

Andresen believes that the roughness of this front will be higher under aqueous conditions than under humid air conditions.

Some additional conclusions were drawn regarding the high-aspect-ratio pits that are expected to develop under high pH conditions. The manner in which these pits would grow is a function of the frequency and persistence of drips, Dr. Shoesmith believes. Unless drips are frequent and persistent, he would expect stifling of the pits to occur, followed by development of new pits and not regrowth of existing pits to ever-increasing depths. Dr. McCright noted that pH 9 to 10 is at the transition from active corrosion to passivation in carbon steel, thus suggesting that other chemical species and factors will affect the processes of localized corrosion. He suggested that elevated Cl^- is required for high-aspect-ratio pits to develop under alkaline conditions, which would be the case where salts have been deposited from evaporating drips.

Geometry of Corrosion of CAM. In modeling corrosion of the outer barrier of the waste packages, an important consideration is the geometry or spatial distribution of corrosion processes occurring on the packages. It was generally concluded by the panel that the presence or absence of drips is a controlling aspect of the spatial distribution, both across multiple waste packages and on individual packages. Aqueous corrosion modes are assumed to be possible in the case of dripping water and on the top of the waste packages, defined variously by the panel as the upper 90 to 180° in cross-sectional slice. Some experts also considered the bottom of the package to have the potential for aqueous corrosion, assuming that, after the pedestals have degraded, the bottom of the canister will lie directly on the invert and water running off the sides may accumulate at the bottom. The sides of those packages experiencing drips as well as everywhere on those packages that do not experience drips are generally considered by the panel to undergo humid air corrosion processes. Likewise, the potential for salt deposits from evaporation and high pH conditions are considered possible in the case of dripping conditions.

The importance of this conclusion is not only related to corrosion of the CAM, but also of the inner barrier inasmuch as corrosion of the CAM sets up conditions that enhance or discourage subsequent CRM corrosion initiation. Several experts conclude that the spatial distribution of corrosion modes in the CAM and the condition of the oxide layer will dictate the locations of

enhanced localized corrosion of the CRM. For example, Dr. Scully believes that persistent dripping will lead to enhanced spalling of the protective oxide layer and subsequent localized CRM corrosion. Dr. Shoesmith concludes that persistent drips and the removal of material can cause CAM corrosion rates that are 10X those of aqueous corrosion. Further, he concludes that the time-history of penetration of the CRM will follow the spatial distribution of penetrations through the CAM. Given this conclusion, he estimates that it is highly likely (99%) that the first penetrations of the CRM will be on the top of the canister with the shrink fit design. Dr. Farmer notes that the contact points between the pedestals and the package may form crevices and enhance corrosion processes.

Pit Density and Pit Diameter. Because the corrosion mode for carbon steel under neutral conditions is assessed to be general corrosion, the concept of 'pit' density and diameter is judged to apply only to the case of high pH conditions (from drips). The range of pit densities assessed is about 0.1 to 100 pits/cm², with an average value of about 1 pit/cm². Dr. Scully considers the density of growing pits, which, he concludes, will decrease with penetration depth as pits stifle. His initial pit density is in the range given above, but at depths of 1 - 10 cm, decreases by an order of magnitude. Stifling will occur because of the limited cathode area that is supporting the enlarging anode area as the pit grows. Pit diameters are assessed to be approximately 1 mm, with an uncertainty ranging from 0.01 to 10 mm.

There is some difference of opinion regarding the expected aspect ratios (depth to diameter ratio) for pits in the carbon steel. Drs. Shoesmith and McCright expect aspect ratios to be about 2 and Dr. Andresen suggests that they would be $\gg 10$. Dr. Farmer cites tests conducted for the Swedish high-level repository on pitting of carbon steel and notes that most aspect ratios are less than 7, but have been observed to be as high as 37.

Pitting Factor: Approach and Value. In characterizing the general corrosion rate of carbon steel in TSPA-95, a 'pitting factor' was used to describe the irregularity or roughness of the general corrosion front. The pitting factor is defined as the ratio of the localized corrosion depth (e.g., the maximum depth) to the average general corrosion depth. By associating the pitting factor with the average general corrosion rate for carbon steel, it is possible to estimate the rate at which penetrations will reach a specified depth (i.e., the wall thickness). Because the corrosion modes for carbon steel are judged to differ as a function of pH, the experts

concluded that specific approaches for the neutral and high pH cases are required to characterize the corrosion rate of carbon steel.

In the case of general corrosion (neutral pH), the experts generally concluded that an average penetration rate of the propagating general corrosion front, together with some measure of the roughness of the front, would properly characterize the corrosion rate. Most experts concluded that the roughness or 'localization factor' of the general corrosion front would decrease with depth and become relatively more uniform. Dr. Farmer would expect the local roughness to stay the same with depth and Dr. Andresen concludes that the local roughness of the front would be higher in the case of aqueous conditions than under humid air conditions. Dr. McCright presents abundant observational data gathered over time periods up to 16 years that provide a measure of a localization factor showing a decrease with time.

In the case of high-aspect ratio pitting, it is generally concluded that an appropriate way to express the corrosion rate is with a pit growth law that expresses the penetration depth as a function of time. Dr. Shoesmith concludes that the corrosion rate in the high-pH case is best represented by the sum of the pit growth rate and general corrosion rate. In the high-pH case, the general corrosion rate would be substantially lower than the general corrosion rate under neutral pH conditions.

CAM Corrosion Rate. Based on the approaches discussed above, the experts provided their assessments of the rate parameters and their uncertainties that characterize the corrosion rate of the carbon steel. Under neutral pH conditions, the experts generally concluded that the average general corrosion penetration rate given in TSPA-95 (Figures 5.4-1 and 5.4-2 of that document) provides a reasonable average rate for carbon steel. They concluded that they be used for the average general corrosion rate of carbon steel in humid-air conditions. The model should be updated as additional data are generated, especially for the corrosion rate at elevated temperatures. This average rate would, in turn, be associated with a roughness or localization factor to model the propagating general corrosion front. Dr. Scully notes that the general corrosion rate is much slower than the localized corrosion rates and can be assumed to be linear as a function of time. Dr. Andresen concludes that this average general corrosion rate could be a factor of 2X higher if hydrated salt films or saturated chemistries are present.

In assessing the localized corrosion rate associated with high-aspect ratio pits, the experts recommended the use of a pit growth law generally having the following form:

$$d = kt^n$$

where d is the depth at time t , k is a constant, and n is the power of the growth law. In the case where $n = 1$, the penetration rate is linearly proportional to time; where $n = 0$, no pit growth will occur. In general, the experts concluded that the uncertainty in n -values was significant for pitting in carbon steel, but arrived at preferred values in the range of about 0.3 to 0.6

3.3.2 Alternative CAM: Monel 400

Monel 400 is being considered as an alternative to carbon steel as the corrosion allowance material for the waste package. The experts were asked for their views on the advantages and disadvantages of this alloy as the CAM, including differences in corrosion modes and rates from those of carbon steel

Corrosion Modes and Rates. The panel felt that the available data show that the corrosion rates of Monel 400 under conditions of dry oxidation, humid air corrosion, and aqueous corrosion are all lower than those of carbon steel. Under the expected environmental conditions of the repository the corrosion mode of Monel 400 would be general corrosion and not pitting.

Pros and Cons. The slower corrosion rates are an obvious advantage of Monel 400 over carbon steel. Other advantages noted by the panel are that Cu^{+2} is less subject to acidic hydrolysis than Fe^{+3} , it is less subject to hydrogen embrittlement, and it is less subject to stress corrosion cracking. Disadvantages noted include substantially greater cost, the potential for dealloying in the presence of MIC, and the general lack of experimental data to substantiate claims of superior performance to carbon steel.

3.3.3 Corrosion Resistant Material, CRM

The experts addressed a number of issues related to the corrosion modes and corrosion rates of the corrosion resistant inner barrier of the waste package.

Mechanisms Leading to CRM Corrosion; Corrosion Modes. The experts conclude that the assessment of the corrosion of the CRM inner barrier is tied to the manner in which it is exposed by penetration of the CAM outer barrier and the locations where those penetrations occur. Dr. Shoesmith concludes that, because of the variable penetrations of the CAM in time and space, the sites of initiation of inner-barrier corrosion should be modeled according to the evolution of pit penetrations through the outer barrier (which is currently planned for TSPA-VA). The CAM will be penetrated by either general corrosion or pitting (depending on pH, which, in turn, depends on the presence or absence of dripping conditions). It is concluded that the probability of pit or crevice initiation in the CRM is a function of the availability of water, Cl^- concentration, pH, Fe^{3+} , and oxygen. Given the candidate CRM materials of Alloys 625 and C-22, it is concluded that under humid air conditions and the expected environmental conditions only very slow general corrosion of the CRM will occur. To develop localized corrosion, the aggressive conditions that might result from dripping conditions, including high-aspect ratio pits in the CAM, must be present, otherwise only general corrosion will occur. Therefore, those packages subjected to drips and those parts of the package experiencing high-aspect ratio pitting (discussed earlier) are the locations having a potential for localized attack of the CRM. The most likely corrosion mode for the CRM is judged to be crevice corrosion, with the possibility of high-aspect ratio pitting and SCC.

It is generally postulated that the low pH conditions and presumably high Cl^- within a crevice or pit in the CAM can lead to crevice corrosion along the crevice at the margins of the pit. Dr. Farmer notes that if significant exfoliation of the CAM occurs, large parts of the CRM will be exposed to bulk environmental conditions (i.e., neutral or high pH and J-13 Cl^- concentrations) and localized attack of the CRM will not occur. Drs. Andresen and McCright conclude that water will likely penetrate and travel along the narrow gap between the inner and outer barriers. Dr. Andresen suggests that volume expansion of the CAM by corrosion along this gap and the irregular contact between the barriers may lead to tensile stresses and possibly SCC.

Galvanic Protection. The present design calls for a shrink fit between the inner and outer barriers (by heating of the CAM) to allow for 90% contact between the two barriers. The potential exists, therefore, for galvanic protection of the inner barrier as the outer barrier is penetrated. While acknowledging that galvanic protection is possible for a limited period of

time, all of the experts concluded that the period is too short to be of much significance over the time periods required for the repository. The panel believes that the extent of galvanic protection is determined by the ionic conductivity and geometry of CAM penetration and crevice. The throwing power or distance given the electrolyte conductivity is assessed to be on the order of millimeters or, at most, a few centimeters. Therefore, for the expected CAM penetration by a general corrosion front, large areas of the CRM will be exposed at close to the same time, thus quickly exceeding the throwing distance. In the case of high-aspect pitting of the CAM, the period of galvanic protection is expected to be longer, but still not significantly long relative to the period of performance of the waste package (a few hundred years, at most).

Pit Density, Pit Diameter. Because of the paucity of data regarding the candidate CRM alloys, it is very difficult to estimate the density of pits/crevices to be expected on the CRM. Dr. Scully notes that the initial pit density or, equivalently the probability of pit initiation, needs to be established from experimental data. He would expect the growing pit density to decrease with time/depth of penetration. Dr. Shoesmith suggests that for purposes of waste package degradation modeling the probability of pit/crevice initiation should conservatively be assumed to equal 1.0 given penetration of the CAM and temperatures $\geq 65^{\circ}\text{C}$, and assumed to be equal to 0 at temperatures $\leq 55^{\circ}\text{C}$. Dr. Farmer provides an estimate of pit density based on short-term experiments with Alloy 825. Dr. Shoesmith suggests that the pit/crevice density should be comparable to that assessed for the case of high-aspect ratio pitting of the CAM.

Pit/Crevice Growth Rates. Due to the general lack of experimental data or experience with these relatively new alloys, all of the experts expressed uncertainty in characterizing the rates of general or localized corrosion of the CRM materials (Alloys 625 and C-22). The experts characterize the rates of general corrosion as being very low and Dr. McCright suggests that the general corrosion rates determined from experimental data for Alloy 825 would be comparable to or higher than those expected for the candidate alloys.

Given pit/crevice initiation, which to the experts occurs under conditions of dripping on the waste packages, the rate of pit/crevice growth or penetration is characterized by a linear penetration rate or growth law. Drs. Andresen and Farmer provide linear penetration rates (i.e., $n = 1$). Dr. Andresen provides these as a function of temperature, Cl^- , and pH, and Dr. Farmer provides extrapolations of empirical penetration rates derived from experimental data

under various environmental conditions for n-values of 1 and 0.5. Most of the experts conclude the n-values will generally lie in the range of 0.25 to 0.75, with preferred values of about 0.4.

3.3.4 Microbiologically Influenced Corrosion (MIC)

Most of the members of the expert panel acknowledged limited expertise in the assessment of the potential for and impact of MIC. Fortunately, Dr. Little provided a detailed evaluation of her assessment of MIC. The following summary reflects strongly her assessments, supplemented by those of other members of the panel.

Conditions Leading to MIC. The potential for MIC is related to the formation of a biofilm, which is controlled by the availability of nutrients, water and electron acceptors. All of these conditions must be met in order to have the potential for MIC. Dr. Little notes that at the present time a mass balance inventory has not been carried out for the repository, which would establish the limiting conditions in terms of a material inventory, energy-producing reactions, water availability, etc. These limiting conditions could then be used to assess the potential for MIC considering the waste package material, environmental conditions, and MIC mechanisms.

Until the repository has cooled to temperatures below 100°C and relative humidity above 60%, the potential for MIC will not be present. The potential for MIC is greatly affected by the presence or absence of drips on the containers; if there are no drips, there will not be adequate water or, likely, nutrients available to support the microorganisms.

MIC Mechanisms. Dr. Little reviews the possible MIC mechanisms that may potentially occur in the repository, including manganese oxidation, iron oxidation, metal-reducing bacteria, sulphate-reducing bacteria, acid-producing and slime-producing bacteria, fungi, and ennoblement. Fungi require an organic carbon and are unlikely to grow under Yucca Mountain conditions. She suggests that iron-reducing bacteria may be the most important organisms to consider for the carbon steel.

It is noted by some experts that it may be difficult for microorganisms to penetrate the thick layer of corrosion products to reach the interface with the CRM. However, Dr. Little concludes that microbes can penetrate the corrosion products and the ease with which the

corrosion products are permeated will depend on the surface area and the crystal structure of the iron oxide. If the corrosion products have a high ability to hold water (due to drips and surface characteristics) the potential for MIC will be enhanced.

In order for MIC to be operative in the corrosion of the CRM, there must be drips. MIC can cause ennoblement and lead to an enhance probability of localized corrosion of the inner barrier.

Impact on Corrosion Rates. It is generally concluded that the importance of MIC is in the probability of initiation of localized corrosion and the pit/crevice density, rather than affect the rate once corrosion has begun. MIC can maintain the proper conditions (e.g., low oxygen, low pH) for continued pit/crevice growth. Drs. Scully and Little note that MIC can increase the open circuit potential to +200 - 300 mV_{sce}, thus enhancing the probability of pit/crevice initiation. The likelihood that this increase in potential will cause pit/crevice initiation is a function of the materials being considered. Drs. Little and Shoesmith note that some of the candidate materials (e.g., C-22) have not been associated with documented cases of MIC.

3.3.5 Other Issues

Welds. The experts were asked to consider the effect that welds might have on the potential for, or localization of, corrosion. Two potential problems that were identified as being associated with welds are SCC related to residual stresses and localization of MIC. The anticipated welding technique is narrow gap welding with full stress anneal of all assembly welds. The closure weld may or may not be annealed, but will be protected from dripping water by a skirt in the container. Thorough inspection of all welds is also anticipated. Most of the experts conclude that this procedure will mitigate against most problems related to residual stresses. Dr. McCright notes, however, that undetected weld cracks or changes in microstructure in the fused zone may lead to localized corrosion. Dr. Little notes that microbes attach preferentially to welds and rough areas, but she would not expect bacteria to increase the probability of localized corrosion of the materials being considered for the waste package.

Ceramic Coating. The experts were asked to consider the potential performance and benefits/disadvantages of a non-porous ceramic coating placed over the outer barrier. In

general, the panel is skeptical that such a ceramic coating would provide a significant benefit and are doubtful that such a coating is practical. Most of the experts concluded that a ceramic surface would be subject to cracking during handling, from defects, from thermal expansion, or from mechanical loads like rock falls. These cracks and defects would then be sites of corrosion of the CAM, leading to additional cracking and likely spalling of the ceramic coating.

Stress Corrosion Cracking. All of the experts felt SCC is a potentially important process for localized corrosion, but felt that it is difficult to quantify its potential effect. Dr. Andresen suggested that the proper way to consider the phenomenon is to look at the stresses, microstructures, and environments that could lead to SCC. He, and others, identified the residual stresses associated with welds as potential sources of SCC, which can be mitigated by proper weld procedures. Drs. Andresen, McCright, and Farmer identified the shrink-fit process as possibly leading to stresses. It is suggested by some that, given the limited benefit to be gained by galvanic protection, a larger gap be considered between the inner and outer barrier, thus precluding the need for a shrink fit and allowing for possible volume expansion of the CAM along the gap between the barriers. Dr. Shoesmith suggests that one way to consider SCC in the waste package degradation models is to assume that, after penetration of 2/3 of the inner barrier by general or localized corrosion, the final one-third of the barrier will fail more quickly by SCC mechanisms.

Radiolysis. The experts considered the potential for enhanced corrosion due to radiolysis. Dr. Farmer notes the potential importance of radiolytic effects observed for thin-walled containers in high-radiation fields. While acknowledging these known effects, the experts generally conclude that because of the rate of radioactive decay of the inventory (assuming a half-life of 30 years of Cs-137 and Sr-90, which are the dominant radionuclides most contributing to the radiation dose), the radioactive dose will be too low to affect the corrosion processes by the time the waste packages have cooled sufficiently (below the boiling point) and relative humidities have risen sufficiently to initiate humid air corrosion of the packages.

Recommendations for Additional Work to Reduce Uncertainties. The experts provided their perspectives on additional work, including testing, experiments, calculations, and analyses, that they felt could significantly reduce the uncertainties associated with the key

waste package degradation issues. These recommendations are summarized in Table 3-2 and are discussed in the elicitation summaries for expert in Appendix D.

Uncertainty and Spatial Variability. The issue of stochastic models applicable to characterizing the uncertainty in degradation and spatial variability was discussed during the workshops and within each of the elicitations with the experts. Although there was a general consensus that stochastic variability is expected (both from package to package and from location to location on each waste package), each expert found it difficult to quantify this variability, with the exception of the variability attributed to the likelihood of dripping water on the waste package and the spatial distribution of aqueous and humid air corrosion modes on the waste package. There was general belief that other environmental factors (e.g., local geochemical variability) would also be important.

TABLE 3-1
ASSUMED ENVIRONMENTAL AND DESIGN CONDITIONS
FOR WASTE PACKAGE DEGRADATION EXPERT ELICITATION

For the experts on the Waste Package Degradation Expert Elicitation project to address various key issues related to corrosion of the waste package, certain reference conditions must be assumed. In some cases these conditions are themselves uncertain and, in those cases, some predicted profiles are presented as being representative of the expected conditions. In most cases, the reference environmental conditions are "bulk" conditions (that is, they do not reflect the conditions that might occur locally on the waste package surface or within a particular pit or crevice). The location of the condition (e.g. drift wall, canister surface) is given. Please refer to the attached figure and the overhead transparencies presented by D. Stahl and D. Sassani at WPDEE Workshop 2 for additional information.

ENVIRONMENTAL CONDITIONS

Temperature

The range of expected temperature conditions at the surface of waste packages with different waste types (10-year old spent nuclear fuel [SNF], 26-year old SNF, and defense high-level waste [DHLW]) is given by the temperature-time evolution in the attached figure.

Relative Humidity

The range of expected relative humidity conditions at the surface of waste packages with different waste types (10-year old SNF, 26-year old SNF, and DHLW) is given by the temperature-time evolution in the attached figure.

TABLE 3-1 (continued)**Water Seepage Flux**

Assume the following water contact scenarios:

- (1) First 1,000 years: the range in relative humidity (RH) at the waste package surface as given in the attached figure; no drips on waste canisters.
- (2) 1,000 - 10,000 years:
 - (a) water film on most waste canisters.
 - (b) local drips on some waste canisters (as much as 2 m³/yr for one-week period during year—subject to change).
- (3) 10,000 - 100,000 years:
 - a) water film on most waste canisters.
 - b) local drips on some canisters (as much as 20 m³/yr for one week period during year—subject to change).

Water Chemistry

Assume that the chemistry of the water entering drifts ranges from 0.1X to 10X J-13 water throughout the 100,000-year time period. Note that the water "film" on the waste package surface could be concentrated with salts due to evaporation during the thermal perturbation period. For example, chloride concentration of the water film potentially could increase to about 1000X J-13 water chloride concentration.

pH: assume near 10 for the first few thousand years for water dripping through concrete linings under degradation, then gradually return to ambient pH (7 to 8) for water contacting the waste package.

Dissolved oxygen and carbonate concentrations: oxygen and carbon dioxide fugacities will follow the air mass fraction profile given in D. Sassani's presentation at the second workshop (subject to change). After a few thousand years, the fugacity levels will return to normal values.

TABLE 3-1 (continued)**DESIGN CONDITIONS****Waste Package**

- Dimensions of waste package: 1.8-m diameter and 5.3-m length.
- Two-barrier canister wall: 10-cm-thick corrosion allowance outer barrier (CAM) and 2-cm-thick corrosion resistant inner barrier (CRM).
- Assume horizontal emplacement of waste package.
- Assume the same waste package design for defense high-level waste (DHLW) packages.
- Pedestal contacts consist of tubes of carbon steel; there are two points of contact with canister for each pedestal.

Materials/Alloys

- CAM: carbon steel (reference) or Monel 400
- CRM: alloy 625 (reference) or C-22

Mechanical Loads

- Assume local rockfall of up to 8 tons (1.9 m) of rock.
- Closure welds: narrow gap tungsten inert gas (TIG) welding.
- Residual stress relief of welds will be conducted.

Fabrication and Assembly

- Fabricated from plate or sheet that is rolled and welded.
- Outer and inner barriers constructed from two or three segments welded together.
- Shrink-fit by heating outer CAM and slipping over inner CRM.
- Lids welded using a narrow-gap welding technique.
- Thorough inspection of welds.

Radiation/Waste Package Shielding

- Assume shielding for protection from radiation-enhanced corrosion (during some period, perhaps 10,000 years).

TABLE 3-1 (concluded)

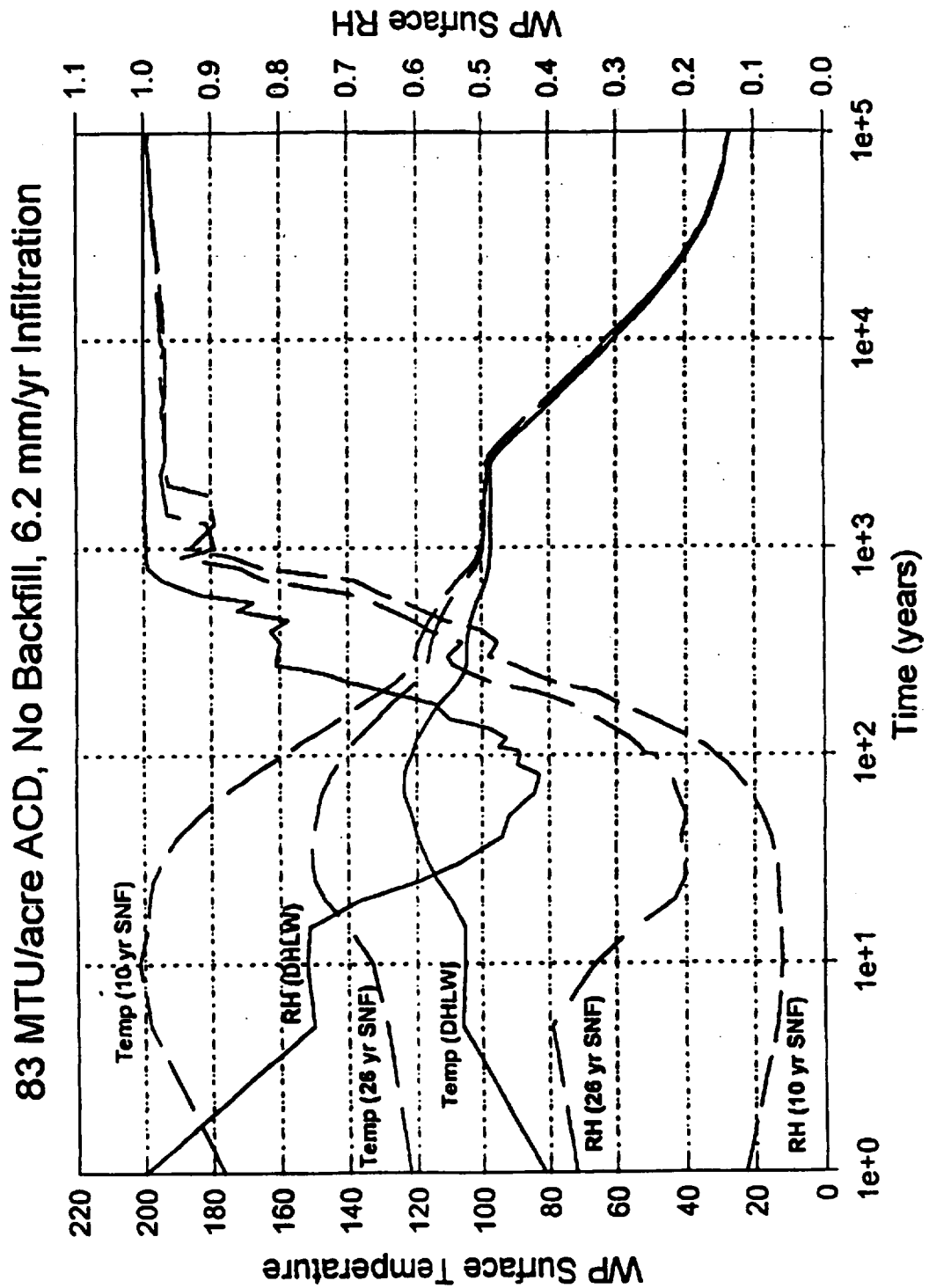


TABLE 3-2 - SUMMARY OF KEY ISSUES

	David Shoesmith	Joe Farmer	Peter Andresen	John Scully	Dan McCright	Brenda Little																		
Carbon Steel CAM																								
Oxidation of CAM	+Very thin oxide layer will develop (microns thick) during dry, hot period; very slow rate of corrosion +Limiting thickness achieved by high-field ion conduction process +Temperatures are too low (200°-140°C) for significant oxide spalling. +Oxygen may be depleted, but unlikely to have significant influence during dry oxidation period.	+Initially, layer formed during oxidation will be adherent, compact, and protective; eventually will become thick, non-adherent, flaky, and porous. +Spalling probably will occur, with exfoliated areas becoming further oxidized. +Doubtful repository will be oxygen-depleted for significant period; expect oxygen transport into drifts through pores and fractures in the rock.	+No appreciable corrosion initially. Rates controlled by T, RH, O ₂ & spallation. +Expect a thin, tenacious oxide film. initially, then will thicken & may spall. +High temperatures, boiling will lower O ₂ , CO ₂ partial pressures; atmospheric gas exclusion could have pronounced influence on onset of CAM humid air & aqueous corrosion & perhaps concrete carbonation.	+Oxygen partial pressures will control corrosion rate by dry oxidation during hot, dry period +Slow, dry oxidation process will give rise to brittle corrosion product susceptible to eventual spalling +Degree of spalling: low (0.1) moderate (0.6) high (0.3) +Location and degree of eventual spalling will localize subsequent humid-air corrosion	+Low-temperature dry oxidation will lead to thin oxide film +Do not expect significant flaking or spalling +Oxygen deficiency might cause oxidation of CAM to lower oxidation states (e.g., Fe ₃ O ₄)																			
Temperature threshold for corrosion of CAM	+Temperature is essentially boiling point of water contacting surface, which is affected by presence or absence of salts. +Temperature 110 ± 10°C accounts for presence of salts from evaporated drips.	Assuming no salt film: 100°C (100%) 125°C (1%) 150°C (0%) Assuming salt (NaCl) film: 100°C (100%) 125°C (99%) 150°C (50%) 175°C (10%) 200°C (0%)	+At ≥100°C, there will be no convection within boiling front; assume water is deaerated due to boiling. +Below 100°C, the RH thresholds apply.	+100°C, subject to salt film modification.	105°C (100%) 101°C (50%) 97°C (0%)																			
Importance of drips to CAM Corrosion	+Above boiling point, any drips will react with iron oxide, hydrolyze it, and reprecipitate iron oxy-hydroxides; persistent drips will lead to removal of oxide and onset of enhanced corrosion +Frequency and persistence of drips will have pronounced effect on CAM corrosion (increased water residence time)	+Drips onto hot waste packages will evaporate and leave salt deposits; redissolution of salt deposits can result in presence of concentrated electrolyte on surface of CAM. +Significant effect on temperature threshold for onset of corrosion of CAM.	+Spatial distribution of drips, drip rate, and frequency are important - effects spalling, and transition to and rates of humid air & aqueous corrosion. +Can lead to saturated chemistries, hydrated salt deposits as function of temperature.	+Pronounced effect on corrosion of CAM +At 100°C, RH>50%, drips will leave salt deposits: HAC +At RH>95%, drips lead to alternating aqueous and HAC; salt caking maintains aqueous condition longer	+Drips are very important to both CAM and CRM degradation; frequency and amount control time package stays wet +Concrete liner will degrade thermally and through carbonation before dripping, thus elevation of pH 9-10 will not be as high as new concrete +Salt deposits left from evaporating drips, mix with dust and concrete debris, leading to saturated solutions																			
Threshold of relative humidity (RH) for humid-air corrosion (HAC)	+Normal distribution between 65% and 75%.	<table><tr><td>RH</td><td>CDF</td></tr><tr><td>80%</td><td>100%</td></tr><tr><td>60%</td><td>50%</td></tr><tr><td>20%</td><td>5%</td></tr></table>	RH	CDF	80%	100%	60%	50%	20%	5%	+Normal distribution between 65% and 75%.	+Threshold depends somewhat on degree of spalling of oxidation products through capillary condensation and drips +50% for spalling, with drips +60% for no spalling, no drips	+RH thresholds is a function of the constituents; surface with dust, debris, salt has lower threshold than clean carbon steel <table><tr><td></td><td>RH</td></tr><tr><td>Condition</td><td>(mean, range)</td></tr><tr><td>Oxides, salts, dust</td><td>65% (60-70%)</td></tr><tr><td>Oxides, dust</td><td>75% (70-80%)</td></tr><tr><td>Dust</td><td>85% (80-90%)</td></tr></table>		RH	Condition	(mean, range)	Oxides, salts, dust	65% (60-70%)	Oxides, dust	75% (70-80%)	Dust	85% (80-90%)	
RH	CDF																							
80%	100%																							
60%	50%																							
20%	5%																							
	RH																							
Condition	(mean, range)																							
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Oxides, dust	75% (70-80%)																							
Dust	85% (80-90%)																							

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TABLE 3-2 - SUMMARY OF KEY ISSUES
(Continued)

	David Shoesmith	Joe Farmer	Peter Andresen	John Scully	Dan McCright	Brenda Little																														
Carbon Steel CAM																																				
Threshold of relative humidity (RH) for aqueous corrosion	+Aqueous corrosion appropriate for immersion in water, thus will occur only where there are drips (especially frequent and persistent). +Normal distribution between 85% and 95% as in TSPA-95	<table><tr><th>RH</th><th>CDF</th></tr><tr><td>100%</td><td>100%</td></tr><tr><td>95%</td><td>90%</td></tr><tr><td>90%</td><td>50%</td></tr><tr><td>85%</td><td>5%</td></tr><tr><td>80%</td><td>0%</td></tr></table>	RH	CDF	100%	100%	95%	90%	90%	50%	85%	5%	80%	0%	+Normal distribution between 85% and 95%. +"Immersion" conditions if there are drips or pooled water (RH 100%).	+95% on top only with drips.	<table><tr><th>RH (w/ oxides)</th><th>RH (oxides+salt)</th><th>CDF</th></tr><tr><td>100%</td><td>95%</td><td>100%</td></tr><tr><td>97%</td><td>90%</td><td>90%</td></tr><tr><td>95%</td><td>85%</td><td>50%</td></tr><tr><td>90%</td><td>80%</td><td>10%</td></tr><tr><td>85%</td><td>79%</td><td>0%</td></tr></table>	RH (w/ oxides)	RH (oxides+salt)	CDF	100%	95%	100%	97%	90%	90%	95%	85%	50%	90%	80%	10%	85%	79%	0%	
RH	CDF																																			
100%	100%																																			
95%	90%																																			
90%	50%																																			
85%	5%																																			
80%	0%																																			
RH (w/ oxides)	RH (oxides+salt)	CDF																																		
100%	95%	100%																																		
97%	90%	90%																																		
95%	85%	50%																																		
90%	80%	10%																																		
85%	79%	0%																																		
Corrosion modes for CAM	+Pit morphology is function of pH +Neutral pH (~4-9), "pits" will start as hemispherical and coalesce to form rough front and uniform corrosion mode. +At high pH (10) high-aspect-ratio pits. +Persistent and frequent high pH drips will enhance continued pit growth; infrequent drips (wetting and drying) will lead to stifling and start of new pits (not regrowth of existing pits). +Gradual decrease in pH with time will lead to decrease in aspect ratio, no new pits, and uniform corrosion.	+Corrosion mode function of pH; CAM will experience general corrosion at pH<10; water passing through the concrete may have pH>10 and will cause pitting of carbon steel. +Expect high pH conditions only where there are drips.	+Assuming pH 4-9, non-dripping: general corrosion w/ non-uniform surface. +Mean roughness factor: 1.1 for humid air; 1.5 for aqueous. +Assuming pH 10-13 and drips: high-aspect-ratio pits.	+Governed by pH conditions of water; no drips or HAC, pH assumed to be neutral; drips through concrete assumed to be alkaline (pH >9) +Assuming neutral pH: cratering and uniform corrosion +Assuming pH ≥9: high-aspect-ratio pits	+Mode is function of pH; pH 4-9 will have general corrosion; pH 9-10 could have pitting, depending on chemistry +pH 9-10 range is transition from active corrosion to passivation, thus other chemical species and factors will affect localized corrosion +Elevated Cl ⁻ required for high-aspect-ratio pits in alkaline conditions; thus, drips required and pH will decrease with time; nitrate ion presence will mitigate chloride ion effects																															
Geometry	+At RH 85%-95%: •where have drips, upper 120° of package can have aqueous conditions. •where no drips, and along sides and bottom, will be HAC. +Where have frequent and persistent drips, have enhanced corrosion rate of 10x aqueous corrosion rate. +Site of failure of CAM will influence corrosion process of CRM; >99% likely to be on top of canister.	+Top of package is where drips will impinge and lead to greater corrosion +Supports at bottom of package may form crevices.	+Top of WP defined as 20-30-degree angle, growing to 90 degrees with corrosion. +Bottom is 20-30-degree angle and support pedestals. +Humid-air corrosion on sides, accelerated somewhat by salt film "traces" from drip motion.	+Assuming drips occur, upper 120°-180° of package will have aqueous conditions and high pH. Angle depends on roughness developed +HAC, neutral pH on sides and bottom of packages with drips, and all over non-dripping packages +Enhanced pit initiation probabilities at locations of spalling of oxide layer but only slight reduction in probability, if any, in non-spalled regions depending on oxide porosity +Supports, bottom may also support bulk water conditions	+Oxides will be present on entire canister surface +Salt deposits present only where there are drips and on upper 180° of surface +Aqueous conditions only where there are drips and on top (upper 60°) and bottom (lower 60°) where water can accumulate +HAC where no drips and on sides where there are drips																															

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TABLE 3-2 - SUMMARY OF KEY ISSUES
(Continued)

	David Shoesmith	Joe Farmer	Peter Andresen	John Scully	Dan McCright	Brenda Little
Carbon Steel CAM						
Pit density and pit diameter	Assuming high pH conditions: +Pit density (pits/cm ²) log-normal distribution: 1 (median, 50 th percentile) 0.1 (5 th percentile) 10 (95 th percentile) +This pit density will persist throughout lifetime of CAM. +Aspect ratios of about 2 are expected, maximum would be 4.	Assuming high pH conditions: +Pit diameter: ~1mm +Pit density (pits/cm ²): 100 (99%) 10 (50%) 1 (5%) 0.1 (0%) +Aspect ratios observed are generally less than 7, although known to be as high as 37.	Assuming high pH conditions: +Pit diameter: few mm's expected; 10 mm max +Pit density (pits/cm ²) CDF: 10 (99%) 5 (95%) 1 (50%) 0.05 (20%) 0.01 (1%) +Aspect ratio can be >10:1	Assuming high pH conditions: +Growing pit density decreases as function of time/depth +At depth 0.001 to 1 cm, no. pits/cm ² is: 10 (99.9%) 1-2 (90%) 0.5 (50%) +At depth 1 to 10 cm, no. pits/cm ² is: 2 (99.9%) 0.1-0.2 (90%) 0.01-0.02 (50%) +Pit diameter (mm) 10 (99.9%) 5.6 (95%) 1.7 (75%) 0.8 (25%) 0.2 (1%) +Pit shape is function of potential and other factors	+Aspect ratio for high pH pits is about 2; shape is roughly spherical with narrow mouth +Low aspect ratio consistent with corrosion localization factors calculated from long term exposures	
Pitting factor: approach & value	+Do not use pitting factor for corrosion rate of CAM. +Neutral conditions: use general corrosion rate, zero pitting rate. +High pH: total penetration depth is sum of general corrosion depth and pitting depth (different general rate than neutral conditions).	+Pitting factor to describe propagating corrosion front is not appropriate +Two alternatives: (1) use average general corrosion rate, divide area of waste packages into patches and assume they have same average rate but different distributions; or (2) use "roughness" factor to describe variation in morphology of front and assume it stays constant with depth. [what is roughness factor??]	For general corrosion: +Humid air: 1.2 (+2σ) 1.1 (mean) 1.0 (-2σ) +Aqueous: 2 (+2σ) 1.5 (mean) 1.0 (-2σ)	+Pitting factor not appropriate under neutral conditions: use general corrosion rate +Under high pH use pit growth law	+Prefer to consider a localization factor expressed as either the ratio of the average pit depth to the average corrosion penetration, or ratio of deepest pit depth to the average corrosion penetration +Localization factor will decrease with time/depth	
CAM corrosion rate	+Assuming neutral pH: use general corrosion rate in TSPA-95. +Assuming high pH: •General corrosion rate is lower than neutral case (Scale from TSPA-95 and Marsh's plot) •Pitting rate: n-values: (normal distribution) 0.48 (mean) 0.33 (5 th percentile) 0.67 (95 th percentile) 0 (0 percentile) 1.0 (100 th percentile) k-values (from Marsh's data) +Because temperature will not change much during period of pitting, don't need temperature-dependence of rate.	+Assuming neutral conditions, use TSPA-95 to define average general corrosion rate. [What is rate for high-aspect-ratio pits?]	+Assuming neutral pH 4-9: rate used in TSPA-95 is OK (Figures 5.4-1 and 5.4-2) for general corrosion +If have hydrated salt films or saturated chemistries, 2x higher	+Assuming neutral pH: general corrosion rates in TSPA-95 (much slower than localized corrosion and assumed to produce linear penetration, At) +High pH: pit growth law $d = At + Bt^{n+1}$ n-values: -1.0 99.9%) -0.66 (95%) -0.5 (75%) -0.33 (25%) -0.25 (5%) 0 (0.1%) +At $t_c = 1$ day, B-values (μm/day) ⁿ⁺¹ : 10,000 (99.9%) 1,000 (90%) 800 (60%) 200 (40%) 100 (10%) 10 (0.1%)		

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TABLE 3-2 - SUMMARY OF KEY ISSUES
(Continued)

	David Shoesmith	Joe Farmer	Peter Andresen	John Scully	Dan McCright	Brenda Little
Carbon Steel CAM						
Alternative CAM: Monel 400						
Corrosion modes, rates	+Sparse data suggest lower corrosion rates.	+Monel 400 is more corrosion-resistant than carbon steel. +Presence of dissolved copper in crevice solution might produce penetration rates comparable to those in "Green Death" solution.	+Very slow general corrosion, not pitting	+Very slow (passive diss.) uniform corrosion in acidic, neutral, and slightly alkaline pH +Slower dry air oxidation, HAC, and aqueous corrosion than carbon steel	+Does not develop deep pits +Experimental data show general corrosion and pitting rates less than carbon steel	+Sulfide may be produced by sulphate-reducing bacteria, but probability is relatively low because of aerobic conditions
Pros and cons	+Don't recommend for these reasons: <ul style="list-style-type: none">•Order of magnitude more expensive•Available data to establish rates for carbon steel, not for Monel 400•Would remove extensive carbon steel data base and weaken credibility.		+Passive in most environments, including high pH +Performs poorly in H ₂ S and nitric acid, which aren't likely to develop	+Minimal pH suppression due to hydrolytic acidification +Resistant to SCC and hydrogen embrittlement +May undergo dealloying in presence of MIC; >4x rate increase +Localized corrosion can occur by ion concentration cell mechanism +Cu content will not degrade resistance of Ni-Cr-Mo alloys	+Cu ⁺² less subject to acidic hydrolysis than Fe ⁺³ +Sulphate-reducing bacteria tend to cause de-alloying +Is an intermediate material with performance between carbon steel and CRMs +Perhaps could have thinner section than 10 cm proposed for carbon steel	+Probability of developing a biofilm on Monel 400 CAM is comparable to carbon steel
Corrosion-Resistant Material, CRM						
Mechanisms leading to CRM corrosion; corrosion modes	+Initiation of localized corrosion sites occurs according to evolution of pit penetrations through the CAM. +Given CAM penetration, probability of pit/crevice initiation function of availability of water, Cl ⁻ , pH, Fe ³⁺ , temperature, and O ₂ ; thus most likely at top of package and under dripping conditions. +For high Mo Ni alloys general passive corrosion most likely mode +However, judicious to assume crevice corrosion occurs +Given CAM penetration, probability of crevice initiation = 1.0 at ≥ 65°C, and = 0 at ≤ 55°C, with exponential decrease between 65° and 55°C. +Assume that no crevice will stop growing.	+Attack of the CRM will begin with penetration of the CAM and exposure to the near-field environment and the CAM-CRM crevice solution. +If general corrosion leads to significant exfoliation and exposure of CRM, neutral or high pH and J-13 [Cl ⁻] of contacting water will lead to slow general corrosion. +Crevice corrosion is only process that can lead to significant penetration of CRM. +If high-aspect-ratio pits in CAM, may lead to pH suppression, high Cl ⁻ and CRM pitting, intergranular attack, and SCC. +Tight crevices will result in higher corrosion rates; geometry determined by fabrication technique (shrink fit, weld cladding, etc.).	+Water will penetrate and travel along the gap between the inner and outer barriers +Water in gap will remain deaerated until large penetrations in CAM occur, but slow corrosion of CAM from inside will oxidize entire ID wetted surface. +Volume expansion of CAM (2-3x) and irregular contact may lead to tensile stresses (even in CRM from buckling) and SCC +No significant corrosion of CRM under humid-air conditions; only under aqueous film or immersion, which are associated with drips	+CRM corrosion only under aqueous conditions +High-aspect ratio pitting and crevice corrosion modes as a function of temperature, pH, Fe ³⁺ , O ₂ , H ₂ O ₂ , biofilm ennoblement on top of package under drip pools. No justified stifling scenario	+General corrosion is expected under expected bulk environmental conditions +Localized corrosion requires drips, elevated Cl ⁻ , and low pH within a crevice/pit +Given drips, T=80°-30°C, pH 4-9, expect less than 4% of canisters to have localized corrosion of CRM +Moisture may get in and move along the narrow crevice between inner and outer barrier	

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TABLE 3-2 - SUMMARY OF KEY ISSUES
(Continued)

	David Shoesmith	Joe Farmer	Peter Andresen	John Scully	Dan McCright	Brenda Little
Carbon Steel CAM						
Galvanic protection	+Period of galvanic protection will be limited due to low aspect ratio of pits and short throwing distances (few millimeters). +For general corrosion, period of galvanic protection 50-150 years; for high-aspect ratio pits, period of ~300 years	+Extent of galvanic protection (throwing power) determined by ionic conductivity and geometry of CAM penetration and crevice. +Doubtful that galvanic protection will be significant. +Passivation of crevice wall formed by CAM may not be possible at pH and potential at mouth of crevice.	+Throwing distance related to ionic coupling, limited by copious iron oxide corrosion products +Throwing distance ~1cm or less; protection especially ineffective for general corrosion (large exposure areas) +Any benefit to CRM is quite limited spatially and temporally +Wiser to select material with greater resistance to pit/crevice corrosion (e.g., C-22, C2000)	+Galvanic suppression direct function of thin electrolyte film and aspect ratio of pits/general corrosion front +Throwing distances on order of millimeters or centimeters +In neutral conditions, general corrosion front will expose large surfaces of CRM, limiting galvanic suppression to tens of years +Assuming high pH, period may to 200 - 400 years	+Effectiveness of galvanic protection is function of throwing power, which is related to electrolyte conductivity +Throwing distance of no more than a few centimeters +In neutral conditions, large parts of CRM exposed at same time, thus limited protection time +In high pH conditions, aspect ratios are ~2, thus won't have long protection period	
Pit density, pit diameter	+Pit/crevice density is same as for CAM in high pH case.	+Initial pit density difficult to estimate for alloys 625 and C-22 because of limited test data; have short-term test for 825 +Pit density (pits/cm²): 400 (100%) 200 (75%) 80 (50%) 50 (25%) 10 (5%)	Density of localized corrosion broadly similar to CAM at high pH because of cathodic current requirements	+Must establish the initial growing pit density, or probability of pit initiation, with experimental data (similar to CAM high pH case)		
Growth rates	+In absence of growth laws for CRM candidate materials, use laws for Ti-2, which is susceptible to crevice corrosion. n-value P(µm) = kt(hrs) - x₀ k = 750 ± 290 x₀ = -1200 ± 800	+Penetration rate for CRM: n-value CDF 1.0 100% 0.7 90% 0.5 75% 0.3 10% 0. 0% [Empirical rates are used to develop penetration plots shown on Figures JF-3 to 6].	+Given drips, high-aspect ratio pits in CAM, high Cl⁻, pH 3 (0.1): 100°C 50°C CDF 50 mil/yr 5 mil/yr (99.9%; 1 0.1 (70%) 0.3 0.03 (50%) 0.01 0.001 (5%) +Given drips, general corrosion of CAM, mixed anions, pH4-10 (0.9): [Lower than above rates by order of magnitude]	+Pit growth law d = Bt ⁿ⁺¹ B-values: same as for CAM, high pH condition n-values: (differ as function of alloy, must be established from experiments): •expected to lie within -0.75 and -0.25 •might be truncated at -0.5 if diffusion-limited pit growth +Passive dissolution rates; will decrease with time by orders of magnitude •Assuming aggressive T, pH: Initially =>500 µm/yr Later => 5-50 µm/yr •Assuming neutral, 20°C: Initially => 5-50 µm/yr Later => 0.05-0.005 µm/yr	+General corrosion rates from experimental data of Alloy 825 in J-13 water, T=50°-150°C range from 0.03 to 0.21 µm/yr; Ni-Cr-Mo alloys should show similar or lower rates [Need CDF] +For localized corrosion, once pit/crevice initiates, pit growth law p = Kt ⁿ n-values (for C-22, 625) normal distribution: 0.4 (mean) 0.3, 0.5 (±2σ) 0.2, 0.65 (limits)	

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TABLE 3-2 - SUMMARY OF KEY ISSUES
(Continued)

	David Shoesmith	Joe Farmer	Peter Andresen	John Scully	Dan McCright	Brenda Little
Carbon Steel CAM						
Microbiologically Influenced Corrosion						
Conditions leading to MIC	+After RH is sufficient for HAC, MIC can occur +Without drips, potential for MIC is low because free water is low beneath porous oxide on CAM and hard to get nutrients to interface; with drips, access to interface is enhanced	+Fungi are capable of growth at RH 60%-90%, bacteria at >90%.	+Not present >100°C; not likely >70°C	+Temp <100°C, RH>60% +Maximum area affected is area subjected to drips	+At temp <100°C, RH>60%-70%, fungi and bacteria can grow +Fungi can grow at RH<60% but require organic carbon, which is limited	+Potential for MIC is related to biofilm formation, which is controlled by availability of nutrients, water, and electron acceptors; all must be present +Temp <100°C, RH>60% MIC begins and is greatly influenced by presence of drips (no drips, no MIC) +Mass balance would show availability of nutrients, redox reactions, etc., and establish limiting conditions
Mechanisms		+Iron-oxidizing bacteria have been isolated from Yucca Mountain samples +Acid- and sulfide-producing bacteria may also exist.	+Carbon sources associated with repository development and emplacement +Likely no significant carbon sources in dripping water	+Effect on CAM is to lower the pH to 4	+MIC is one condition that might, with time, lead to lower pH in repository +Controlled by availability of water and nutrients, which are in limited supply	+Potential MIC mechanisms include: manganese oxidation, iron oxidation, sulphate-reducing bacteria, acid-producing and slime-producing bacteria, fungi, and ennoblement +Iron-reducing bacteria may be most important organisms to consider for carbon steel +For CRM, drips are required and MIC may cause ennoblement and localized corrosion (probabilities given in elicitation summary)
Impact on corrosion rates	+MIC affects the probability of initiation and not the rate of corrosion (already assuming conservative initiation probability). +Dismiss MIC as consideration for the CRM, except in cases of drips. +Choice of materials can influence likelihood; MIC is not seen on C-4 or C-22.	+MIC could push CRM to more anodic potentials, closer to critical pitting potential. +Possible production of acid will exacerbate both general and localized corrosion.	+Expect very thin biofilm and limited shift in local chemistry beneath biofilm	+2x to 5x multiplier on CAM corrosion rate +Increase open circuit potential to +200-300mV _{sce} , enhancing probability of pit or crevice initiation on CRM; probably over local area	+May have large effect on CAM, but most CRM materials appear to be immune	+Importance of MIC is in probability of initiation of localized corrosion and pit/crevice density, rather than effect on rate once corrosion has begun +MIC can maintain proper conditions (low oxygen, low pH) for continued pit/crevice growth. +Can affect the spatial distribution of localized corrosion (e.g., at drips) +Salts that develop on surface from evaporating drips may not be conducive to microbial growth

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TABLE 3-2 - SUMMARY OF KEY ISSUES
(Continued)

	David Shoemith	Joe Farmer	Peter Andresen	John Scully	Dan McCright	Brenda Little
Carbon Steel CAM						
Other Issues						
Welds	+Don't expect enhanced corrosion of CAM welds if done properly. +Perhaps enhancement at CRM welds, but already assuming conservative initiation probability.	+Welds will have residual stresses approaching the yield stress. +Will be prime location for initiation and propagation of stress corrosion cracks. +Sensitization will increase probability of failure.	+High residual stresses at welds commonly lead to SCC +Narrow gap welding and full stress relief anneal will reduce SCC problem +Do not expect weld, if performed properly, to enhance general or localized corrosion of CAM or CRM	+Abstract behavior of CRM welds by considering in terms of C_{reqiv} relative to base alloy	+Assuming assembly welds will be annealed; small residual stresses or cracked welds may lead to localized corrosion. +MIC may localize at CAM welds +Welds could lead to localized corrosion due to microstructure in fusion zone +Low interstitial content, good welding practices, and quality control will reduce likelihood	+Although microbes attach preferentially to welds and rough areas, do not expect bacteria to increase probability of localized corrosion of materials being considered
Ceramic coating	+Don't recommend; failure at one site would destroy its effectiveness. +Difficult to claim containment for significant period of time.	+Coatings expected to have porosity and will crack due to thermal expansion, impact during movement, impact and deformation from rock fall, and formation of corrosion products at interface with CAM. +Could form crevice with CAM, exacerbating corrosion. +Stress risers in ceramic may lead to SCC in CAM.	+Creating porosity- and crack-free coating over large surface is impractical and improbable +Water penetrating coating will corrode CAM and volume expansion will cause spalling +Benefit is limited to years or tens of years	+Should limit area affected by corrosion processes until significant fraction have spalled +All coatings have defects (cracks and flaws) +CAM corrosion modes not affected +Voluminous corrosion products will spall coating +Cracks may be sites for early capillary condensation	+Vulnerable to cracking and spalling due to handling and contact with debris and pedestals; won't provide protection when needed +Possibility of coating inside of the CRM as alternative	
Stress corrosion cracking	+May assume that cracks develop at base of well-developed pit/crevice and accelerate pitting/crevice process. +Assume 2/3 of wall thickness of CRM is available for crevice corrosion; after that SCC causes rapid failure.	+CAM will be stressed from shrink fit. +SCC is a possible corrosion mechanism for the CRM.	+Look at stresses, microstructures, and environments that lead to SCC +Reduce potential by annealing welds, no shrink fit, and larger gap between inner and outer barriers to avoid oxide wedging	SCC windows of susceptibility must be defined. When SCC growth rate < passive dissolution rate, SCC is no longer relevant. Minimize tensile stresses	+Possible susceptibility of carbon steel at pH 9-10 when passivation is incomplete, due to carbonate and nitrate present +Residual thermal stresses due to shrink-fit procedure may lead to SCC; perhaps should have a larger gap between inner and outer barriers	
Radiolysis	+Radioactive decay will have lowered dose by the time conditions reach 110°C and RH ~65%	+Important in thin-walled containers with high radiation fields. +Can form oxidizing agents such as H_2O_2 , which can elevate the potential of CAM or CRM several hundred millivolts. +Gamma radiolysis can produce nitrogen oxides that react with copper-based alloys.	+Atmospheric gas exclusion will reduce presence of nitrogen +Radioactive decay over first 1000 years will greatly reduce threat from radiolysis	+Radioactive dose will be low by the time there are high pH drips; probably not a significant effect		

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TABLE 3-2 - SUMMARY OF KEY ISSUES
(Continued)

Carbon Steel CAM	David Shoesmith	Joe Farmer	Peter Andresen	John Scully	Dan McCright	Brenda Little
Recommendations for Additional Work	<ul style="list-style-type: none"> +Establish drip frequency, volume and distribution under repository conditions. +Determine volume of water which must permeate through concrete before pH of water is not made alkaline. +Experiments could be conducted to evaluate the potential for stiffling crevices in the CRM, as a function of temperature and materials. 	<ul style="list-style-type: none"> +Results of the ongoing testing program should be used to establish parameters of probabilistic and deterministic models of localized corrosion rates for the CRM. +More research is needed to reduce the uncertainty in the time-dependence of CRM corrosion rates (i.e., the n-values). 	<ul style="list-style-type: none"> +Improve hydrology scenarios and estimates for water arrival rate at waste package. Then define likely near-field and local (waste package) water composition vs. time, including effects of refluxing, concrete, dripping/evaporation, and corrosion. +Establish the time-history of oxygen partial pressures +Evaluate the potential for high pH conditions from the standpoint of saturation, CO₂ exclusion, species dissolved from the concrete, etc. +Consider larger annular gap between inner and outer barriers +Need to evaluate experiential "vignettes" that imply that radiolysis-enhanced corrosion occurs at low RH 	<ul style="list-style-type: none"> +Testing of CAM in high pH conditions to establish pit density, growth rate of high-aspect-ratio pits +Testing of CRM at various applied potentials to establish probability of pit initiation, growing pit density rates, and n-values +Low temperature 100°-200°C oxidation studies on CAM at various O₂ partial pressures to establish growth laws (logarithmic vs. parabolic?) and factors governing spalling. +Establish whether localized corrosion stiffling criteria exist for CRM C-22, alloy 625 materials. Define mechanism of stiffling. 	<ul style="list-style-type: none"> +Ongoing studies of possible carbonate- and nitrate-induced SCC of carbon steel are important, as are studies of concrete degradation and their effect on water chemistry +TSPA should incorporate scenarios that include very rare or long-term processes 	<ul style="list-style-type: none"> +Mass balance inventory should be conducted for repository, including material inventory; energy-producing reactions; evaluation of MIC potential considering container material, environmental conditions, and mechanisms +Tests should be conducted to assess the effect of concentrated salt solution (1000x J-13) on growth of ESF isolates; should also be evaluated at 100°C

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4.0 SUMMARY AND CONCLUSIONS

The Waste Package Degradation Expert Elicitation (WPDEE) project is one of a series of projects involving the elicitation of experts to characterize the knowledge and uncertainties in key inputs to the Yucca Mountain Total System Performance Assessment (TSPA). The objective of this project was to characterize the spatial and temporal distribution of degradation of the waste package, including uncertainties. An understanding of waste package degradation processes is critical to evaluating the performance of the potential high-level nuclear waste repository at Yucca Mountain.

A major goal of the project was to capture the uncertainties involved in assessing the waste package degradation processes. To ensure that the analysis included a wide range of perspectives, multiple individual judgments were elicited from members of an expert panel. The panel members, who were experts from within and outside the Yucca Mountain project, represented a range of experience and expertise. A deliberate process was followed, consistent with available procedural guidance regarding expert elicitation methodologies, in facilitating interactions among the experts, in training them to express their uncertainties, and in eliciting their interpretations. The resulting assessments and probability distributions, therefore, provide a reasonable aggregate representation of the knowledge and uncertainties about key issues regarding waste package degradation.

The principal steps followed in the WPDEE project were the following:

- Development of Project Plan
- Selection of the Expert Panel
- Data Compilation and Dissemination
- Meetings of the Expert Panel
- Elicitation of Experts
- Feedback of Preliminary Results
- Finalization of Expert Assessments
- Preparation of Project Report

The assessments made by the WPDEE experts included evaluation of several key technical issues related to waste package degradation. A brief summary of the expert interpretations is given below.

Corrosion of Carbon Steel CAM

The experts addressed the issue of corrosion of the carbon steel as a function of the temperature, relative humidity, water dripping, and chemistry of the dripping water within the repository. The first assessment is the nature of oxidation of the carbon steel CAM during the initial period where the repository is at its hottest temperatures and relative humidities are lowest. The experts generally agree that the dominant process during this period would be dry oxidation of the carbon steel and consequent very slow corrosion. There are differences of opinion regarding the nature and thickness of the oxide film that would develop on the waste package during this period, and the potential for spalling of the oxide layer. Some of the experts conclude that, because the temperatures are relatively low (relative to 500°C where carbon steel oxidation has been observed), a thin oxide layer would develop that is not flaky and prone to spalling. Others believe that a thick, non-adherent, flaky, and porous oxide layer will form that will become prone to spalling.

As the temperature of the repository cools, there will be a threshold temperature below which dry oxidation of the carbon steel will be replaced by humid-air or aqueous corrosion, depending on the exposure conditions. All of the experts concluded that the threshold temperature was essentially the boiling point of water that contacts the waste package surface. Below that point, the relative humidity will be important to corrosion processes.

A persistent theme across the panel is that drips are very important to the corrosion processes and rates of corrosion of the CAM (as well as the CRM). Important aspects are the spatial distribution, persistence through time, and frequency of drips. All experts noted that drips during the time that the waste packages are relatively hot will evaporate and leave behind hydrated salt deposits, whose constituents would include concentrated J-13 water as well as contributions from the degrading concrete liner. Persistent drips onto these salt deposits could lead to saturated chemistries. Importantly, the presence or absence of drips is also judged to control to a large extent the pH of water on the package surface, which, in turn, controls the mode of corrosion of the carbon steel.

In general, the relative humidity threshold at which humid air corrosion (HAC) processes become operative is believed by the experts to be a function of the nature of the surface that

will exist at the time that relative humidities rise. Assessments of the RH threshold range from about RH 60% to 80% across the panel, depending on the nature of the surface. Therefore, the RH threshold for the onset of aqueous conditions is generally in the range of RH 85-100% and drips or pooled water are required to achieve aqueous corrosion conditions.

Assuming the onset of corrosion, the mode of corrosion of the carbon steel CAM is judged to be governed by the pH of the water contacting the surface. The experts conclude that the expected corrosion mode of the carbon steel in the case of no drips and neutral pH is uniform or general corrosion, and in the case of high pH drips is high-aspect ratio pitting.

It was generally concluded by the panel that the presence or absence of drips is a controlling aspect of the spatial distribution of corrosion both across multiple waste packages and on individual packages. Aqueous corrosion modes are assumed to be possible only in the case of dripping water and on the top of the waste packages, defined variously by the panel as the upper 90 to 180° in cross-sectional slice. Some experts also considered the bottom of the package to have the potential for aqueous corrosion.

In the case of general corrosion (neutral pH), the experts concluded that an average penetration rate of the propagating general corrosion front, together with some measure of the roughness of the front, would properly characterize the corrosion rate. In the case of high-aspect ratio pitting, it is generally concluded that an appropriate way to express the corrosion rate is with a pit growth law that expresses the penetration depth as a function of time. The experts provided their assessments of the rate parameters and their uncertainties that characterize the corrosion rate of the carbon steel.

Alternative CAM: Monel 400

Monel 400 is being considered as an alternative to carbon steel as the corrosion allowance material for the waste package. The panel felt that the available data show that the corrosion rates of Monel 400 under conditions of dry oxidation, humid air corrosion, and aqueous corrosion are all lower than those of carbon steel. Other advantages noted by the panel are that Cu^{+2} is less subject to acidic hydrolysis than Fe^{+3} , it is less subject to hydrogen embrittlement, and it is less subject to stress corrosion cracking. Disadvantages noted include substantially

greater cost, the potential for dealloying in the presence of MIC, and the general lack of experimental data to substantiate claims of superior performance to carbon steel.

Corrosion Resistant Material, CRM

The experts addressed a number of issues related to the corrosion modes and corrosion rates of the corrosion resistant inner barrier of the waste package. The experts conclude that the assessment of the corrosion of the CRM inner barrier is tied to the manner in which it is exposed by penetration of the CAM outer barrier and the locations where those penetrations occur. It is concluded that the probability of pit or crevice initiation in the CRM is a function of the availability of water, Cl^- concentration, pH, Fe^{3+} , and oxygen. Given the candidate CRM materials of Alloys 625 and C-22, it is concluded that under humid air conditions and the expected environmental conditions only slow general corrosion of the CRM will occur. To develop localized corrosion, the aggressive conditions that might result from dripping conditions, including high-aspect ratio pits in the CAM, must be present. Therefore, those packages subjected to drips and those parts of the package experiencing high-aspect ratio pitting are the most likely locations of localized attack of the CRM. The most likely corrosion mode for the CRM is judged to be crevice corrosion, with the possibility of high-aspect ratio pitting and SCC.

While acknowledging that galvanic protection is possible for a limited period of time, all of the experts concluded that the period is too short to be of much significance over the time periods required for the repository. The panel believes that the extent of galvanic protection is determined by the ionic conductivity and geometry of CAM penetration and crevice. The throwing power or distance given the electrolyte conductivity is assessed to be on the order of millimeters or, at most, a few centimeters. The short throwing distance, combined with the morphology of the general corrosion front, will preclude significant galvanic protection over large parts of the exposed CRM.

Due to the general lack of experimental data or experience with these relatively new alloys, all of the experts expressed uncertainty in characterizing the rates of general or localized corrosion of the CRM materials (Alloys 625 and C-22). Given pit/crevice initiation, which to most of the experts occurs under conditions of dripping on the waste packages and high-aspect ratio pitting of the CAM, the rate of pit/crevice growth or penetration is characterized by a linear

penetration rate or growth law. Most of the experts conclude the n-values will generally lie in the range of 0.25 to 0.75, with preferred values of about 0.4.

Microbiologically Influenced Corrosion (MIC)

The potential for MIC is related to the formation of a biofilm, which is controlled by the availability of nutrients, water and electron acceptors. All of these conditions must be met in order to have the potential for MIC. The potential for MIC is greatly affected by the presence or absence of drips on the containers; if there are no drips, there will not be adequate water or, likely, nutrients available to support the microorganisms. It is generally concluded that the importance of MIC is in the probability of initiation of localized corrosion and the pit/crevice density, rather than affect the rate once corrosion has begun. Drs. Scully and Little note that MIC can increase the open circuit potential to +200 - 300 mV_{scc}, thus enhancing the probability of pit/crevice initiation. The likelihood that this increase in potential will cause pit/crevice initiation is a function of the materials being considered and the experts note that some of the candidate materials (e.g., C-22) have not been associated with documented cases of MIC.

Other Issues

In addition the primary issues discussed above, the experts were asked to provide their interpretations regarding a number of other issues including importance of welds to corrosion process, the pros and cons of a ceramic coating on the waste package, stress corrosion cracking, and radiolysis influenced corrosion.

In addition, the experts provided their assessments of the data collection and analyses that could be conducted to reduce uncertainties in the key issues.

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APPENDIX A

BIOGRAPHIES OF EXPERT PANEL MEMBERS

BIOGRAPHIES OF MEMBERS OF THE EXPERT PANEL

Dr. Peter L. Andresen has been a corrosion scientist with GE Corporate Research & Development Center in Schenectady, New York since 1978 where he has worked in the area of corrosion and environmental effects on mechanical properties of structural materials. He has received two Whitney Gallery of Achievers Awards and the Dushman Award from GE, the Speller Award from NACE, and was selected as one of "50 Stars to Watch" by Industry Week (12/16/96). Dr. Andresen is the author of over 90 publications and conference proceedings and is a Fellow of the American Society for Metals. He serves on the Board of Editors for Corrosion Journal and on the Executive Committee of the International Cooperative Group on Environmentally Assisted Cracking. He has also served in numerous capacities as an expert consultant and advisor to a variety of major international programs. Dr. Andresen completed his B.S., M.S. and Ph.D. degrees in Materials Engineering at Rensselaer Polytechnic Institute.

Dr. Joseph C. Farmer is Group Leader of the Electrochemical Processing Group, Chemistry & Materials Science at the University of California Lawrence Livermore National Laboratory where he has been employed since 1987. Dr. Farmer has more than 20 years of experience in basic and applied research involving: glass and ceramic processing; electrochemical processing; corrosion science; electroplating; sputter deposition; optical characterization of films adsorbed and deposited on electrode surfaces; high-pressure homogeneous catalysis; and separations. He is the author of over 100 publications, and has been a recipient of several awards from international scientific and technical organizations, including: 1996 Award for Best Paper, International Thermoelectrics Conference; 1995 R&D 100 Award; 1986 Norman J. Hackerman Award for Young Authors, Electrochemical Society. Dr. Farmer holds Ph.D. in Chemical Engineering from the University of California at Berkeley, and a B.S. in Chemical Engineering from Virginia Polytechnic Institute and State University.

Dr. R. Daniel McCright is a metallurgical engineer at the University of California Lawrence Livermore National Laboratory. He is currently assigned to the Yucca Mountain Project as the Technical Area Leader for Engineered Barrier Materials Characterization. In this assignment, he provides technical leadership to a group of 18 scientists, engineers, and technologists for testing, evaluating, and modeling the behavior of candidate materials for high-level nuclear waste and spent fuel containers. McCright has been employed at Lawrence Livermore National Laboratory since 1976, and most of his work experience has been in corrosion and electrochemistry. He holds a B.S. in Metallurgical Engineering from

the University of Cincinnati, and a Ph.D., also in Metallurgical Engineering, from the Ohio State University.

Dr. Brenda J. Little is a Senior Scientist for Marine Molecular Processes at the Naval Research Laboratory at Stennis Space Laboratory in Mississippi, where she has been employed since 1986. Dr. Little has adjunct faculty positions at Montana State University and the University of Southern Mississippi. At the Naval Research Laboratory she serves as the Section Head for the Microbiologically Influenced Corrosion Section. She has published over 60 research papers, 13 book chapters and one book on that subject. Dr. Little received a Ph.D. from Tulane University in chemistry and a B.S. from Baylor University in biology and chemistry.

Dr. John R. Scully is Associate Professor in the Department of Materials Science and Engineering at the University of Virginia. His current research includes studies on localized corrosion, passivity and repassivation, stress corrosion and hydrogen embrittlement of Al, Ti, Fe and Ni-based alloys as well as intermetallics compounds. Prior to joining the University of Virginia in 1990, he was a Senior Member of Technical Staff at David Taylor Naval Ship R&D Center, A.T. & T. Bell Labs and Sandia National Labs for a total of nine years. He has conducted electrochemistry, corrosion, passivity and environmental fracture studies in the marine, battery, microelectronics, aerospace, electric power, and defense-related fields. Dr. Scully chaired the Electrochemical Corrosion Methods Subcommittee of ASTM for 7 years. He is chairman of the NACE Research Committee and serves as an associate editor for Corrosion Journal and Metallurgical and Materials Transactions. He has edited two conference proceedings and two books, and published over 60 papers. Dr. Scully is an NSF Presidential Young Investigator, and he has received the A.B. Campbell and H.H. Uhlig Awards from NACE, the Blum Award from ECS, and has given over 30 invited talks on his work. Dr. Scully holds B.S., M.S., and Ph.D. degrees in Materials Science and Engineering from Johns Hopkins University.

Dr. David W. Shoesmith is a principal scientist with Atomic Energy of Canada (Whiteshell Laboratories) and Head of the Corrosion and Electrochemistry section in the Physical and Environmental Science Division. He has been with Atomic Energy of Canada for the last 24 years and in his present position for the last 12 years. He is responsible for programs on wasteforms (used fuel) and waste containers and the development of models to predict their behavior under disposal conditions. Dr. Shoesmith is a fellow of NACE International and the Canadian Chemical Society, and a rabid member of "The Toon" supporters club. He is the author/coauthor of 90 refereed publications, 8 book chapters and over 60 company reports. He has a degree in chemistry and a Ph.D. in electrochemistry from the University of Newcastle upon Tyne (United Kingdom).

APPENDIX B

REFERENCES DISTRIBUTED TO EXPERT PANEL MEMBERS

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APPENDIX C
WORKSHOP AND FIELD TRIP SUMMARIES

SUMMARY
WORKSHOP ON SIGNIFICANT ISSUES AND AVAILABLE DATA
WASTE PACKAGE DEGRADATION
EXPERT ELICITATION PROJECT

March 25 and 26, 1997
The Orleans Hotel and Casino
Las Vegas, Nevada

The Workshop on Significant Issues and Available Data was the first of three workshops to be conducted for the Waste Package Degradation Expert Elicitation (WPDEE) project for Yucca Mountain, Nevada. The project is sponsored by the U.S. Department of Energy (DOE) and managed by Geomatrix Consultants. The purposes of this workshop were to (1) introduce the expert panel members to the WPDEE project, (2) summarize the significant issues regarding corrosion of waste packages and modeling of the process for the Total System Performance Assessment (TSPA), and (3) summarize the data sets related to these significant issues. The workshop involved one and one-half days of technical presentations and discussions of the data sets developed during the past several years to characterize waste package degradation in the proposed repository at Yucca Mountain. This workshop provided an opportunity for the expert panel members to gain a first-hand understanding of the data, the associated uncertainties, and the course of the rest of the project.

The overhead transparencies shown during this workshop are included with this summary (Attachment 1), along with brief summaries of the speakers' technical presentations.

DAY 1 - TUESDAY, MARCH 25

An introduction to the workshop and an overview of the WPDEE project were given by several members of the project's methodology development team (MDT). David Haught (DOE) welcomed workshop participants and observers on behalf of the DOE. Kevin Coppersmith (Geomatrix), the WPDEE project manager, presented a talk titled "Overview of Process and Guidelines for Workshops." He discussed the project objectives, organization, procedures, and schedule, including the steps for conducting the project and selecting the expert panel members. He then introduced the panel members: Dr. Peter L. Andresen (GE Corporate R&D); Dr. Joseph C. Farmer (Lawrence Livermore National Laboratory [LLNL]); Dr. Brenda J. Little (Naval Research Laboratory, Stennis Space Center); Dr. R. Daniel McCright (LLNL); Dr. John R. Scully (University of Virginia); and Dr. David W. Shoesmith (Atomic Energy of Canada Limited). The MDT, which plans and conducts project activities, consists of: Dr. Kevin J. Coppersmith (Geomatrix); Mr. David Haught (DOE); Dr. Joon H.

Lee (M&O/INTERA); Dr. Peter A. Morris (Applied Decision Analysis, Inc.); Ms. Martha Pendleton (M&O/Woodward-Clyde Federal Services); Dr. Roseanne C. Perman (Geomatrix); Dr. David Stahl (M&O/ Framatome Cogema Fuels); and Dr. Robert R. Youngs (Geomatrix).

Martha Pendleton (M&O/WCC) then presented a talk titled, "Overview of OCRWM, Viability Assessment and the Yucca Mountain Site." She discussed the key high-level waste regulations and requirements, the Yucca Mountain Site Characterization Plan, attributes of the waste containment and isolation strategy, the positive aspects and complicating features of the Yucca Mountain site, and future plans for the Yucca Mountain project.

D.G. McKenzie, III (M&O/MK, Manager for Subsurface Repository Design), then presented a talk titled, "Overview of Mined Geologic Disposal Systems (MGDS): Operations & Issues." His talk focused on the project design phases, physical characteristics of the potential repository and waste canister packages, and proposed operations, including repository closure. He focused on several key design issues: waste handling, remote operations, criticality control, thermal management, retrievability, and post-closure performance. Jerry McNeish (M&O/INTERA) gave the next presentation (substituting for Bob Andrews, M&O/INTERA). His talk, titled "Overview and Objectives of Total System Performance Assessment - Viability Assessment," focused on the overall objective of the Yucca Mountain project, and objectives of the Total System Performance Assessment (TSPA) for viability assessment (VA) that must be completed in 1998. The U.S. Congress plans to assess the viability of licensing and constructing a geologic repository at the Yucca Mountain site based on the TSPA-VA of the probable behavior of the proposed repository relative to overall system performance standards. Waste package degradation is a key aspect of waste isolation and thus of the TSPA-VA, and the expert panel convened for the WPDEE project has an important role in characterizing uncertainties involved in evaluating this issue.

David Stahl (M&O/Framatome Cogema Fuels [FCF]) then presented a talk titled, "Corrosion Modes Relevant to Waste Package Degradation in the Yucca Mountain Repository." He discussed the key elements of the waste containment and isolation strategy, the waste package environment at Yucca Mountain, materials and fabrication considerations in design of waste packages, and the status of the project's testing and modeling programs for corrosion.

Following a lunch break, Joon Lee (M&O/INTERA) continued the presentations with a talk titled, "Waste Package Degradation Modeling and Abstraction in Previous TSPAs and TSPA-VA." His discussions focused on performance measures for a waste package, the assumptions used for waste package degradation modeling and abstraction in previous TSPAs, the key issues and uncertainties to be resolved in a TSPA-VA, and the general scope of the elicitation process for the WPDEE project. Following the talk, members of the expert

panel and the MDT discussed the level of detail that will be needed for modeling; this issue will be discussed further at Workshop 2 in May.

The next presentation was given by Joel Atkins (M&O/INTERA). His talk, titled "Variability and Uncertainty in Waste Package Performance Assessment," focused on sources of uncertainty in the repository environment and in waste package modeling. He addressed issues of variability (in waste package performance and in environmental factors affecting degradation); uncertainty in the repository environment; and sources of model uncertainty, including conceptual and representational uncertainty.

Greg Gdowski (LLNL) gave the next talk: "Corrosion Allowance: Outer Barrier Corrosion Data Collection." He discussed the aqueous corrosion testing and the humid air corrosion testing being conducted on a variety of corrosion allowance and corrosion-resistant materials. Ajid Roy (M&O/FCF/LLNL) then described the results he has obtained from studies of electrochemical cyclic potentiodynamic polarization, electrochemical potentiostatic polarization, electrochemical galvanic corrosion, and fracture-mechanics-based stress corrosion cracking. Denny Jones (M&O/UNR) gave the final technical presentation of the day on "Microbiologically Influenced Corrosion Research Plan and Accomplishments." He summarized the research plan for the Yucca Mountain project and the results obtained to date.

The day concluded with a few short questions and comments from the workshop observers. Dr. Daniel Bullen, a new member of the U.S. Nuclear Waste Technical Review Board, commented briefly on several items, including the need to consider failure of juvenile waste packages.

DAY 2 - WEDNESDAY, MARCH 26

Joe Farmer (M&O/LLNL) gave the first presentation of the day by continuing the discussion on corrosion of corrosion-resistant inner barriers. His talk focused on published corrosion models, how corrosion modes are linked, the stochastic pitting model developed for the Yucca Mountain project, and reaction kinetics. He discussed the difficulties in coupling pitting models with crevice corrosion models, and reviewed the conclusions of the recent TSPA-VA waste package abstraction/testing workshop. Joanne Horn (M&O/LLNL) then presented a talk titled, "Microbially Induced Corrosion (MIC) Studies of Nuclear Waste Package Materials." She discussed the goals of the MIC research program for the Yucca Mountain project and briefly described the experiments being conducted to answer questions about MIC.

Following a short break, Narasi Sridhar (CNWRA) presented a talk titled, "Prediction of Waste Package Performance: Studies by NRC/CNWRA." He discussed the NRC's major program objectives with respect to the Yucca Mountain project, including independently analyzing key issues such as waste package performance and conducting confirmatory work. He described some of the research the CNWRA has conducted during the past nine years, including studies of localized corrosion processes, failure mechanisms, and determination of corrosion potential. He concluded that performance assessment models require a mechanistic base.

Kevin Coppersmith then led a short discussion with the expert panel on the availability and distribution of data sets relevant to the WPDEE project. He discussed the objectives and organization of future workshops, and reviewed the roles of project participants. The workshop concluded with a few short questions and comments from the observers.

**SUMMARY
WORKSHOP ON ALTERNATIVE MODELS
AND INTERPRETATIONS**

**WASTE PACKAGE DEGRADATION
EXPERT ELICITATION PROJECT**

**May 20-21, 1997
The Orleans Hotel and Casino
Las Vegas, Nevada**

The Workshop on Alternative Models and Interpretations was the second of three workshops to be conducted for the Waste Package Degradation Expert Elicitation (WPDEE) for the Yucca Mountain project, Nevada. The purposes of this workshop were to: (1) present and discuss alternative models for treating aspects of waste package degradation, including crevice and pitting corrosion, stress corrosion cracking, galvanic protection, and microbiologically influenced corrosion (MIC); (2) discuss the key uncertainties associated with assessing waste package degradation at the proposed Yucca Mountain repository; and (3) discuss the issues that will be addressed in the elicitations. The workshop involved two days of technical presentations and discussions about alternative models and interpretations. In addition to technical presentations by invited specialists, presentations were given by each of the six members of the expert panel.

Copies of the overhead transparencies shown during this workshop are included with this summary as Attachment 1.

DAY 1 - TUESDAY, MAY 20

An introduction to the workshop was given by Kevin Coppersmith (Geomatrix). He reviewed the objective of the WPDEE project: to characterize the uncertainties associated with the spatial and temporal distribution of degradation of the corrosion allowance and corrosion-resistant layers of the waste package. He reviewed the key issues to be considered and noted that the study is a technical evaluation of our present knowledge and uncertainty; it will say nothing, for example, about the adequacy or completeness of the experimental data base, or the suitability of Yucca Mountain as a potential repository. Dr. Coppersmith emphasized that panel members, having been selected by their peers, are in the best position to characterize uncertainties regarding key technical issues. Joon Lee (M&O/INTERA) gave the next talk, describing the issues to be addressed in the elicitations. He noted that the knowledge and experience of the expert panel will be the basis for the elicitations, and that the elicited models/products should be

in “abstracted form(s)” rather than detailed process-level models. Dr. Lee then reviewed models/abstractions for localized corrosion of the corrosion-resistant inner barrier, and for microbiologically influenced corrosion (MIC) of the carbon steel outer barrier and the corrosion-resistant inner barrier.

Three presentations on reference conditions followed the introductory talks. David Sassani (M&O/INTERA) presented the first talk: “The Near-Field Geochemical Environment in Total System Performance Assessment: Waste Package Degradation Focus.” He described the near-field conditions anticipated within the drifts, specifically aqueous phase, gas phase, solids and colloids, and how to define the phases that would react with the waste packages. He described the “ambient” system flux with respect to water, gas, and colloids; potential effects of thermal perturbation (including temperature dependencies and boiling/refluxing); and potential effects of introduced materials (variations in water and gas composition, solids evolution, and colloid generation). He then showed schematic diagrams of base-case evolution for temperature, air mass fraction, dissolved oxygen, dissolved carbonate, pH, and dissolved chloride, and discussed associated uncertainties and variability. He noted that these time-evolution relationships are being developed for the Yucca Mountain project now and, therefore, are at a preliminary stage.

R. Daniel McCright (M&O/LLNL) gave the next presentation: “Alloy Selection Issues.” He gave a brief history of waste package materials studied for the Yucca Mountain project, and reviewed the activities aimed at selecting the advanced conceptual design (ACD) for the waste package container. In the ACD activity, weighting factors were developed for 34 selection criteria; materials performance topics were assigned 70% weight; fabricability, cost, and other engineering topics were assigned 30% weight. Dr. McCright then reviewed the candidate materials, and described how efforts in testing and modeling provide support for materials selection and performance prediction for the waste package. David Stahl (M&O/FCF) discussed reference conditions that the WPDEE panel should assume in the proposed repository. He presented preliminary temperature and humidity profiles for a 100,000-year period, and discussed water seepage flux, water chemistry, mechanical loads, radiation/waste package shielding, and container fabrication and assembly issues. He then described waste package design goals.

Two talks were presented on the topic, “Relevant Experience—Canada.” David Shoesmith (AECL, WPDEE panel member) discussed the proposed repository in Canada, outlining the environmental conditions and proposed design considerations (e.g., use of a clay backfill to enhance oxygen removal from the vault; waste package to withstand extreme pressure conditions from a possible future episode of glaciation). He described the evolution in waste vault conditions over time and the expected effect on corrosion processes. The potential corrosion scenarios for titanium containers and copper containers were outlined. An important conclusion of the presentation was that the damage functions Canadian researchers have

developed for a variety of materials and aspects of corrosion (e.g., crevice corrosion) tend to have similar shapes. Simcha Stroes-Gascoyne (AECL) then gave a presentation titled, "Predicting the Effects of Microbial Activity on the Corrosion of Copper Nuclear Waste Disposal Containers." She described Canadian microbial and corrosion studies related to MIC, specifically describing the various tests conducted and their results.

Brenda Little (Naval Research Laboratory) then gave an overview of microbiologically influenced corrosion. She reviewed types of bacteria and described the biofilms that bacteria create, a research area that is her particular interest. Dr. Little described several case studies of MIC, which produces localized corrosion, depending on environmental and material properties. She concluded that biofilms probably will not occur in the potential repository at Yucca Mountain, but the amount of water present and the nutrient availability will be critical controls.

Peter Andresen (GE Corporate R&D) presented the first of four talks on modeling issues related to waste package degradation. His topic, "Stress Corrosion Cracking (SCC)—Initiation and Growth," incorporated the insights he has gained from working on light-water reactors. He stated that stress, material, and environment are interdependent variables that control the rate of SCC. He discussed these variables and their effects on SCC initiation and growth. John Scully (University of Virginia) presented the next talk: "An Assessment of Uncertainties in Current Approaches and Alternatives for Addressing the Effects of Pitting and Crevice Corrosion on Containment of Nuclear Waste." Corrosion-resistant materials (CRM) for inner barriers were the focus of his talk. He emphasized that the CRM corrosion control strategy and materials selection should guide experimental and modeling approaches for localized corrosion. Specifically, he identified two strategies: (1) define and identify "windows of susceptibility" relating the potential for corrosion to environmental conditions as a function of alloy, and (2) develop an assessment of the rate of corrosion (e.g., damage functions), taking into account pit/crevice initiation and stifling probabilities.

DAY 2 - WEDNESDAY, MAY 21

Presentations on modeling issues continued on the second day of the workshop. David Shoesmith gave a talk titled, "Container Corrosion Scenarios—Electrochemical Procedures to Develop Container Corrosion Models." He noted the need to develop a probability distribution for pit initiation, and how maximum depth and stifling rules can be obtained from growth laws. A major point of his talk was that criteria can be developed for repassivation, and that electrochemical procedures can be developed and adjusted to vault conditions and used to develop damage curves. Narasi Saridhar (CNWRA) gave the next talk: "Chloride Concentration in the Near Field and Its Effect on Waste Package Performance." The bulk chloride concentration at Yucca Mountain is expected to be relatively constant over time, but concentrations on the waste package surfaces will vary because of evaporation and refluxing and localized corrosion.

Modeling studies indicate that localized corrosion results in an increase in chloride concentration and a decrease in the pH in pits and crevices. A major conclusion of the presentation was that a wide range of chloride concentrations should be considered in modeling waste package failure.

“Modeling Inner Barrier Corrosion” was the next talk, presented by Joe Farmer (LLNL). He discussed alternative corrosion models, including a pitting model based on stochastic probability theory, a pitting model based on heterogeneous reaction theory, and a crevice model. He concluded that modeling the performance of a wet inner barrier is possible by integrating approaches published by various researchers, but a major source of uncertainty will be the corrosion scenario (e.g., environmental conditions).

Three talks were given on the topic of Galvanic Protection and Electrochemical Modeling. John Scully gave the first talk, reviewing factors that govern galvanic interactions (such as solution conductivity, geometry and electrochemical characteristics of anode and cathode) and how these factors govern current and potential galvanic distributions. He discussed examples of modeling potential distribution and its use to predict susceptibility to localized corrosion. Joe Payer (Case Western University) discussed the chemical and electrochemical interactions between waste package barriers. He described galvanic action, and focused on the area effect or “throwing power” of galvanic protection. For the waste packages in the potential repository, the galvanic effect likely will extend approximately a few millimeters. He discussed data needs and modeling approaches and described morphologies of corrosion.

Alberto Sagues (University of South Florida) gave the final talk on electrochemical modeling issues (Dr. Sagues is also a Nuclear Waste Technical Review Board Member, but stated clearly that he was speaking at the workshop as a faculty member of the university and not as a representative of the board). He discussed contact-resistance galvanic protection, mixed-metal crevice corrosion under various conditions, and the implications of shared potential. He stressed the importance of focusing on observed conditions and not on assumed “worst-case” conditions that have never been observed (e.g., deep corrosion pits in superalloys). Dr. Sagues also briefly discussed his experience with concrete culverts and the relevance to the proposed repository.

Kevin Coppersmith asked for comments from observers. Bill Halsey (LLNL) stressed a need to distinguish between variability and uncertainty—Dr. Coppersmith stated that this issue would be reviewed with the panel during the elicitation training at WPDEE Workshop 3. Dan Bullen stated a concern with identifying near-field environmental conditions, including oxygen potential near the waste packages, and the importance of defining realistic critical failure criteria. After additional discussion, Dr. Coppersmith thanked the workshop participants, and the meeting was adjourned.

SUMMARY
WORKSHOP ON PRELIMINARY INTERPRETATIONS

WASTE PACKAGE DEGRADATION
EXPERT ELICITATION PROJECT

June 10 and 11, 1997
Embassy Suites - South San Francisco

The Workshop on Preliminary Interpretations was the last of three workshops to be conducted for the Waste Package Degradation Expert Elicitation (WPDEE) for the Yucca Mountain project, Nevada. The purposes of this workshop were to (1) provide an opportunity for the experts to present and discuss their preliminary interpretations and uncertainties regarding key issues in waste package degradation processes, (2) provide feedback to the experts regarding their preliminary interpretations prior to the elicitation sessions, and (3) provide elicitation training to the experts to help them quantify their uncertainties.

DAY 1 - TUESDAY, JUNE 10, 1997

Kevin Coppersmith (Geomatrix) began by describing the purpose and approach of the workshop, stating that this was a working meeting, with preliminary ideas that would be subject to change, free-form discussion of alternative views, and hand-drawn graphics. Most importantly, he stated that elicitation of expert judgments had begun and would continue until the elicitation documentation is finalized in early August of 1997. Dr. Coppersmith then reviewed the questions to be addressed in the WPDEE elicitation interviews and the schedule for the key activities during the remainder of the project.

Peter Morris (Applied Decision Analysis and MDT member) introduced probability assessment to prepare the experts for the upcoming elicitation interviews. His talk focused on using probability to quantify uncertainty, representing and manipulating probabilities, and assessing probabilities.

Joon Lee (M&O/INTERA) gave the first of his two talks on "Key Technical Issues and Uncertainties to be Addressed in Elicitations." He described performance measures for the waste package: waste containment, and controlled/gradual release of radionuclides. He showed example time-history plots of waste package failure and pit depth distributions. Dr. Lee had viewgraphs describing the five primary issues to be covered in the workshop, and it was decided to use these to introduce each of the five issues.

Dr. Lee gave the next talk: "Modeling Localized Corrosion of Carbon Steel Outer Barrier in TSPA-1995." He described the pitting factor approach employed in TSPA-1995, and showed plots of general corrosion depth vs time for corrosion allowance materials and predicted pit depth distribution under humid-air, in water, and under constant aqueous conditions. His concluding remarks indicated that the pitting depth factor approach used in TSPA-1995 may have been too conservative. This opinion was shared by the panel members, and there was a general discussion of the value in using the term "safety factor," the use of growth laws, and the issue of stifling.

Dr. Coppersmith reviewed the questions associated with Dr. Lee's Primary Issue I - Corrosion of Carbon Steel Outer Barrier and Primary Issue II - Pitting Factor for "Localized Corrosion" of Carbon Steel Outer Barrier. Since these topics had been covered by Dr. Lee in the previous two talks, there was little discussion. The discussion of Primary Issue III - Corrosion of Alternative Corrosion Allowance Material (Monel 400) then began. Dan McCright (M&O/Livermore National Laboratory) gave the first talk, beginning with a description of reasonable alternative materials to carbon steel for the outer barrier and their relative costs (Monel 400 is a relatively expensive candidate material). He discussed the advantages and disadvantages of Monel 400, and showed results of general corrosion tests. David Shoesmith gave the next talk on Monel 400. He described expected advantages and the expected susceptibilities to pitting, crevice corrosion, and microbiologically induced corrosion under various environmental conditions. After describing various studies conducted on this alloy, Dr. Shoesmith concluded that many uncertainties exist in assessing the performance of Monel 400, particularly given the small data base. If a material is to be sacrificed, he stated that it should be a relatively inexpensive one.

Daniel Bullen (University of Iowa/Nuclear Waste Technical Review Board) described some experiments he and a student performed on Monel 400. A general discussion of the potential environmental conditions in the repository followed. Joe Farmer suggested several topics that he would like the elicitations to cover; he gave a list of these topics to Dr. Coppersmith, who said he would type it for discussion on the second day of the workshop.

DAY 2 - WEDNESDAY, JUNE 11

This day began with a session on pitting and crevice corrosion of the candidate corrosion-resistant materials (CRM). Dr. Coppersmith reviewed the elicitation questions for this issue. John Scully gave the first presentation on the topic, and began by reviewing the factors that would influence each probability. He discussed how probabilities would differ with geologic time or environmental conditions, the probability of stifling, and the rate of pitting/crevice corrosion as a function of various parameters. Dan McCright spoke briefly on how limiting currents stifle cathodic reactions.

The next session was on microbiologically influenced corrosion (MIC). Brenda Little began by noting the difference between survival of microbes and growth of the microbes in a given environment. She reviewed the tolerance of various microbes to extreme environmental conditions, and the most favorable environments for growth. Some of the results of the Swiss and Canadian repository programs were discussed, and the need for mass balance calculations for essential elements (e.g., C, N, P, S) was stressed. Dr. Little concluded that if free water (or standing water) exists in the potential Yucca Mountain repository, there will be microbial activity, and biofilms will form.

Dr. Coppersmith reviewed the fifth key issue: "Representation of Uncertainty and Variability in Stochastic Waste Package Degradation Modeling." Dr. Shoesmith began by reviewing the uncertainties in environmental conditions and their effects on oxygen availability, formation and redissolution of deposits, salinity, and other factors. He reviewed the potential modes of corrosion, their relationship to humid-air and aqueous conditions, and the associated uncertainties. Peter Andresen next discussed variability, time evolution, and uncertainty. He described local environment and package fabrication as the most critical issues; he stated that the uncertainty in the local environment dominates other issues. He discussed the properties of candidate materials and experimental data on corrosion rates.

Dr. Andresen began the session on welds with a talk titled "Issues in Welding and Coating." He reviewed various issues related to welding and made recommendations on how welding should be accomplished. He also discussed issues of stress corrosion cracking.

In the final session of the workshop, on ceramic coatings, Dr. Scully described probable candidate materials and their expected behaviors.

A discussion of Joe Farmer's list of suggested topics for the elicitation followed. Some of the topics were addressed in Day 2 of the workshop; others were deemed to need input from other participants in the Yucca Mountain project.

The workshop was opened to comments from observers. The importance of TSPA-VA was discussed. Dr. Coppersmith adjourned the meeting.

APPENDIX D
ELICITATION INTERVIEW SUMMARIES

ELICITATION SUMMARY

PETER L. ANDRESEN

OVERVIEW OF WASTE PACKAGE CORROSION PROCESSES

The spatial and time evolution of the environment and the associated corrosion degradation mechanisms are complex and inter-dependent. Evaluating possible responses is made substantially more complex because engineering data, experience, and intuition are predominantly based on time scales of <10 years, not >1000 years. Corrosion phenomena are complex and very sensitive to "subtleties" of environment, stresses, and metallurgical chemistry and processing. However these complexities and uncertainties are, in this case, overwhelmed by the lack of detailed analyses and experiments that define the likely or possible nature of the "near field environment" or, more importantly, the local environments that form on a waste package. This increases the speculation content of the assessments, creates high levels of uncertainties in estimating corrosion response, and drives engineering judgment toward materials and techniques of construction which would likely be deemed excessively conservative if more knowledge of the environment existed.

The elicitation process and summaries have had to deal with "work in progress", such as the lack of a detailed description of the hydrology (this elicitation will occur later), multiple materials (e.g., Alloy 825, Alloy 625, and various Hastelloy C alloys for the CRM; and carbon steel and Monel 400 for the CAM), incomplete information on fabrication (e.g., welding procedures and resulting microstructures and residual stresses, and characteristics of the ceramic coating) and design (e.g., possible use of a drip shield, and the uncertain nature of the concrete liner composition and its likely life), variations in estimates for the temperature - humidity - water availability profile vs. time, etc. Many of these issues and associated design judgments are complex and would benefit from close interaction among specialists in various fields, especially hydrology, corrosion, and container design / fabrication.

The trajectory of the repository conditions vs. time will clearly involve a shift from a period of moderate temperature and relatively low humidity (e.g., 200 - 140 C, <50% RH), to a period of lower temperature and higher humidity (e.g., 105 - 140 C, >60% RH), to a period of high humidity (e.g., 80 - 105 C, >85% RH), to a period of episodic wetting from dripping and/or condensation, which could range from 30 C to >100C. Major areas of speculation include:

- the role of and range of conditions that give rise to atmospheric gas exclusion, which might affect the repository for thousands of years, potentially in the dry oxidation, humid air corrosion, and aqueous film - dripping - "pooled water" corrosion via its effects on O₂ availability (which affects corrosion potential) and N₂ availability (which affects radiolysis by permitting "fixing" N₂ to, e.g., nitrites and nitrates, which can affect corrosion potential, pH, and have a specific role in the degradation of some, e.g., Cu, alloys).
- the likelihood and periodicity of water dripping on waste packages, which can occur from periods of high water influx to the mountain, or from refluxing of water as it is heated / boiled by the thermal flux from the waste packages then condenses elsewhere in the mountain. Because fracture flow can be the dominant mechanism for water transport in rock, it is unclear whether dripping can be excluded even under the initial, hot (e.g., 200 C) repository conditions—although clearly dripping will be more likely at lower temperatures. The capillary properties of the rock near the drifts, tendency for thermal expansion of the rock (and perhaps some closing of the fracture "gaps"), the concrete liner (and its degradation vs. time), and any (as yet undecided) use of a local drip shield can substantially affect the likelihood of dripping, at least early in the life of the repository.
- the nature of the local environment, should dripping occur. The time evolution of the water composition/pH reaching the repository is not well defined, including for refluxing conditions, as water travels through the concrete liner, as water falls on the package and boiling / evaporation occurs, and as general and localized corrosion processes occur (which affect the local chemistry). While the mixture of anions likely always present will make acidic shifts (e.g., below pH = 5) more difficult, and therefore reduce the prospects of accelerated corrosion processes (the rate of general corrosion and likelihood of localized corrosion can increase rapidly at lower pH), at this point there is insufficient information to exclude the possibility of low pHs.

Atmospheric Gas Exclusion. The modes and rates of corrosion during the life of the repository system are extremely sensitive to the profiles vs. time of temperature, relative humidity, water dripping, nominal water composition and evaporative concentration, and oxygen conditions within the system. During the early period of the repository, high temperature / thermal flux from the waste will drive off water from the repository rock, causing boiling. The volume expansion of liquid water to vapor is very large (e.g., between 650 - 1200X, depending on temperature); and this vapor will substantially mix with the gases (i.e., O₂, N₂, and CO₂) initially in the repository, and (since the repository will not pressurize) gases must move out of the repository, causing dilution of these initial gases. If perfect mixing of the gases is assumed to occur, and the flux of gases (including water vapor) by convection out of the repository (from boiling and mixing) exceeds the natural permeation (diffusion) rate of gases into the repository (the rate at which the repository "breathes"), then the O₂ (or N₂ or CO₂) level in the repository will decrease to e^{-v} , where "v" is the number of "volume equivalents" of the repository gas space that has been created by water boiling. Based on reasonable assumptions, this should lead to a long period of atmospheric gas exclusion, likely extending to the time required for the package to cool to about 100 C.

The lack of O₂ (and N₂ and CO₂) availability during the thermally-elevated period may have the most pronounced influence on the potential for and rates of corrosion for a substantial period of time. As a result of reduced O₂ and N₂ (for radiolysis), the early period of corrosion may be significantly lowered.

CAM Corrosion. Corrosion of a carbon steel corrosion allowance material (CAM) is very sensitive to the temperature, relative humidity, water dripping, nominal water composition and evaporative concentration, and oxygen conditions within the system vs. time. With decreasing temperatures (~150 - 100 C) and increasing relative humidity (~40 - 60%), and perhaps increasing possibility for O₂ transport into the repository (the importance of oxygen is difficult to assess because it is a common feature of most studies at <150 C, e.g., on atmospheric corrosion), enhanced dry oxidation of the carbon steel corrosion allowance material (CAM) will occur. Initially a relatively thin, tenacious oxide film will develop, rather than a thicker scale that is observed at much higher temperatures under dry oxidation

conditions; thus, oxidation rates should initially be quite slow. It is difficult to assess the prospects for oxide film spallation (oxide debonding from lifting or flaking), which is controlled by the oxide thickness and the volume expansion as the oxide is formed (Pilling-Bedworth ratio). For short term exposure (years), this should not be a large concern, but after dozens and hundreds of years, it is hard to dismiss. Spallation locally "resets" the corrosion "clock" to time zero, so that much higher corrosion rates will occur, which again slowly decay with time. Spallation can be greatly enhanced by alternate wet / dry conditions, as might be expected in most dripping scenarios.

The corrosion rate of the CAM would then increase through processes of humid air corrosion, thin film aqueous corrosion, aqueous corrosion in "pooled" regions of perhaps very concentrated chemistry (if there are drips), and corrosion under the remote possibility of total immersion. However, these processes need to be considered in light of the availability of water, dissolved species, and oxygen (perhaps best expressed as a time-history of oxygen partial pressures) to properly model the corrosion rates.

The influence of pH on the corrosion of the CAM is very important for estimating the expected corrosion modes. Under relatively neutral pH conditions (pH at temperature of 4 - 10, see Uhlig, page 96), general corrosion (exhibiting some surface irregularities) of the carbon steel is expected. Pitting of carbon steel in neutral Cl⁻ has been reported, although its likelihood greatly increases for pHs above 10 - 11, which could occur from dripping through the concrete and subsequent boiling / evaporation. The mix of dissolved species plays a large role in both general corrosion and pitting of carbon steel, and not only because they affect pH.

A potentially important issue is that the onset of high pH conditions might be delayed if there is little water coming through the concrete and/or little oxygen is present. If drips are believed to be possible, it is important to know the rate and frequency of dripping (e.g., constant dripping on the waste package that might prevent concentrated chemistries from forming - vs.- regular dripping where the solution becomes saturated - vs. - very intermittent wetting / drying that might lead to partially hydrated salt films) and the spatial distribution of

dripping conditions. Drips are expected to have their greatest effect on the upper surface where drips hit and could pool, at the base of the package where water accumulates and may drip off of the package, and where the package may be in contact with the invert or the support pedestals. Depending on the surface temperature of the waste package and the flow of water (evaporation vs. flowing around and off the package), the drips may lead to saturated chemistries and deposited salts that can enhance corrosion. The presence of specific anions in the drips can also enhance the CAM corrosion rate.

Gap Between CAM and CRM—Shrink Fit. A potentially important consideration is the gap or crevice that will exist between the CAM outer barrier and the corrosion resistant material (CRM) inner barrier. If a shrink fit or other tight fit is pursued to help maintain electrical contact between the two barriers (e.g., for galvanic protection), it is expected that the gap between the two barriers will still fill with water from capillary action once the CAM is penetrated. If the gap is fairly large, water will tend to flow to the bottom. Oxygen should be fully consumed in the creviced region, and corrosion will proceed at a relatively low rate (unless acidic conditions develop, since corrosion of carbon steel increases rapidly below a pH of 4). However, in any tight fit design the volume expansion associated with the formation of iron oxide will likely produce large wedging forces that are capable of producing significant deformation and buckling of the inner package. Stresses cannot be assumed to be compressive in all areas, and this, among other sources of stress, could lead to stress corrosion cracking or perhaps even mechanical failure.

Note that in a "wide-gap" design, the contact of the bottom of the CAM with the CRM should afford electrical conductivity (the oxides of iron and nickel alloys are reasonably good semi-conductors), at least providing the opportunity for some galvanic protection (if any does exist), subject to the limitation of the size of gap between the upper surfaces of the containers. Even in a "shrink fit" design, the occasional metal-to-metal contact points that are formed by the shrink fit would likely be oxidized soon after water ingress to the gap occurred; thus, subsequent electrical conduction would rely on an oxide semiconduction path.

Corrosion of the CRM. The primary factors that control the initiation period and corrosion rate of the CRM are the temperature, pH, oxygen, Cl⁻, and nature of the corrosion of the CAM. Because of the presence of mixed anions, general corrosion of the CAM may not produce acidic conditions (e.g., pH <4) as corrosion penetrates to the interface with the CRM. The likelihood of an acidic pH being produced is higher at the interface (crevice) between the inner and outer barriers, or in high-aspect ratio pits in the CAM. This could produce a localized pH of 3 or lower (depending on the mix of anions and the temperature effect of the iron ion hydrolysis reaction, e.g., $\text{Fe}^{2+} + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_2 + 2\text{H}^+$). With appropriate assessments of the temperature, oxygen, and Cl⁻ conditions, the corrosion rate of the CRM can be estimated from the available experimental data, although uncertainties in the (low) general corrosion rate (passive current density) of the CRM complicate this. Note that at a pH of about <3 and with significant chloride, materials like Alloy 625 and perhaps even Hastelloy C276 could readily pit at the temperatures of interest (e.g., 50 - 105 C). Selection of more resistant alloys, like Hastelloy C22 or C2000 is advisable because they help eliminate this concern, although proof that the "threshold" conditions of pH, chloride, oxygen and temperature will not be approached could make Hastelloy C276 or even Alloy 625 stronger candidates. Careful evaluation of their general corrosion rates under ranges of relevant conditions is needed since the multi-thousand year lifetime that is desired translates to very low general corrosion rates (a 1 mil per year corrosion rate, generally considered excellent, results in total failure in <1000 years).

Stress Corrosion Cracking. The potential for stress corrosion cracking (SCC) should be carefully evaluated by looking at the environments that might form. Because SCC can occur at very low rates, assessing its potential is somewhat analogous to estimating the general corrosion rate of highly resistant materials. The experimental data suggest that SCC is relatively rare at temperatures below about 125 C but, because of the long time periods considered for the repository, the potential for SCC must be considered. Most of the literature involves accelerated or screening tests which only identify conditions where SCC susceptibility is severe. The only significant attempts to characterize the very low crack growth rates that might be remotely relevant to the long lifetimes needed for radioactive waste are those related to light water reactor environments. In alloys like stainless steel and

Alloy 600, SCC growth rates of concern have been reported at 25 to 200 C, although crack initiation is difficult. Of course, despite their "nickel-base" commonality, the behavior of Alloy 600 and Hastelloy C can not be assumed to be similar.

All sources of stress need to be identified and minimized or eliminated, including weld residual stresses on the waste package, possible shrink-fit between the inner and outer barriers, volume expansion due to oxidation of the CAM in the gap between the CAM and CRM, contacts with the pedestals, cap welds, etc.

Ceramic Coating. In my judgment it is unlikely that a porosity- and crack-free ceramic coating can be applied over a large engineering surface (especially one that is heavy and must be extensively handled and implaced). I believe the best possible ceramic coating will have at least dozens of locations on the waste package where water could penetrate to the CAM, causing corrosion. The large volume expansion of the iron oxide will quickly induce spalling of the ceramic coating, eliminating its value. This could occur within months or years of exposure to dripping or high humidity, and could render a substantial fraction of the package surface unprotected within years or tens of years. Given the enormous cost of the process, the severe handling complications that would result, and the limited benefits, I don't believe this is a worthwhile approach to pursue.

Welding Considerations. Welding of materials like carbon steel, Monel, and Hastelloy C22 should pose no engineering challenge (apart from the size and length of all of the welds that are required). However, welds are responsible for a large fraction of the cracking in structural components. Welding produces high residual stresses and can make the metallurgical microstructure more susceptible to cracking. Narrow gap (or "fine line") techniques should be strongly considered, and should be coupled with a full stress relief anneal for the container fabrication welds. Techniques for accomplishing some stress relief on the final closure weld of the CRM should also be considered, because it may be hard to ensure that this closure weld will not be exposed to water once the CAM is penetrated.

CORROSION OF CARBON STEEL OUTER BARRIER

Introduction. Corrosion of carbon steel in water is moderately complex. At room temperature, the corrosion of carbon steel is approximately linear with dissolved oxygen, at least up to values somewhat above air saturation (about 9 ppm), at which point the corrosion rate decreases. This "threshold" level (at which increasing oxygen produces decreasing corrosion) is higher as temperature of Cl^- is increased. In neutral, deaerated water at 25 C, the corrosion rate is about 0.2 mils/y, about 10 - 100X lower than in aerated solutions. At pHs below 4, or in moderately concentrated Cl^- (like sea water), the corrosion rate of carbon steel increases greatly, although with increasing Cl^- the corrosion rate drops off a little.

When oxygen is present the corrosion rate increases about 2X every 30 C, although above 80 C the corrosion rate decreases because the dissolved oxygen levels drops (in open systems). When hydrogen evolution controls corrosion, the corrosion rate doubles as quickly as every 10 C (e.g., this is true in HCl). The general corrosion rate is not cathodically limited in the neutral range (pH 4 - 10) at 25 C under full immersion conditions, although cathodic availability certainly can influence pitting and pit distributions. The corrosion rate can drop dramatically if CaCO_3 is present as a result of the formation of a highly protective film of CaCO_3 (in drinking water this is measured as a "saturation index").

Alkali salts (Li/Na/K combined with Cl/I/Br/ SO_4) have a broadly similar effect of the general corrosion of carbon steel, although if hydrolysis occurs to form acid or base, substantial differences are observed. Under humid air conditions, the presence of hygroscopic salts is important, and the critical relative humidity level for the onset of "atmospheric corrosion" ranges from 93% for Na_2SO_4 , to about 80% for KCl, NaCl, and NaNO_3 , to about 60% for NaNO_2 and NaBr, to 43% for NaI, and to 15% for LiCl. The presence of impurities contributes very strongly, both in instantaneous corrosion rate, and the rate vs. time (i.e., it can be linear rather than parabolic).

"Atmospheric gas exclusion". Given the elevated temperatures and low relative humidities during the early period of the repository lifetime, the corrosion (oxidation) rate will be quite

low and principally controlled by temperature and the concentration of water, O_2 and perhaps CO_2 . During the period when the temperature in the repository is above about 100 C, a boiling / evaporation front will exist in the rock at some distance from the drifts. The heat flux will produce evaporation of water, a substantial fraction of which will move into the repository space (the liquid water tends to impede its path away from the drifts. The water vapor will mix with any non-condensable gases (such as O_2 , N_2 and CO_2) and, since the repository will not pressurize, this mixture will move by convection through pores and fractures in the rock out of the mountain. Since the amount of water vapor that is expected to be produced by the heat flux is estimated to represent more than thousands of times the volume of the repository volume, the initial non-condensable gases will be diluted and convected out of the repository (if perfect mixing of evaporated water and the gases in the repository are assumed, then the remaining fraction of an initial gas can be expressed as e^{-v} , where "v" the number of repository volume equivalents of water vapor that has been produced).

That is, if the repository is 10^7 m^3 of gas space, by the time this volume of water vapor has been created by boiling, the O_2 level will decrease down to the fraction of e^{-1} , or to 0.37 of its original (20.9% in air) value; by the time 3 volumes have been created, the O_2 will be 0.049 of its original value, by the time 10 volumes have been created (10^8 m^3 of water vapor), the O_2 will be 4.5×10^{-5} of its original value, and by 100 volumes, the O_2 level will be reduced to 3.8×10^{-44} of its original value. Precisely what fraction of the water vapor that is produced ends up condensing before it exists the mountain is difficult for me to estimate, but the boiling process will drive the condensation point well away from the repository open space, and then it must be determined whether the "back diffusion" of O_2 and CO_2 will be faster than the convection produced by constant boiling / evaporation of water, at least during the first thousand or so years.

One must also factor in changes in atmospheric pressure (if the mountain is assume to be homogeneous, then this should simply move the "boundary condition" for atmospheric concentrations of gases from the surface of the mountain, to a distance part way into the mountain), and the possibility of fracture flow of water (since water move more slowly than

gases, and doesn't carry much dissolved gas with it, this shouldn't contribute consequentially to the influx of atmospheric gases) and gases (this could affect the "breathing" of the mountain a lot, and thus the likelihood that "atmospheric gas exclusion" would occur over long periods of time).

As long as the water boiling / evaporation rate remains greater than the "breathing" (gas transport) rate into the mountain, the concentration of species like O_2 , N_2 and CO_2 should remain very low. This scenario is complicated by considering the condensation of the boiled / evaporated water at some point beyond the boiling / evaporation front in the rock, but the action of water evaporation (as opposed to simple migration of the water front away from the repository) would appear to ensure a net flux of water (vapor) out of the mountain, or at least well beyond the boiling / evaporation front in the rock. This should ensure that the "creation / mixing / transport" of gases from the repository required by this "atmospheric gas exclusion" concept is achieved.

Conceptually, to achieve and maintain O_2 exclusion conditions, it is necessary that any oxygen that would otherwise tend to enter the mountain by diffusion in fractures in the rock would be overwhelmed by convection associated with water boiling / evaporation. This is analogous to having a long, small diameter tube between two chambers, one filled with N_2 and one with O_2 . If the N_2 flow rate is above some small value (depending on how long and how small the diameter of the tube is), no O_2 will be able to back-diffuse up the N_2 convection stream because convection overwhelms Brownian motion that is responsible for diffusion. This phenomenon is used, e.g., to produce ultra high vacuum in space, because the residual gases in space cannot diffuse into the region behind a baffle / shield when the space craft is traveling at many thousands of mile per hour. Similarly, oxygen should not diffuse into the drifts as long as boiling continues at an adequate rate.

Even as temperatures fall to below the boiling point, the availability of oxygen (i.e., the dissolved oxygen level in water) will be limited by the partial pressure of water vapor. For example, at 95 C, the vapor pressure of water is 0.83 atm, leaving 0.17 atm for dissolved gases (thus, the oxygen partial pressure is 0.036 atm assuming the air maintains the same

composition as atmospheric air of 20.9% O₂). Compared to about 9 ppm dissolved oxygen in pure water at 25 C, its level is only about 0.9 ppm at 95 C (note that both the partial pressure of water vapor and the Henry's Law constant change with temperature). Likewise, at 80 C the saturated pressure of water vapor is 0.47 atm leaving 0.53 atm for air (the oxygen partial pressure is 0.11 atm, and the dissolved oxygen level in water is 2.8 ppm).

Because of the importance of this issue and the boiling / evaporation of water vs. the "breathing" rate of the mountain, the associated time-history of oxygen partial pressures during the lifetime of the repository should be assessed in detail. This information can then be taken into account in assessing the corrosion mechanisms and rates for the carbon steel. I suspect that a relatively long period of depleted O₂ and CO₂ conditions will delay the onset of dry oxidation of the CAM, slow the rate of aqueous corrosion, delay degradation of the concrete liner by carbonation, and perhaps also delay the onset of high-pH dripping conditions. In the absence of any explicit incorporation of this information into the corrosion model, it would certainly be conservative to consider only the temperature and relative humidity thresholds for controlling corrosion processes of the CAM.

Specific CAM corrosion issues. Under the initial temperature, humidity, and oxygen conditions in the repository, little initial corrosion ("dry oxidation") of the carbon steel would be expected. I would expect the oxide film that forms initially to be fairly thin and adherent. With sufficient time (e.g., >10 years) the oxide layer will thicken, and the possibility of spalling, which will cause increased corrosion, can't be dismissed. Spallation would be enhanced significantly by dripping (alternate wet / dry cycles). As the temperature drops, the "dry oxidation" will decrease, although the tendency for dripping will increase (and thereby the net corrosion rate could increase).

As the relative humidity rises to above about 60% (see earlier discussion on critical relative humidity as a function of the presence of specific salts), a more heavily hydrated film and perhaps local capillary condensation in the outer layer of the oxide could develop and humid air corrosion processes will initiate. As the relative humidity approaches 85 - 90%, a water film will develop and there will be more significant anode-cathode coupling. Because there

is heat flux out of the package, I would consider it to be conservative to assume that aqueous corrosion processes begin at a relative humidity threshold of 85%. Depending on the temperatures, boiling / evaporation conditions will continue to play a role below 100 C, leading potentially to oxygen-depleted conditions. In the case of dripping conditions, local "immersion" conditions will prevail from persistent drips and/or pooled water on the surface of the waste package.

In terms of temperature thresholds for corrosion mechanisms of the CAM, it is reasonable to assume that at temperatures above 100 C, any water in contact with the waste package will be deaerated due to boiling. Below 100 C, the relative humidity thresholds will define the corrosion behavior of the carbon steel. A smooth normal distribution between 65 and 75% RH can be used to define the uncertainty in the threshold between dry oxidation and humid air corrosion; and a similar distribution between 85 and 95% to define the threshold between humid air and aqueous (thick water film) conditions. Local "immersion" conditions are expected in the case of drips or pooled water at relative humidity of 100%.

Assuming pH 4 - 10, non-dripping conditions, and temperatures below 100 C, the corrosion of the carbon steel outer barrier will occur as general corrosion which is somewhat non-uniform on the surface. The "roughness" of the general corrosion front will likely differ between humid air and aqueous conditions, with the expectation that the front will be more uniform in the humid air condition than the aqueous. To express this assessment, the ratio of the average depth of the corrosion front to the maximum depth (i.e., the "surface roughness factor") for the humid air and aqueous cases is estimated below. The expected ratio for the humid air case is 1.1 and for the aqueous case is 1.5. The uncertainty in the assessment is represented by a normal distribution centered on these best estimates (mean and medians) with the ± 2 sigma values also indicated. The basis for expecting a more irregular pattern of corrosion damage for aqueous exposure is that there is a much greater opportunity for coupling of anodic and cathodic areas, for metallurgical inhomogeneities to play a role, and for water to pool in random areas (causing preferential corrosion).

<u>Humid Air Case</u>	<u>(Ave/Max) Roughness Factor</u>
+ 2 σ	1.2
Mean, median	1.1
- 2 σ	1.0

<u>Aqueous Case</u>	<u>(Ave/Max) Roughness Factor</u>
+2 σ	2
Mean, median	1.5
-2 σ	1.0

As free water passes through the concrete as drips, the potential exists for high pH (~9 - 10) conditions, perhaps higher if concentration from evaporation occurs. The potential for drips is important—particularly the drip rate and frequency, which can range from continuous to intermittent to very infrequent. The evaluation of the effect of drips should include not only the number of waste packages that might experience drips, but also the spatial distribution of drips on individual waste packages. I would divide the spatial distribution into the top, sides, and bottom of the waste package. The top could be defined as the upper 30 - 50 degree included angle of the package, with the angle likely growing to perhaps 90 degrees as corrosion occurs. The bottom is defined as the lower 20 - 30 degrees included angle, as well as the support pedestals, which are prone to trap water or promote capillary condensation. The bottom or sides may also become important as the pedestals holding the package degrade and the package eventually ends up lying directly on the invert. In this case water that drips on the surface may evaporate or accumulate at the bottom of the package, or perhaps at longer times be wicked up through the invert (although it is more likely that the invert will help draw water away).

A key issue associated with drips is the degree to which they might lead to saturated chemistries. Until the waste package cools to near room temperatures (below ~30 C), drips will continue to evaporate even at high relative humidities, leaving behind hydrated salt deposits and/or concentrated solutions. The degree to which this occurs is a function of the temperature: at temperatures of 100 C or greater, drips will quickly evaporate and leave behind salt deposits; at 100 to 75 C, saturated chemistries, or hydrated deposits because there will be little water (and potentially little O₂); at 75 to 45 C, there will still be evaporation,

with saturated chemistries (vs. hydrated deposits) more likely to form because of greater availability of water and O_2 ; and at 45 to 30 C, there will be less evaporation and perhaps less tendency to form saturated chemistries depending, of course, on the frequency of dripping.

In the above scenarios, the 75 to 45 C case may be the worst condition for corrosion of the carbon steel because of there is a higher likelihood of forming a combination of saturated chemistries and somewhat elevated temperatures which promotes chemical reactions, although this will strongly depend on the dripping conditions. The degree of chemical saturation in all cases is highly dependent on the drip rate, and the resultant solution pH is dependent on the mix of species in solution, temperature, and precipitation. Concentrated chemistries that might be envisioned include concentrated J-13 water (e.g., up to 1000X J-13) and pH 10.5 - 11; saturated solutions of J-13 are also likely in areas where evaporation is high compared to repetitive dripping, and require more detailed analysis and experimental evaluation for nominal and off-chemistry conditions. At various pHs, the possibility of precipitation of species (like $CaCO_3$) must be accounted for because they may act to reduce the pH.

Assuming that a high-pH (10 - 13) condition can develop (this needs to be evaluated from the standpoint of saturation, CO_2 exclusion, contribution of species dissolved from the concrete, etc.), high aspect ratio pits may develop on the carbon steel. As in other highly passive materials, these pits could have an aspect ratio $\gg 10:1$, and the expected diameter of the pits is a few millimeters.

Pit Density

The pit density expresses the number of pits per unit area on the carbon steel CAM. In the case of neutral pH conditions (pH 4 - 10), corrosion is much more likely to proceed as the propagation of a rough front rather than by high aspect ratio pitting (although pitting is possible in this pH regime, e.g., at high Cl concentrations). However, at high pH (pH >10 - 11), high aspect ratio pits are much more likely to develop, and the following cumulative distribution function represents my assessment of the pit density and its uncertainty:

<u>Percentile of CDF</u>	<u>Pit Density (pits/cm²)</u>
99%	10
95%	5
50%	1
20%	0.05 (1 pit/20 cm ²)
1%	0.01 (1 pit/100 cm ²)

Assuming that an aqueous environment exists, the dominant process that governs the pit density is the microstructure of the carbon steel. At high pH the pit density is likely controlled by cathodic availability (especially if only a thin film or "shallow pool" of water exists), with the number of pits (and their depths) limited by the cathodic area available to support individual pits.

CORROSION RATES OF CARBON STEEL

The corrosion rates applicable to carbon steel are a function of the pH, temperature, Cl⁻ (and other ions) concentration, and oxygen availability. The general corrosion rates used in TSPA-95 appear to be applicable to neutral pH conditions, J-13 Cl⁻ concentrations, and abundant oxygen availability. I broadly agree with the relationship used, which is a function of temperature (Figure 5.4-2); it does, however, assume a relatively constant chemistry—that may not be maintained. If hydrated salts films or saturated chemistries form, the rates may be higher and initiate at lower relative humidity. For example, if NaCl is present in high concentrations, the corrosion rates may be a factor of ~2 higher. The extent to which anions concentrate in a crevice is a function of their initial concentration. Because there are several dissolved anionic species in the saturated solution, pit initiation may be much more difficult. By contrast, in solutions of increasing conductivity (even with mixed anions), CAM general corrosion rate will likely be enhanced. The effect of saturated chemistries may be counteracted at higher temperatures because oxygen availability is lower in concentrated solutions and in hotter solutions.

Quantitative treatment of general corrosion and pitting corrosion of carbon steel can be handled by the "pit" penetration laws (penetration is proportional to t^n) described in John

Scully's talks. As the value of the "n" exponent approach 0, these laws describe general corrosion; thus, the spectrum of localized corrosion under higher pH conditions, and general corrosion under "neutral" pH conditions can be . Temperature variations are sensibly handled using an Arrhenius expression for thermal activation, although the reduced solubility of O₂ in water must be accounted for above about 75 C.

ALTERNATIVE CORROSION-ALLOWANCE MATERIAL

Monel 400, the alternative CAM being considered for the repository, is dramatically different from carbon steel in its corrosion resistance. The alloy is passive in most environments and even if corrosion occurs, rates should be quite low and thus little acidification should develop in any eventual crevice between the CAM and CRM interface. Monel 400 performs exceedingly well in many environments including under high pH conditions, but can perform poorly in a few environments such as 10% H₂S and nitric acid, and may not be considered adequately corrosion resistant in sea water. It is unlikely that these aggressive conditions will form on the waste package surface, although lower levels of problematical species might form from MIC activity (e.g., H₂S) or radiolysis (HNO₃). The expected corrosion mode in the YM conditions is very slow general corrosion and not pitting.

Drawbacks to the use of Monel 400 include:

- cost—but a thinner CAM layer could be considered since radiation levels and radiolysis effects may not be a problem
- lack of available data and therefore reliability / credibility of the performance assessment—using a poorer material whose response is somewhat better defined should be questioned
- concern for the effects of copper ion on the corrosion response of the CRM—but it's not at all clear that copper ion will directly affect the performance of materials like Alloy 625 or Hastelloy C22; that it will cause an elevation in corrosion potential because O₂ and iron ions are already present with the carbon steel design; or that it would enhance the tendency for acidification (again, compared to carbon steel).

Thus, I view Monel 400 as a fully satisfactory choice. It should provide substantial advantages over carbon steel in terms of corrosion life, and its cost may be less of a detriment if a thinner wall can be employed (other benefits related to handling lighter packages could also accrue). However, a final decision regarding the use of either CAM material is probably more important than which one is chosen.

CORROSION OF CORROSION-RESISTANT INNER BARRIER

Once the CAM is penetrated, corrosion of the CRM inner barrier becomes important, and the possibility of galvanic protection of the CRM by the remaining CAM needs to be considered. Provided electronic (metallic) and ionic contact is maintained between the two materials, some galvanic protection should occur, although probably only over limited distance and for a limited time. The distance limitation is related to the ionic coupling, which is greatly limited by the expected presence of copious iron oxide at any area where the CAM is penetrated; even highly concentrated solutions are expected to provide limited "throwing power" when extensive corrosion products are present.

The degree and time over which galvanic coupling protects the CRM is also a function of whether a carbon steel CAM has degraded by general corrosion or high-aspect ratio pitting (which, in turn, are a function of pH). In either case, galvanic protection would be spatially limited to an annular region near the (changing) outside diameter of the CAM (perhaps within a cm or so), and would be temporally limited to perhaps years or tens of years, controlled by the rate of corrosion of the CAM. The throwing power of a galvanic couple of two metals is large in open sea water, but in a system with significant amounts of oxide (or, more so, limited water), the throwing power can decrease by 100 - 1000 times. Thus, a reasonable estimate of the throwing distances at the CAM-CRM metal interface is one centimeter or less; that is, assuming a simple cylindrical hole / pit through the CAM, galvanic protection would only occur in the annular area on the CRM from the outer diameter of the hole / pit inward by 1 cm. The region of the exposed CRM more than 1 cm away from the CAM would benefit minimally from galvanic protection. The CRM under the areas where the CAM is intact (water is likely to be present in this gap once the CAM is penetrated

anywhere) will also conceptually benefit from galvanic protection—however, there is less need for galvanic protection since this region is a restricted geometry, little or no oxygen is present (it is consumed as it migrates into the crevice), and it may not be nearly as susceptible a location as the area directly exposed to the environment (depending, e.g., on the extent to which the entire inner-to-outer package gap takes on an aggressive, acidified “pit / crevice” chemistry).

Galvanic protection will be more significant in the case of high aspect ratio pits, where the high acidity at the base of the pit may lead to more localized attack of the CRM, as discussed below. Thus, if high aspect ratio pitting is considered the dominant CAM penetration mechanism, then some galvanic protection of the CRM may exist (although it probably is not needed if the right CRM alloy is chosen). From polarization data, it isn't obvious that some lowering of the corrosion potential of the CRM by galvanic protection is going to significantly affect passive current densities (general corrosion rates)—the largest expected benefit is associated with maintaining the CRM potential below the pitting or crevice corrosion potential, and it would appear to be wiser to select a material that has greater intrinsic resistance to pitting and crevice corrosion (e.g., Hastelloy C22 or C2000 rather than Alloy 625 or Hastelloy C276).

The basic concern for the galvanic protection concept is that it probably will not provide any consequential protection in instances where the corrosion of the CAM begins exposing areas larger than about 1 cm in diameter, and other side effects of the shrink fit design would likely lead to severe problems, as discussed below. Since corrosion of the CAM in the annular gap between the CAM and CRM will occur, I'm not convinced that purely metallic (electrical) contact will be maintained for any prolonged length of time; however, the oxides of iron and nickel have good semi-conductivity (e.g., the electrochemical reactions that control the corrosion potential and most of the polarization behavior in hot water occur on the oxide surface, not on the metal), and adequate electrical contact (for electron flow between the CAM and CRM) will likely be present for just as long if the CRM is simply set in the CAM (e.g., a large annular gap is used).

Given the alloys being considered for the CRM, I would not expect any significant corrosion of the CRM to occur under humid air conditions. The high chromium and molybdenum content of the CRM assists in the development of the highly protective passive films, and essentially no corrosion will occur. Corrosion of the CRM should only be considered under aqueous film or immersion (locally, or of the entire package) conditions.

As breakthrough of the CAM occurs, either due to general corrosion or high-aspect ratio pitting, I would expect water to penetrate and travel along the gap between the inner and outer barrier. Even if the contact between the barriers is "90%" as planned, the actual contact occurs at surface irregularities / asperities, leaving microscopic gaps where water will infiltrate in the gap. While oxygen will be consumed near the areas where the CAM has been penetrated (i.e., the crevice or pit "mouth"), the CAM will still undergo corrosion, albeit at a lower rate than if oxygen were present. As discussed later, the volume expansion of Fe to Fe_3O_4 is large (roughly 2 - 3X) and will almost certainly lead to very high stresses between the inner and outer barriers. Since the CAM is very thick-walled, and it's possible that penetration has occurred, e.g., by pitting (so that a significant fraction of the CAM wall remains in most regions), the large stresses would put the CRM container in compression. Since the stresses would not be fully symmetrical, there is a reasonable concern for buckling of the CRM; thus, while the stresses are nominally compressive, there is certainly the possibility that their non-uniform nature would produce local tensile stresses in the CRM, contributing to the possibility of SCC (residual stresses from closure welds or container fabrication welds will also contribute, if they're not fully stress relieved).

In evaluating the experimental data related to corrosion rates of the corrosion resistant materials (i.e., Hastelloy C-22), most of the experiments are carried out under aggressive conditions of low pH, saturated Cl^- concentrations, high oxygen, and elevated temperatures. Further, the reported corrosion rates for some of the superalloys such as C-22 are often given as "<2 mil/yr" rather than an actual rate. Because at least somewhat less aggressive conditions are expected within the repository (although in some scenarios the chemistry at the base of pits and crevices in the CAM could produce $\text{pH} < 3$ and reasonably high Cl^- under

elevated temperature conditions) the assessment of corrosion rates for the candidate CRMs is difficult and uncertain.

For example, given pH ~3, high Cl⁻, and available oxygen, the following table summarizes the critical temperatures at which pitting and crevice corrosion initiates, and the temperature at which the general corrosion rate reaches 5 mil/yr (125 µm/yr) for various alloys:

Alloy	T _{pitting/crevice} °C	T _{2 mil/yr} °C
C-22	100-120	60
C276	65-75	50
625	45-50	30

As can be seen, general corrosion occurs at lower temperatures than pitting or crevice corrosion, and the exact values for general corrosion rates are speculative because most investigators have been content to characterize the lower limit of general corrosion as "< 2 mils/y", a value that is not entirely comforting when designing for a multi-thousand year life. However, I expect that, except perhaps at the most extreme environmental conditions (approaching those conditions that cause pitting and crevice corrosion in a given alloy), the general corrosion rate is in fact very much below that lower limit rate of 2 mils/y.

To express the uncertainty in the corrosion rates for the CRM, two sets of conditions are assumed:

1. High-aspect ratio pits within the CAM, high Cl⁻ concentrations, and pH 3 at the base of the pits. This condition is unlikely for several reasons. First, high-aspect ratio pits are primarily expected in the case of high pH conditions related to drips through the concrete. High Cl⁻ would only result from conditions on the top of the waste package where salts and concentrated solutions have developed. Low pH would develop at the base of the pits, although this is not likely given the mix of anions (especially, abundance of OH⁻ ions in high pH solution) expected in the solution (note that much of the data has been obtained simply in NaCl, not mixtures of anions - such as is characteristic of J13 water - which are almost always less aggressive). Given dripping conditions, I estimate that there is less than a 10%

probability that the associated Cl⁻ and low pH conditions would occur. It's possible, as has been shown in various systems (including by SWRI in Alloy 825), that the mix of anions present (e.g., Cl, SO₄, NO₃, etc.) would make pitting in the CAM or CRM exceedingly unlikely.

2. General corrosion of the CAM, mixed anions, and pH 4 - 10 conditions. This condition is expected over all of the waste packages that do not experience consistent, localized dripping and, for those packages that do experience drips, over all of the surface except the top (and perhaps bottom) of the waste package, and at time periods following the degradation of the concrete when pHs have fallen to neutral levels. Given dripping conditions, I estimate that there is more than a 90% probability that the associated Cl⁻ and neutral pH conditions would occur.

Given the first condition above, which is the most aggressive, I estimate the general corrosion rate for C-22 at temperatures of 50 and 100 C and the associated uncertainties with the cumulative distribution functions listed below. Note that much of the uncertainty relates to a poor definition of the possible solution composition and pH conditions that might exist.

<u>Percentile of CDF</u>	<u>Rate at 100 C (mil/yr)</u>	<u>Rate at 50 C (mil/yr)</u>
99.9%	50	5
70%	1	0.1
50%	0.3	0.03
5%	0.01	0.001

Note that these rates are for general corrosion; pitting and crevice corrosion of C-22 can occur in some environments, generally at temperatures >100 C. At these elevated temperatures, the relative humidities in the repository will be too low to result in aqueous corrosion processes. The CDF above for the 100 C case would apply for Hatelloy C276 at about 65 C and for Alloy 625 at about 45 C. For the second condition above, the corrosion rate of the CRM will be lower by about one magnitude.

MICROBIOLOGICALLY INFLUENCED CORROSION

The likelihood of MIC playing a consequential role under the repository conditions is best answered by Brenda Little and others, although clearly there are carbon sources associated with opening the repository and emplacing the waste packages (machine oils, worn rubber from the conveyer belt, etc.). If we assume that biofilm formation is possible, it is necessary to estimate the conditions when it could play a large role (e.g., not above 100 C, and likely not above 70 C). Since most of the contamination will be on the tunnel or drift hole floor, it is not expected that any dripping water will contain significant carbon sources. Thus, any biofilms are expected to be very thin, and likely produce only a limited shift in the local chemistry under the biofilm.

RADIOLYSIS

Because of the average (or "equivalent") half-life of the radioactive contents of the waste package is estimated at 35 years, and the expected dose is 50 R/hr when implaced, radiolysis can't be automatically ignored. My primary concern is for formation of nitric acid when liquid water and (atmospheric) nitrogen are present. Note, however, that the "atmospheric gas exclusion" scenario described above (where boiling / evaporation of water dilutes / displaces other gases that were initially present) would be applicable to the radiolysis concern as well—that is, no atmospheric nitrogen is likely to be present, and water dripping on packages is likely to be low in nitrogen (from being "stripped" of gases on its way to the package) or will have the nitrogen stripped very soon after it drips onto the package (by boiling deaeration). Radiolysis can also produce oxidants, but only in very limited quantities vs. time because gamma radiation is relatively inefficient (compared to alpha, proton, and neutron radiation) in depositing energy in water. In both instances (nitrate and oxidants), the concentrations are expected be low, and they will be consumed with time (oxidants, in raising the corrosion potential, are themselves reduced)—in the case of nitrate, this reduction reaction produces ammonia, which is an alkaline buffer.

There apparently are data to show some corrosion enhancement in metals exposed to 50 - 100 R/h gamma, although this was not discussed or reviewed in detail. There have also been

experiential “vignettes” (e.g., by Bill Clarke at LLNL) that transportation casks have experienced corrosion (or indirect evidence of it based, e.g., on “wiping” tests for radiation contamination of the surface). These need to be evaluated more carefully. The problems may be associated with the shift in pH as nitric acid forms—however, acidification is likely to be very difficult in J13 (or concentrated J13) water, since substantial amounts of nitric acid would have to be generated to counteract the natural alkalinity of the J13 water. It is also interesting to note that SWRI has shown that the presence of nitrate was beneficial in their tests (for pitting on Alloy 825, I believe). Finally, the likely exclusion of atmospheric nitrogen over more than one thousand years, coupled with radioactive decay (a 35 year half life reduces the radiation level from 50 R/h by 1000 times at 350 years, and by about a billion times at 1000 years) combine to greatly reduce the overall likelihood of a threat from radiolysis.

WELDS

Welds have been the source of a huge fraction of the failures in structural components for decades, either from inadequate initial quality or (more commonly) from the high weld residual stresses. Welding materials like carbon steel, Monel, and Hastelloy C22 should pose no engineering challenge (apart from the size and length of all of the welds that are required). However, the prospect of having numerous container fabrication welds in addition to the final closure weld is not an attractive one unless proven techniques to ensure weld quality and to eliminate weld residual stresses are employed.

I recommend the use of techniques such as narrow gap (or “fine line”) welding techniques, coupled with a full stress relief anneal for the container fabrication welds. Techniques for accomplishing some stress relief on the final closure weld of the CRM should be developed, because it’s not easy to ensure that this closure weld will not be exposed to water once the CAM is penetrated (for the CAM, the current design “shields” the closure weld by insetting the closure cap and weld, so the skirt that extends beyond the closure weld makes it essentially difficult for water to contact the weld (water from splashing / dripping can still contact the weld, but it should run off because this is a vertical surface).

Since any welding defects that exist at emplacement could permit access to moisture and/or water to the CAM/CRM gap early in life, it is prudent to consider non-destructive techniques to help ensure weld quality. It may also be valuable to consider use of "tracer" inert gases for the CAM and perhaps CRM to permit detection of leaks before (or after) the closure of the repository.

CERAMIC COATING

My experience with ceramic coatings (partially stabilized zirconia and alumina) suggest that creating a porosity- and crack-free coating over a large engineering surface (especially one that is heavy and must be extensively handled and implaced) is highly impractical and improbable. Many of the coatings we have examined have intentional cracks and porosity to enhance their resistance to large thermal cycles (e.g., thermal barrier coatings for gas turbines), although we have also examined these coatings for other applications.

Once water penetrates the ceramic coating and contacts the CAM, corrosion will occur, and the large volume expansion of the iron oxide (1.78X for forming FeO, which is relevant only to high temperature oxidation—probably 2 - 3X for Fe₃O₄) will quickly induce spalling of the ceramic coating, totally eliminating its value. I believe that in the best possible ceramic coating there would be at least dozens of locations on the waste package where water could penetrate to the CAM substrate (not to mention areas where the ceramic coating had been seriously mechanically damaged by handling), and that the resultant corrosion and spalling would occur within short time periods (months or years of exposure to dripping or high humidity) and would render a substantial fraction of the package surface unprotected within years or tens of years. Given the enormous cost of the process and the severe handling complications that would result, I don't believe this is a worthwhile approach to pursue. If evaluation of this concept is pursued, I could recommend using large, curved surfaces (e.g., many square meters, to broadly simulate the waste package) and evaluating their permeability by simply soaking the surface in salt water (e.g., 0.1 M NaCl) for a day, then evaluating the ac impedance using electrodes connected to the steel and to a sponge soaked in the salt water.

We use a 60 Hz or 1000 Hz ac bridge. This measurement is highly relevant, because it detects any ionic paths from the bulk solution to the metal surface.

DRIP SHIELD

While the concept of a ceramic coating is not that attractive, any design feature that can reduce the possibility of water dripping on the waste package will produce substantial benefits (at least as long as it remains intact). If the prospect of dripping is deemed to be exceedingly small in the first, e.g., 500 years (because the repository is hot), and the prospect of a drip shield remaining intact after 500 years is small—then clearly it provides little benefit. However, it needs to be recognized that the contribution of dripping water to corrosion of the waste package is likely to be very dominant in most scenarios. Thus, any reasonable approach to minimizing the likelihood of dripping onto the package should be considered.

STRESS CORROSION CRACKING

Dealing with the stress corrosion cracking (SCC) issue is somewhat analogous to estimating the general corrosion rate from experiments that report a rate as " <2 mil/yr." Because the process may be occurring at low rates does not mean that it can be ignored over the long time periods being considered for the repository lifetime. Crack initiation studies have historically been poorly defined (what is crack initiation? what crack size is detectable or detected or meaningful?). Most crack growth studies use the fracture mechanics concept of stress intensity, which is generally proportional to the applied stress times the square root of the crack length. Recent emphasis in the areas of fatigue, corrosion fatigue, and (constant load) stress corrosion cracking has been on recognizing that crack growth concepts and measurements can be applied to account for a very sizable fraction of life in many components provided one accounts for the growth of very small cracks. "True" crack initiation has never been defined, and working definitions range from engineering detectability (by UT, or load drop in strain controlled tests) to the depth at which a crack develops, e.g., the same chemistry as does a long crack. In many alloys, there is no distinct

initiation phenomenon, although in materials that can undergo pitting, SCC is often observed to develop at the base of pits.

To evaluate the potential for SCC, we need to look at the stresses, microstructures, and environments that lead to SCC. Some of these include: welds and heat-affected zone metallurgy, the impact of a shrink-fit process that uses thermal expansion, stresses induced by the volume expansion of corrosion products at the gap between the inner and outer barriers, concentrated and pH-shifted environments that may develop at the base of pits or in crevices of the CAM, etc. For iron and nickel base alloys below about 120 C, getting cracks to initiate is more difficult than getting them to grow. Testing has shown that it can be difficult to initiate and grow cracks at low temperatures and stresses, but this does not mean that it cannot happen. If weld stresses are annealed at temperatures of 800 C as planned, then 80 to 90% of the residual stresses should be removed. The cap welds are difficult to anneal but they are recessed such that they (at least the CAM cap weld) are unlikely to get wet. If a few cm gap is allowed between the inner and outer barriers, the stresses induced from volume expansion should be minimal.

Experimental studies should be focused on demonstrating that SCC initiation is exceedingly unlikely at stresses below, e.g., 150% of yield (a likely upper limit on weld residual stresses). Using actively loaded (at least don't use only wedge or bolt loaded) specimens carefully precracked to make a controlled, gentle transition to constant (or near-constant) loading, studies should be performed to examine the crack growth behavior of the CRM, and perhaps also the CAM. SCC has been repeatedly shown to be difficult to sustain at low stress intensity or in relatively unaggressive environments, and numerous investigators have used very subtle additions of occasional unloading to "encourage" stable, sustained crack growth. While this important area of knowledge is still evolving, it appears that it is the probability of sustaining SCC that varies with stress intensity, environment, and temperature—not an inherent inability to produce SCC. In most industrial applications (such as boiling water reactors) the use of small amounts of unloading can be readily justified since (1) it has little effect on the crack growth rate and (2) load variations are inevitable during operation and with start up and shut down. However, the latter factor cannot be used as a justification in

the waste packages, and this issue will complicate the testing (if fully constant load is used), but also make it unlikely that sustained SCC (or SCC to any consequential depth) will occur, especially if the large sources of stress (weld residual, shrink fit, and oxide wedging) can be substantially eliminated.

REFERENCE

HH Uhlig and RW Revie, "Corrosion and Corrosion Control", Third Edition, John Wiley & Sons, 1985.

ELICITATION SUMMARY
JOSEPH C. FARMER

OVERVIEW OF WASTE PACKAGE CORROSION PROCESSES

The Engineered Barrier System (EBS) being designed for containing spent fuel and high-level waste at the proposed geologic repository at Yucca Mountain, Nevada, is a two-layer canister. In this design, the inner barrier is made of a corrosion-resistant material (CRM) such as Alloys 825, 625, or C-22; the outer barrier is made of a corrosion-allowance material (CAM) such as carbon steel or Monel 400. Initially, the containers will be hot and dry because of the heat generated by radioactive decay. However, eventually the temperature will drop to levels where both humid-air and aqueous-phase corrosion will be possible. As the outer barrier is penetrated, the possibility will exist for crevice formation between the CAM and CRM.

The mechanisms and rates of corrosion will be determined by the temperature and relative humidity (RH) in the potential repository, which will change with time. Immediately following emplacement, the elevated temperature and low RH in the repository will lead to dry oxidation of the corrosion-allowance material (CAM), which is expected to be carbon steel, or perhaps Monel 400. Although oxygen in the potential repository may be consumed by corrosion and microbial growth, it is doubtful that the repository will be oxygen-depleted for any significant period. It is believed that oxygen transport into the drifts through pores and fractures in the rock will be sufficient to keep the repository under oxygenated conditions. In regard to the layer formed during oxidation of the CAM, initially it may be adherent, compact, and protective. However, it is believed that it will eventually become thick, non-adherent, flakey, and porous. Spalling probably will occur, with exfoliated areas becoming further oxidized. Any dust that settles on the waste package may become incorporated into the corrosion scale. Water that drips onto hot waste packages (temperature

greater than the boiling point, which is about 100°C), will evaporate and leave behind a salt deposit. As the waste package cools, it will be possible for liquid water to exist on the surface. Redissolution of salt deposits will then produce a concentrated electrolyte on the surface of the CAM.

It is believed that humid-air corrosion will begin when the temperature of the waste package drops below about 100° to 150°C, provided that there is a source of moisture. In the absence of dripping water, the presence of water molecules on the surface of the waste package depends on adsorption and condensation from the vapor phase. At low surface coverages (less than 1 monolayer), the presence of water on the surface of the waste package probably obeys the Langmuir adsorption isotherm. It is believed that the transition from dry to humid-air corrosion should occur at a RH of about 20 to 80 percent given that it is well known that 1 to 10 monolayers (MLs) of water can exist under those conditions. The threshold RH for humid-air corrosion may be about 60 percent, since 2 to 5 MLs are believed to be present at this level of moisture. The following data are given by Leygraf, 1995.

Relative Humidity (%)	Number of Water Monolayers
20	1
40	1.5 to 2
60	2 to 5
80	5 to 10

Note that the O-H bond length in water is about 0.9584 Angstroms (~0.1 nm), with a corresponding bond angle of 104.45 degrees. Thus, a single ML of water is assumed to be approximately 0.2 nm thick, while 10 MLs are approximately 2 nm thick. The temperature at which condensation occurs depends on the amount of salt on the surface of the container (boiling point elevation phenomenon).

It is believed that a water film of critical thickness must accumulate on the surface of the waste package before classical aqueous-phase corrosion can occur. One can propose several criteria for establishing such a critical thickness. For example, when an electrode is placed in

an electrolyte and polarized at potentials greater than (or less than) the point of zero charge, an electric double layer will form. From the Gouy-Chapman theory, as well as the Stern modification of that theory, it is believed that a fully developed electric double layer on a planar electrode is about 1 to 30 nm thick. In the case of a 1:1 electrolyte in water at 25°C, the characteristic thickness of the diffuse layer ranges from 1 nm at a concentration of 0.1 M to 30 nm at 10^{-4} M (Bard and Faulkner, 1991; Newman, 1991). These estimated double-layer thicknesses correspond to about 5 to 150 MLs of water, and require 60 to 100 percent RH to form. A second criterion can be based on transport-limited current in the water film. For example, sufficient electrolyte must exist on the surface between adjacent anodic and cathodic sites to allow the flow of current at a level that exceeds the passive current density, I_{pass} .

It is believed that the carbon steel outer barrier (CAM) will experience general corrosion at a pH less than 10. It should be possible to express the roughness of this corrosion front mathematically, and to establish an average rate of penetration from experimental data and observations. If water entering the repository passes through concrete, it is conceivable that the pH of water contacting the waste package may be elevated (greater than 10). Under such high pH conditions, pitting of the carbon steel outer barrier may occur. A great deal of excellent work on the pitting of carbon steel has been published by the Swedish company SKB over the years. For example, a report published in 1988 provides a great deal of information regarding the aspect ratios of pits observed in carbon steel, as well as pit distribution data (Marsh et al., 1988). In most cases, aspect ratios were less than about 7, although aspect ratios as high as about 37 were observed in isolated cases. It should be possible to estimate the maximum number of growing pits on a surface (maximum pit density) by assuming that the pits are limited by the cathodic current available to drive cumulative anodic pitting processes. As the surface becomes covered with pits, the cathodic surface area available for oxygen reduction will diminish. According to Marsh:

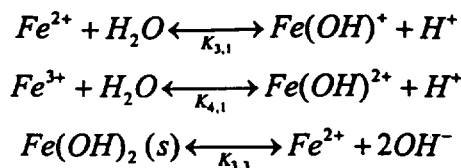
“the minimum requirement for the maintenance of stable passivity is that the small anodic current associated with passive film growth and/or dissolution

must be balanced by a cathodic current produced by the reduction of oxygen or some other oxidizing agent. The latter condition defines the minimum requirement for pitting corrosion to be feasible, and can be expressed mathematically as:

$$\frac{I_{pass}}{4F} \leq D \left. \frac{\partial C(x,t)}{\partial x} \right|_{x=0}$$

A preliminary evaluation of the maximum pitting period based on the above inequality has been made as part of the SKB program and reported separately. This showed that the maximum pitting period was likely to be of the order of 125 years, rather than the full 1000 year container life. However, the analysis showed that this estimate was sensitive to the value of the passive leakage current, I_{pass} . Consequently, careful measurements are being made of I_{pass} before repeating the theoretical analysis."

Eventually, the carbon steel outer barrier (CAM) will be penetrated completely by either general corrosion or localized corrosion, which includes pitting, crevice corrosion, and stress corrosion cracking. After the CAM is breached, corrosive attack of the corrosion-resistant inner barrier will begin. The corrosion-resistant material (CRM) used for fabrication of the inner barrier may be Alloy 825, 625, or C-22. The general corrosion rates for these candidate alloys are extremely low and believed to be insignificant. One of the principal corrosion mechanisms of concern is crevice corrosion. Hydrogen ions produced by the hydrolysis reactions of dissolved iron, nickel, chromium, and other alloying elements will accumulate in a crevice, leading to severe pH suppression. For illustration, relevant hydrolysis reactions for iron are summarized below (Oldfield and Sutton, 1978).



Note that $[\text{Fe}(\text{OH})]^{2+}$ is actually $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$, but is shown without hydration for simplicity. Similarly, other ions are also shown without hydration. Jones and Wilde (1978) prepared solutions of CrCl_3 , FeCl_2 , and NiCl_2 and measured the pH. Their measurements are summarized below.

Salt	0.1 N	1 N	Saturated
FeCl_2	2.1	0.8	0.2
NiCl_2	3.0	2.7	2.7
CrCl_3	1.1	-0.3	-1.4

These valuable data dramatically verify the effects of dissolved FeCl_2 , NiCl_2 , and CrCl_3 on pH suppression. This type of pH suppression can exacerbate corrosion of the CRM in the crevice, and increase the rates of pit initiation and propagation.

Sufficient chloride will be transported into the crevice by diffusion and electromigration to satisfy conditions of electroneutrality. The transport of chloride and other ions is governed by the Nernst-Planck equation, which includes terms for electromigration, diffusion, and convective transport (Newman, 1991):

$$\bar{N}_i = -z_i u_i F c_i \bar{\nabla} \Phi - D_i \bar{\nabla} c_i + \bar{v} c_i$$

where N_i is the flux, z_i is the charge, u_i is the mobility, c_i is the concentration, and D_i is the diffusivity of the i -th ion; Φ is the potential; and v is the convective velocity of the electrolyte. The current density is then defined in terms of the flux:

$$\bar{i} = -F^2 \bar{\nabla} \Phi \sum_i z_i^2 u_i c_i - F \sum_i z_i D_i \bar{\nabla} c_i$$

Transients in concentration can be dealt with through application of the following equation:

$$\frac{\partial c_i}{\partial t} = -\bar{\nabla} \cdot \bar{N}_i + R_i$$

where R_i is a homogeneous rate. By assuming one-dimensional transport, Xu and Pickering (1993) and Nystrom et al. (1994) were able to make the following simplifications:

$$N_{i,x} = -z_i u_i F c_i \frac{d \Phi}{d x} - D_i \frac{d c_i}{d x}$$

$$i_x = -\kappa_x \frac{d \Phi}{d x} - F \sum_i z_i D_i \frac{d c_i}{d x}$$

The conductance of the crevice solution is estimated from a summation of products formed from the valence, mobility, and concentration of each ion.

$$\kappa_x = -F \sum_i z_i^2 u_i c_i$$

The Pickering-Xu model can be used to calculate potential drop in the crevice, which can then be used to establish criteria for depassivation of the crevice wall. This model provides both potential and current distribution along the length of the crevice. It also enables calculation of a critical depth, d_c , for depassivation.

The combination of low pH and high chloride will exacerbate pitting, intergranular corrosion, and stress corrosion cracking of the CRM. These effects will be more pronounced in narrow (tight) crevices than in wide ones. Integrated predictive models are needed to account for the

effects of localized crevice environment on pitting, intergranular attack, and stress corrosion cracking. It is believed that a deterministic calculation is appropriate to estimate the accumulation of hydrogen and chloride ions in the crevice. Probabilistic (or deterministic) models can then be used to predict damage due to pitting and other forms of localized corrosion. Shibata and Takeyama (1977) and Henshall (1992, 1995, 1996) have published a number of relevant papers on the probabilistic modeling of pitting. A "stifling criteria" such as that given in the SKB report by Marsh et al. (date) should also be applied to pitting of the CRM. Obviously, parameters in these models should be determined from available experimental data (published literature and generated by program). Thus, full integration of the testing and modeling activities will be essential.

It should be noted that during a workshop on total system performance assessment, held in January 1997, the following hypotheses were formulated: (1) penetration of the outer barrier comprised of CAM will be by either humid-air corrosion or aqueous corrosion; (2) the inner barrier comprised of CRM will be exposed in patches as the outer barrier corrodes; (3) the crevice region surrounding each exposed patch can be subdivided into three generic zones. These zones are defined as follows: (Zone 1) the CRM will be directly exposed to the near-field environment, via humid air or a thin layer of oxygenated and acidified water; (Zone 2) the CRM will be exposed to a thin layer of acidified water, having a gradient in oxygen concentration; and (Zone 3) the CRM will be exposed to a thin layer of acidified and deoxygenated water. The corrosion phenomena in these zone may progress through two phases: (Phase 1) active corrosion of the CAM crevice wall; and (Phase 2) classical crevice corrosion and pitting of the CRM. These concepts are illustrated on Figures JF-1a through JF-1d.

During Phase 1, the CAM wall will undergo active anodic dissolution, while the CRM wall will be maintained below the damage threshold. As the temperature of the container drops below 100°C, the crevice between the CAM and CRM will be filled with water. This wall will begin to corrode at a rate limited by the availability of cathodic reactants necessary for depolarization of the anodic dissolution reaction. These reactants probably will be dissolved

O₂ entering the crevice through the crevice mouth, or H⁺ from the electrolyte. The pH of this crevice solution (electrolyte) will be suppressed by various hydrolysis reactions involving dissolved iron. The corrosion potential of the CAM at the point of penetration will lie between the redox potentials for cathodic oxygen reduction (or perhaps hydrogen evolution) and anodic iron dissolution. This value, which can be calculated from mixed potential theory, is expected to be below the damage threshold of the CRM. However, the extent of protection (throwing power) will be determined by the ionic conductivity of the electrolyte and the geometry of the penetration and crevice. It is doubtful that the "galvanic protection effect" will be significant. Passivation of the crevice wall formed by the CAM may not be possible at the pH and potential maintained at the mouth of the crevice. The corrosion rate experienced by the CAM is expected to be greatest near the crevice mouth because of the abundance of oxygen. Therefore, the rate of formation of precipitated products from corrosion of the CAM wall also will be greatest near the mouth. These oxides, hydroxides, and/or oxyhydroxides will accumulate near the crevice mouth, eventually filling the space. During Phase 2, a second crevice will form between the precipitated, tightly packed corrosion products and the CRM. Initially, the two walls of this new crevice will be formed by the precipitated solids, which will be relatively dielectric in nature, and the passive surface of the CRM.

CORROSION OF CARBON STEEL OUTER BARRIER

Immediately following emplacement of the waste packages, the elevated temperature and low RH in the potential repository will lead to oxidation of the corrosion-allowance material (CAM), which is expected to be either carbon steel or Monel 400. Although oxygen in the repository may be consumed by corrosion and microbial growth, it is doubtful that the repository will be oxygen-depleted for any significant period. It is believed that oxygen transport into the drifts through pores and fractures in the rock will be sufficient to keep the potential repository under oxygenated conditions. The layer formed during oxidation of the CAM, initially may be adherent, compact, and protective. However, it is believed that it will eventually become thick, non-adherent, flakey, and porous. Spalling probably will occur, with exfoliated areas becoming further oxidized. Any dust that settles on the waste package

may become incorporated into the corrosion scale. Water that drips onto hot waste packages (temperature greater than the boiling point, which is about 100°C), will evaporate and leave behind a salt deposit. As the waste package cools, it will be possible for liquid water to exist on the surface. Redissolution of salt deposits could produce a concentrated electrolyte on the surface of the CAM.

It is believed that the transition from dry oxidation to humid-air corrosion will begin when the temperature of the waste package drops below about 100° to 150°C, provided that there is a source of moisture. The transition from dry oxidation to humid-air corrosion depends on temperature, relative humidity, amount of dripping water present, and whether a salt film exists on the surface. The following cumulative distribution functions (CDFs) reflect some of my uncertainty in the temperature at which the CAM transitions from dry oxidation to humid-air corrosion.

Case 1. No Salt Film on Surface

<u>Percentile of CDF (%)</u>	<u>Transition T (°C)</u>
100	100
1	125
0	150

Case 2. With Salt Film (NaCl) on Surface

<u>Percentile of CDF (%)</u>	<u>Transition T (°C)</u>
100	100
100	125
50	150
10	175
0	200

The transition temperatures are higher with the salt film because of the hygroscopic nature of the salt. The least hygroscopic chloride salt is NaCl, which has a corresponding transition temperature of 125°C. Surface films of other, more hygroscopic salts such as CaCl₂ or MgCl₂ are less likely to be formed, but would have higher transition temperatures if they did. These estimates are based on the experimental data presented by Gdowski (WPDEE Workshop X), as well as subsequent discussions with him. In the absence of dripping water, the presence of water molecules on the surface of the waste package depends on adsorption and condensation from the vapor phase.

As previously discussed, it is believed that the transition from dry to humid-air corrosion should occur at a RH of about 20 to 80 percent, as it is well known that 1 to 10 monolayers (MLs) of water can exist under these conditions. The threshold RH for humid-air corrosion is probably about 60 percent, as 2 to 5 MLs are believed to be present at this level of moisture [Leygraf, 1995]. To express the uncertainty in the RH threshold at which humid-air corrosion begins, the following CDF is estimated:

<u>Percentile of CDF (%)</u>	<u>Relative Humidity (%)</u>
100	80
50	60
5	20

It is believed that a water film of critical thickness must accumulate on the surface of the waste package before classical aqueous-phase corrosion can occur. As previously discussed, one can propose several criteria for establishing the critical thickness. For example, when an electrode is placed in an electrolyte and polarized at potentials greater than (or less than) the point of zero charge, a double layer will form. From the Gouy-Chapman theory, as well as the Stern modification of that theory, it is believed that a fully developed electric double layer on a planar electrode would be about 1 to 30 nm thick (Bard and Faulkner, 1980; Newman, 1991). These estimated double-layer thicknesses correspond to about 5 to 150 MLs of water, requiring 60 to 100 percent RH for formation. A second criterion can be based on transport-limited current in the water film. For example, sufficient electrolyte must exist on the surface

between adjacent anodic and cathodic sites to allow the flow of current at a level that exceeds the passive current density. The following CDF expresses my uncertainty in the RH threshold between humid-air and aqueous conditions.

<u>Percentile of CDF (%)</u>	<u>Relative Humidity (%)</u>
100	100
90	95
50	90
5	85
0	80

Although the effects of temperature and relative humidity are represented by individual CDFs, the separation of these important variables is questionable.

As previously discussed, it is believed that the carbon steel outer barrier (CAM) will experience general corrosion at a pH less than 10. It should be possible to express the roughness of this corrosion front mathematically, and to establish an average rate of penetration from experimental data and observations. If water entering the repository passes through concrete, it is conceivable that the pH of water contacting the waste package may be greater than 10. Under such high pH conditions, pitting of the carbon steel corrosion outer barrier may occur. A great deal of excellent work on the pitting of carbon steel has been published by SKB over the years (Marsh et al., 1988). In most cases, aspect ratios were less than about 7, although aspect ratios as high as about 37 were observed. It should be possible to estimate the maximum number of growing pits on the surface (maximum pit density) by assuming that the pits are limited by the cathodic current available to drive cumulative anodic pitting processes. As the surface becomes covered with pits, the cathodic surface area available for oxygen reduction will diminish. According to Marsh,

“the minimum requirement for the maintenance of stable passivity is that the small anodic current associated with passive film growth and/or dissolution must be balanced by a cathodic current produced by the reduction of oxygen

or some other oxidizing agent. The latter condition defines the minimum requirement for pitting corrosion to be feasible, and can be expressed mathematically as:

$$\frac{I_{pass}}{4F} \leq D \left. \frac{\partial C(x,t)}{\partial x} \right|_{x=0}$$

A preliminary evaluation of the maximum pitting period based on the above inequality has been made as part of the SKB program and reported separately. This showed that the maximum pitting period was likely to be of the order of 125 years, rather than the full 1000 year container life. However, the analysis showed that this estimate was sensitive to the value of the passive leakage current, I_{pass} . Consequently, careful measurements are being made of I_{pass} before repeating the theoretical analysis."

Eventually, the carbon steel outer barrier (CAM) will be penetrated completely by either general corrosion or localized corrosion, which includes pitting, crevice corrosion, and stress corrosion cracking. After the CAM is breached, corrosive attack of the corrosion-resistant inner barrier will begin. The "stifling criteria" given by Marsh et al. accounts only for Fickian diffusion. Given that electromigration is not included, the assumption of a supporting electrolyte having high ionic strength is implicit.

Figure JF-2 is a logic diagram showing possible outcomes or implications for various conditions. The figure identifies several conditions that are important to corrosion of the CAM: temperature, relative humidity, existence of dripping water, existence of salt film, and pH. The probability that a given waste package will experience dry oxidation, humid-air corrosion, or aqueous-phase corrosion must be calculated from information provided by the thermohydrologists, which is not the subject of this elicitation. After my visit to the recently constructed drifts at Yucca Mountain, intuition leads me to believe that relatively few of the waste packages will experience dripping water. However, the rapid migration of certain

chlorine isotopes into the drifts is clear evidence that some sites in the potential repository may experience a sufficiently large flux of water to cause dripping. It is assumed that these isotopes were generated at the surface during aboveground nuclear testing, which occurred less than 53 years ago. Also indicated in the diagram are the expected effects of microbiologically influenced corrosion (MIC). As discussed by other panel members and presenters, fungi are capable of growth at RH of 60 to 90 percent, and bacteria can grow at RH greater than 90 percent. During the potential repository's lifetime, the RH at the surface of several waste packages may exceed these threshold values. Horn has isolated and cultured iron-oxidizing bacteria from YMP geologic samples that might promote MIC. Acid- and sulfide-producing bacteria may also exist.

Little or no pitting of the carbon steel outer barrier is expected at a pH less than 10. Therefore, it is inappropriate to use of a "pitting factor" to describe the propagating corrosion front in such cases ($\text{pH} < 10$). Note that "pitting factor" is defined as the ratio of the pit depth to the overall penetration from general corrosion. It should also be noted that the pitting factor is assumed to be independent of time, which probably is not the case. This approach does not allow for the permanent death or "stifling" of a pit. As an alternative, I visualize the general corrosion front as developing a "roughness" that either increases or diminishes the average penetration. Roughness is believed to reach a maximum, limiting value. I suggest the following two alternative approaches to use of the pitting factor.

1. Use an average general corrosion rate (derived from experimental data, as given in TSPA-95). Divide the area of a waste package into patches and assume that they all experience the same average rate of corrosion but allow each to have a different rate distribution.
2. Use a "roughness" factor that describes the variation in the morphology of the corrosion front and assume that this factor stays constant as a function of depth. Perhaps roughness can be described with a root-mean-square approach.

Pit Density

Given relatively alkaline conditions ($\text{pH} > 10$), pitting of the carbon steel may occur. For TSPA-95, a density of about 10 pits/ cm^2 was estimated (Joon Lee, Private Meeting with Joe Farmer, May 1, 1997, YMP Meeting Notebook, p. 13). Lee cited work by Marsh and Tyler (1988), as well as work by Booth et al. (1963). Is this density reasonable? This question can be evaluated by looking at a pit and the cathodic area needed to support the anodic process at its base. The following assumptions are made.

1. Nine (9) pits exist in a three-by-three (3×3) array in every one square centimeter (1 cm^2) of area.
2. Every pit has a diameter of 1 mm (0.1 cm). The corresponding area at the base of the pit is approximately 0.01 cm^2 ($\pi D^2/4 \sim 7.85 \times 10^{-3} \text{ cm}^2$).
3. Combined anodic and cathodic surface areas for each pit are approximately 0.25 cm^2 ($0.5 \text{ cm} \times 0.5 \text{ cm}$).
4. The cathodic surface area for each pit is approximately 0.24 cm^2 ($0.25 \text{ cm}^2 - 7.85 \times 10^{-3} \text{ cm}^2$).
5. The diffusion-limited oxygen reduction current is approximately $25 \mu\text{A}/\text{cm}^2$.
6. The passive current density at the base of each pit is approximately $100 \mu\text{A}/\text{cm}^2$.

The available cathodic current per pit is therefore:

$$I_{\text{cath}} = (25 \mu\text{A} / \text{cm}^2)(0.24 \text{ cm}^2) = 6 \mu\text{A}$$

The corresponding anodic current level at which the base of each pit will passivate (die) is:

$$I_{\text{pass}} = (100 \mu\text{A} / \text{cm}^2)(7.85 \times 10^{-3} \text{ cm}^2) = 0.79 \mu\text{A}$$

Clearly, the growth of pits is not cathodically limited to 9 pits/cm². The pit density could be about one order of magnitude greater (~100 pits/cm²). At a density of 100 pits/cm², the edges of 1 mm-wide pits would touch, so this is an obvious upper bound. The following cumulative distribution function expresses my uncertainty in the pit density in carbon steel, given high pH conditions (pH ≥ 10):

Percentile of CDF (%)	Pit Density (pits/cm ²)
100	100
50	10
5	1
0	0.1

ALTERNATIVE CORROSION-ALLOWANCE MATERIAL

Although Monel 400 is more corrosion resistant than is carbon steel, the presence of dissolved copper in a crevice solution might produce penetration rates similar to those observed with the "Green Death" solution, as shown on Figures JF-3 through JF-6. See the discussion in the following section.

CORROSION OF CORROSION-RESISTANT INNER BARRIER

The logic diagram that explains my concept of EBS degradation is shown on Figure JF-2. Initially, degradation is dominated by humid-air and aqueous corrosion of the CAM. During this early period, no significant corrosion of the CRM is expected because the CRM will not be exposed to the NFE or any CAM-CRM crevice solution. After the CAM has been penetrated, the CRM probably will be attacked. Because general corrosion of the CRM will occur at extremely low rates, crevice corrosion is believed to be the only corrosive process that can lead to significant penetration of the inner barrier (CRM) over the lifetime of the potential repository. If corrosion of the CAM leads to significant exfoliation and exposure of the CRM, an extensive crevice scenario may not develop. In areas where complete exfoliation occurs, the pH of the water that contacts the CRM will be essentially neutral (or

alkaline if exposed to concrete). The chloride concentration probably will be close to that of J-13 well water. Given these conditions, general corrosion of the CRM will occur at very low rates. Stress corrosion cracking (SCC) may still occur, depending on loading.

Assuming a pH of about 10, pitting of the CAM will occur. These pits, as well as other penetration of the CAM, may lead to crevice corrosion of the CRM. Hydrolysis reactions in the crevice will lead to pH suppression, which will exacerbate pitting, intergranular attack, and SCC. The width of the crevices will be important in defining the rate of crevice corrosion. Tight crevices (0.0755 mm, for example) probably will result in significantly higher corrosion rates than wide crevices. Crevice geometry will be determined by the fabrication technique employed (shrink-fit; weld cladding; etc.).

Clearly, much more work needs to be done on the mechanistic pitting and crevice corrosion models before they can be used reliably to make predictions for the TSPA. In the interim, I recommend the use of empirical rate expressions, based on experimental data and a general knowledge of such transport-controlled processes:

$$d = d_0 \left(\frac{t}{t_0} \right)^n$$

where d_0 is the penetration depth at time t_0 , d is the penetration depth at time t , and n is the power of the growth law. Gdowski's Degradation Mode Survey (1991) has been used as the basis of the predictions shown on Figures JF-3 through JF-6. For Figure JF-3, it is assumed that the penetration rate observed in various crevices, or simulated crevice conditions, is linearly proportional to time (penetration proportional to $t^{1.0}$). In this case, penetration of an inner barrier made of either Alloy 625 or C-276 is predicted within 10,000 years, assuming that the wall is 2 cm thick. In this scenario, both materials would fail within the time of interest to the potential repository. However, if the penetration rate is transport-controlled (penetration proportional to $t^{1/2}$), Alloy C-276 is not penetrated during the 10,000-year period of interest. In contrast, Alloy 625 fails in this case. In cases involving dissolved copper-

based alloys such as Monel 400, tests with the "Green Death" test solution may be more appropriate because 1 percent CuCl_2 is present. In this case, there is evidence that Alloy 686 can pass at temperatures below 135°C . Based on this simple empirical model, it appears that Alloys C-276 and C-22 are better choices for fabrication of the EBS inner barrier than Alloys 825 and 625, which are less resistant to crevice corrosion. Clearly, the exact time-dependence of the penetration rate is critical, but unknown. More research is needed to determine the value of the exponent 'n' in the empirical rate expression. The following CDF represents my uncertainty regarding the value of this parameter.

<u>Percentile of CDF</u>	<u>n-value</u>
100%	1.0
90%	0.7
75%	0.5
10%	0.3
0%	0

The temperature-dependence of these rates must also be determined. If it is assumed that penetration in the crevice is limited by oxygen transport, one can estimate the maximum penetration rate.

The initial pit density for the CRM is difficult to estimate for alloys 625 and C-22 because of limited test data. However, in accelerated short-term exposure tests with Alloy 825, Roy found approximately 68 pits/cm^2 (Henshall, 1996). The following CDF represents my uncertainty regarding the pitting of candidate CAMs.

<u>Percentile of CDF</u>	<u>Pit Density (pits/cm^2)</u>
100%	400
75%	200
50%	80
25%	50
5%	10

MICROBIOLOGICALLY INFLUENCED CORROSION

As discussed by other panel members and presenters, fungi are capable of growth at RH of 60 to 90 percent and bacteria can grow at RH > 90 percent. During the potential repository's lifetime, the RH at the surface of several waste packages may exceed these threshold values. Horn has isolated and cultured iron-oxidizing bacteria from YMP geologic samples that might promote MIC. Acid- and sulfide-producing bacteria may also exist. If iron-oxidizing bacteria are present, the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple could push the CRM to more anodic potentials, closer to the critical pitting potential. The possible production of acid will also exacerbate both general and localized corrosion.

UNCERTAINTY AND VARIABILITY

Because drips will impinge on the top of the waste package, corrosion will be greater on the top. However, supports at the bottom of the package may form crevices and initiate corrosion.

OTHER ISSUES

Radiolysis

This could be important in thin-walled containers exposed to high radiation fields, as in the case with spent fuel. Radiolysis can form oxidizing agents such as H_2O_2 . It is well known that H_2O_2 is an effective depolarizer, capable of elevating the potential of the CAM or CRM several hundred millivolts (anodic polarization) (Glass et al., 1986). It is also known that gamma radiolysis can produce nitrogen oxides such as NO_2 , which can react with copper-based alloys to form blue-green copper hydroxy nitrates. Such deposits have been observed on copper cooling lines around the beam lines of particle accelerators, as well as in radiolysis experiments (Farmer et al., 1988).

Welds

Welds will have residual stresses that approach the yield stress. These areas will be prime locations for the initiation and propagation of stress corrosion cracks. Effects such as sensitization will increase the probability of such failure.

Ceramic Coating

Ceramic coatings are expected to be porous and will crack. Cracks may be due to the differences in thermal expansion of the ceramic and CAM, impact during movement, impact and deformation due to rock fall, and/or the formation of corrosion products at the (porous) ceramic-CAM interface. The imperfect ceramic coating could form a crevice with the CAM, thereby exacerbating corrosion. Stress risers could form at the base of cracks in the ceramic, thereby initiating SCC in the CAM, which will be stressed during shrink-fitting with the CRM.

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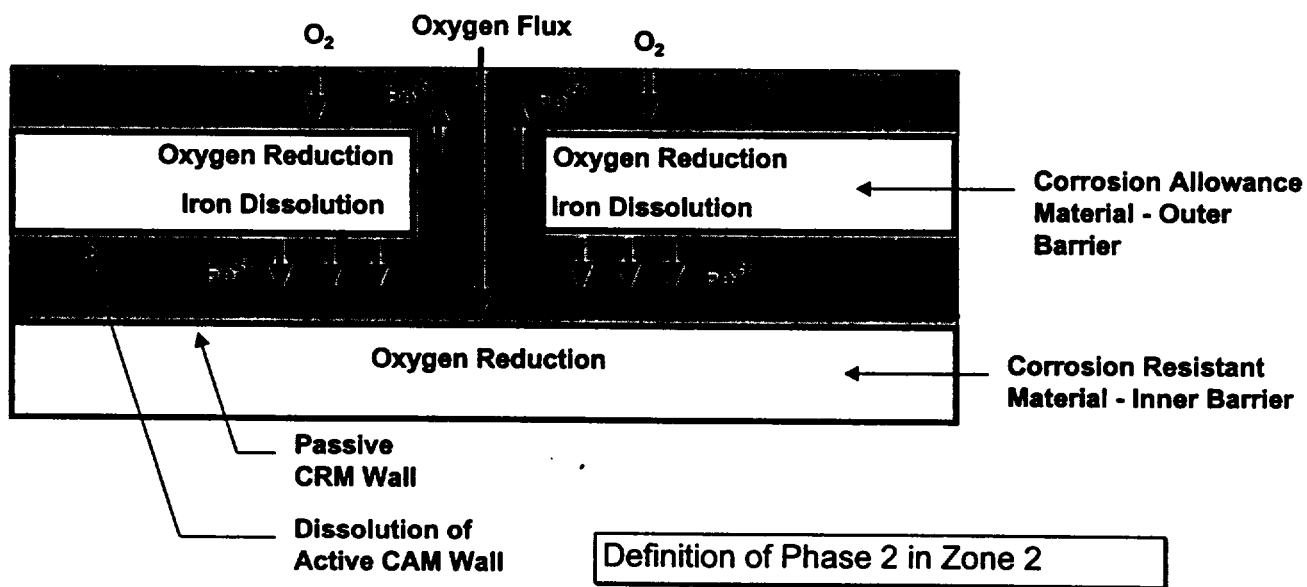
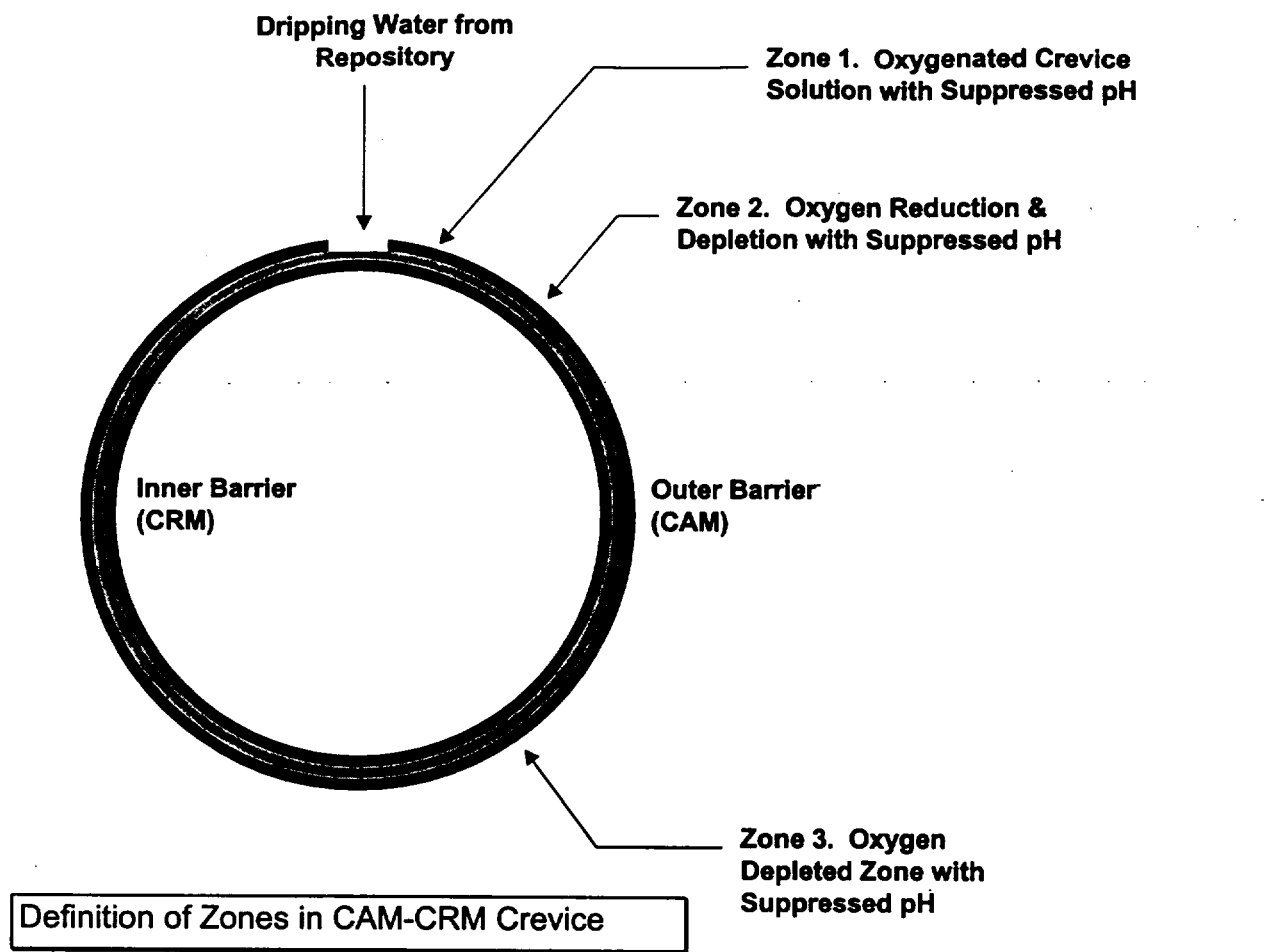
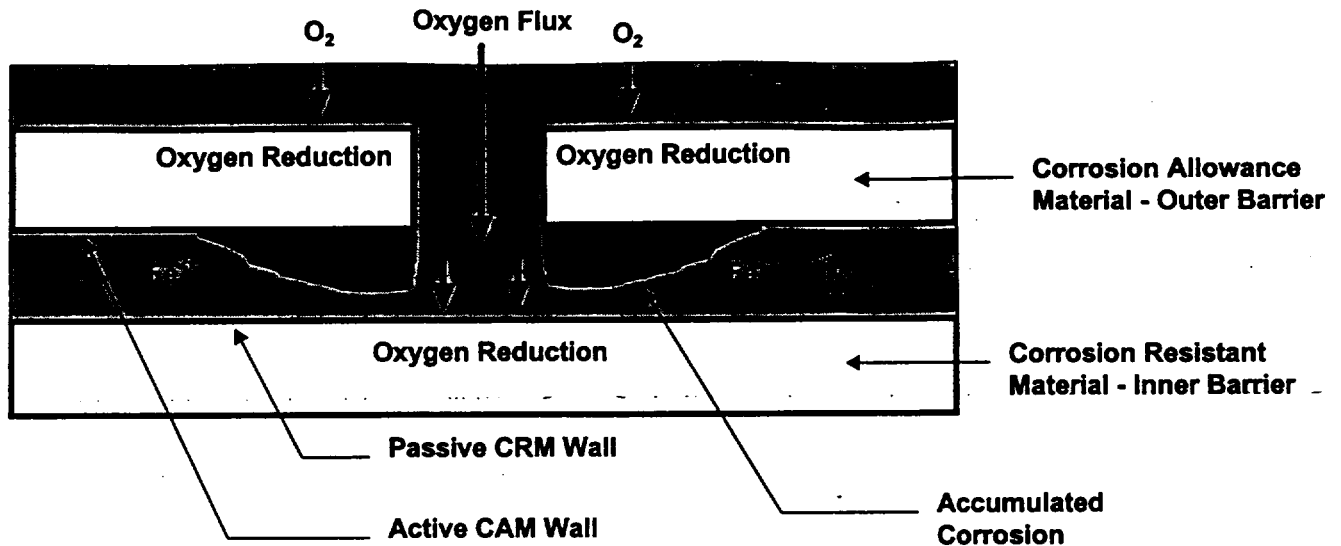
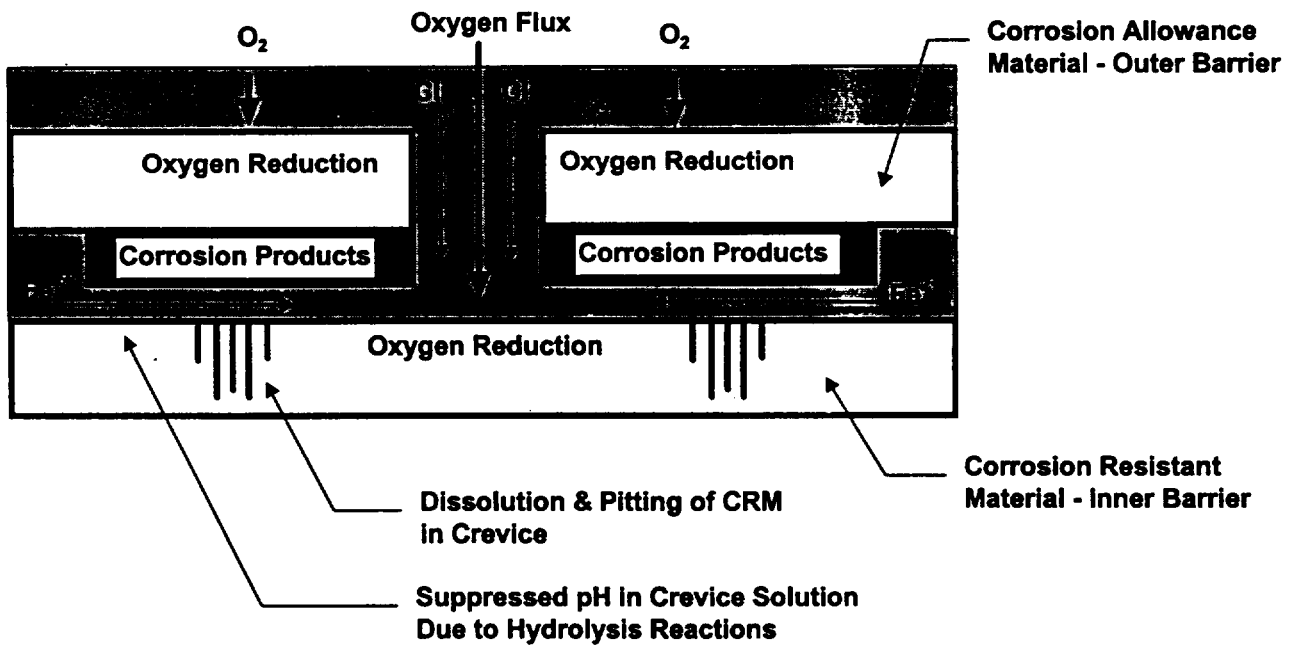


Figure JF-1a and 1b



Definition of Phase 2 in Zone 2



Definition of Phase 2 in Zone 2

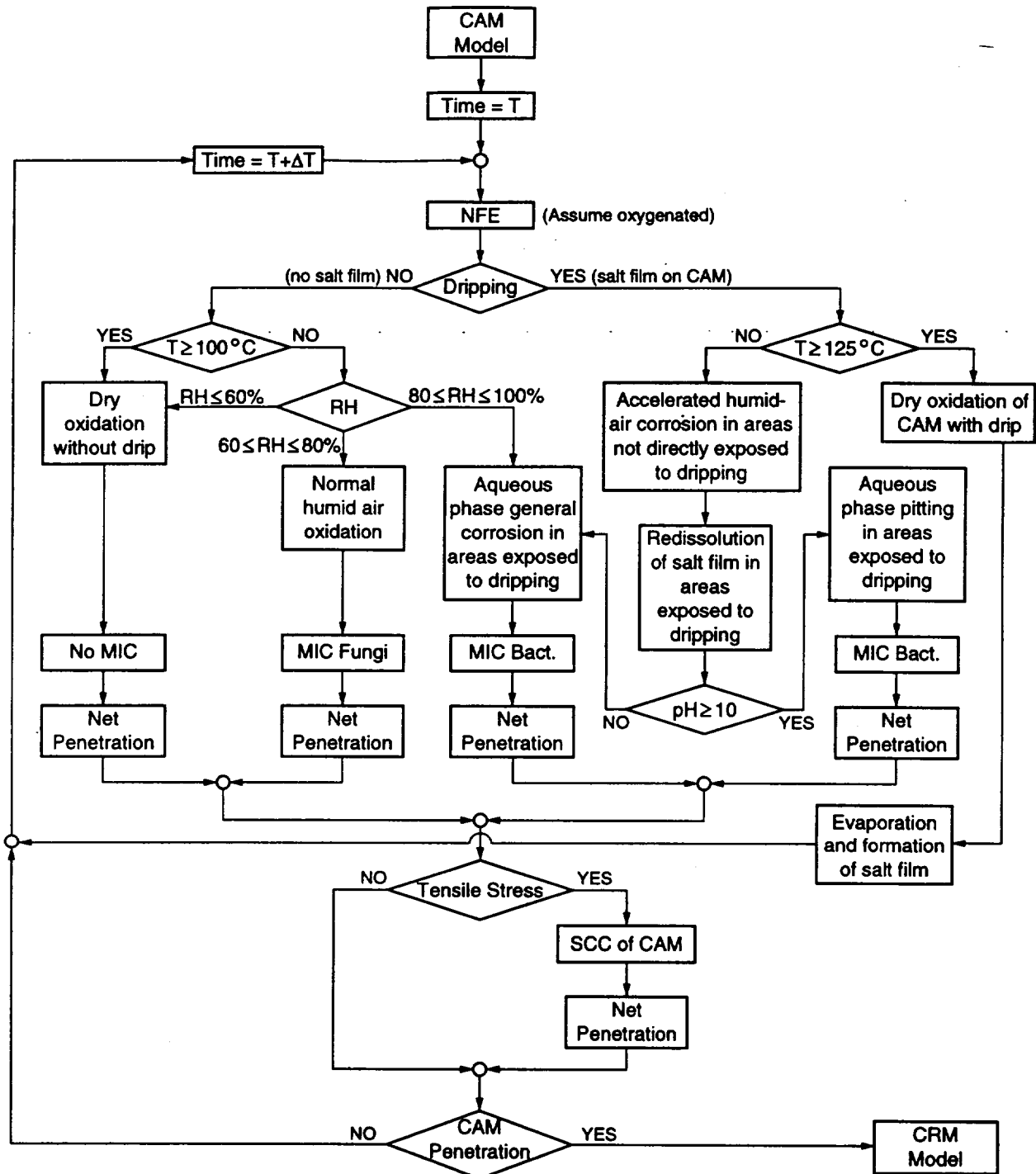


Figure JF-2 Logic diagram showing process affecting the corrosion allowance material (CAM). NFE = near-field environment; RH = relative humidity; MIC = microbiologically influenced corrosion; SCC = stress corrosion cracking; CRM = corrosion resistant materials; EBS = engineered barrier system

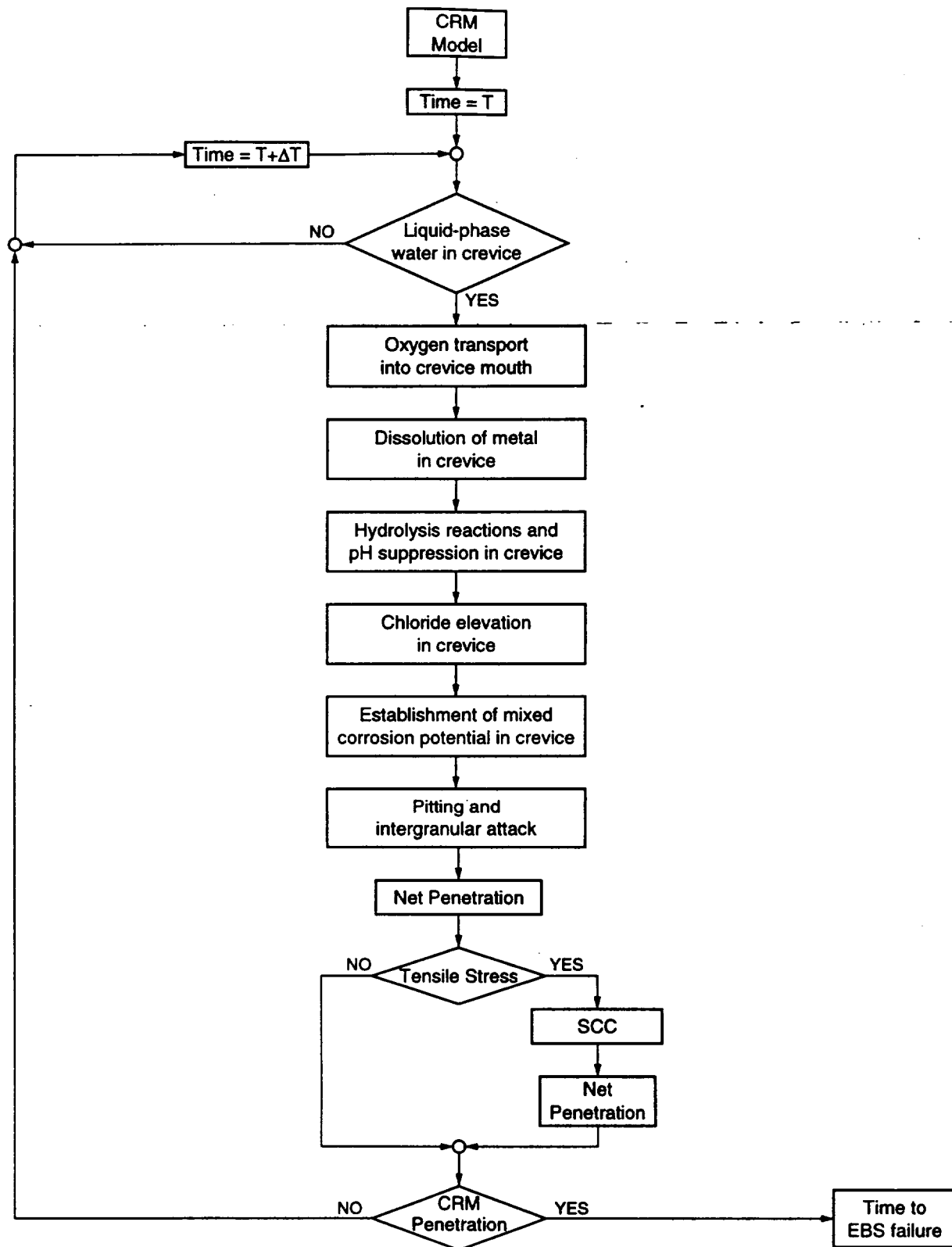
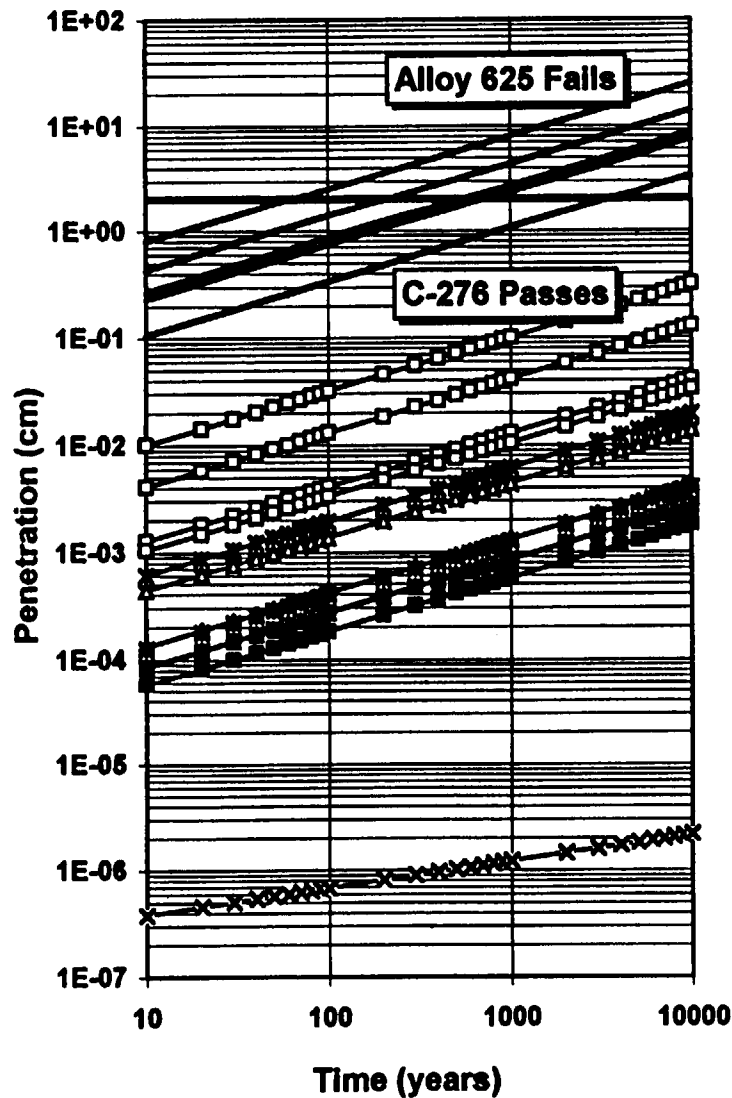


Figure JF-2 (concluded)

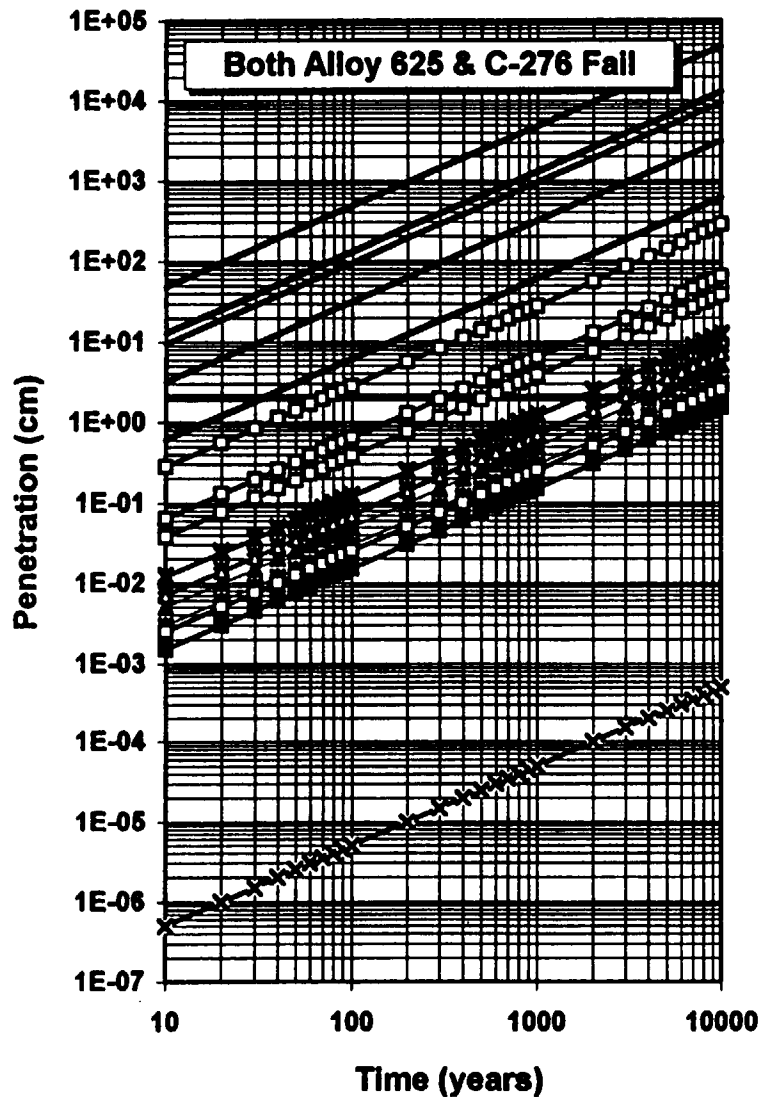
Extrapolation ($t^{1/2}$) of Penetration Rates Observed with Alloy 625 and C-276



- Limiting Value Inner Barrier Wall
- Wide Crevice Data (T20) A-625: 5% FeCl₃ & 25C
- Wide Crevice Data (T20) A-625: 5% FeCl₃ + 5% HCl & 25C
- × Wide Crevice Data (T20) A-625: 5% FeCl₃ & 50C
- × Wide Crevice Data (T20) A-625: 5% CuCl₂ & 50C
- ◆— Wide Crevice Data (T20) A-625: 5% NaOCl & 50C
- Tight (0.0755 mm) Crevice Data (T20) A-625: 5% FeCl₃ & 50C
- Grooved Block Crevice Data (T22) A-625: 10% FeCl₃ & 25C
- Grooved Block Crevice Data (T22) A-625: 10% FeCl₃ & 50C
- Grooved Block Crevice Data (T22) A-625: 10% FeCl₃ & 75C
- Grooved Block Crevice Data (T22) C-276: 10% FeCl₃ & 25C
- ▲— Grooved Block Crevice Data (T22) C-276: 10% FeCl₃ & 50C
- × Grooved Block Crevice Data (T22) C-276: 10% FeCl₃ & 75C
- × General Corrosion (T23) A-625: 7% H₂SO₄ + 3% HCl + 1% FeCl₃ + 1% CuCl₂ & 25C
- Pitting Attack (T23) A-625: 7% H₂SO₄ + 3% HCl + 1% FeCl₃ + 1% CuCl₂ & 102C
- + General Corrosion (T23) C-276: 7% H₂SO₄ + 3% HCl + 1% FeCl₃ + 1% CuCl₂ & 25C
- General Corrosion (T23) C-276: 7% H₂SO₄ + 3% HCl + 1% FeCl₃ + 1% CuCl₂ & 102C
- Sea Water - Crevice (T36) A-625: 0.61 m/s SW & 25C
- Brine - General Corrosion (T47) A-625: Holtville Brine with 3% TDS & 105C
- ×— Brine - General Corrosion (T47) C-276: Holtville Brine with 3% TDS & 105C
- ▲— General, Crevice & Pitting Attack (T50) A-625: Brine A with 306,000 ppm TDS & 250C
- General, Crevice & Pitting Attack (T50) A-625: SW & 250C
- ×— General, Crevice & Pitting Attack (T50) C-276: Brine A with 306,000 ppm TDS & 250C
- ▲— General, Crevice & Pitting Attack (T50) C-276: SW & 250C

Figure JF-3. Data Taken from UCRL-ID-108330

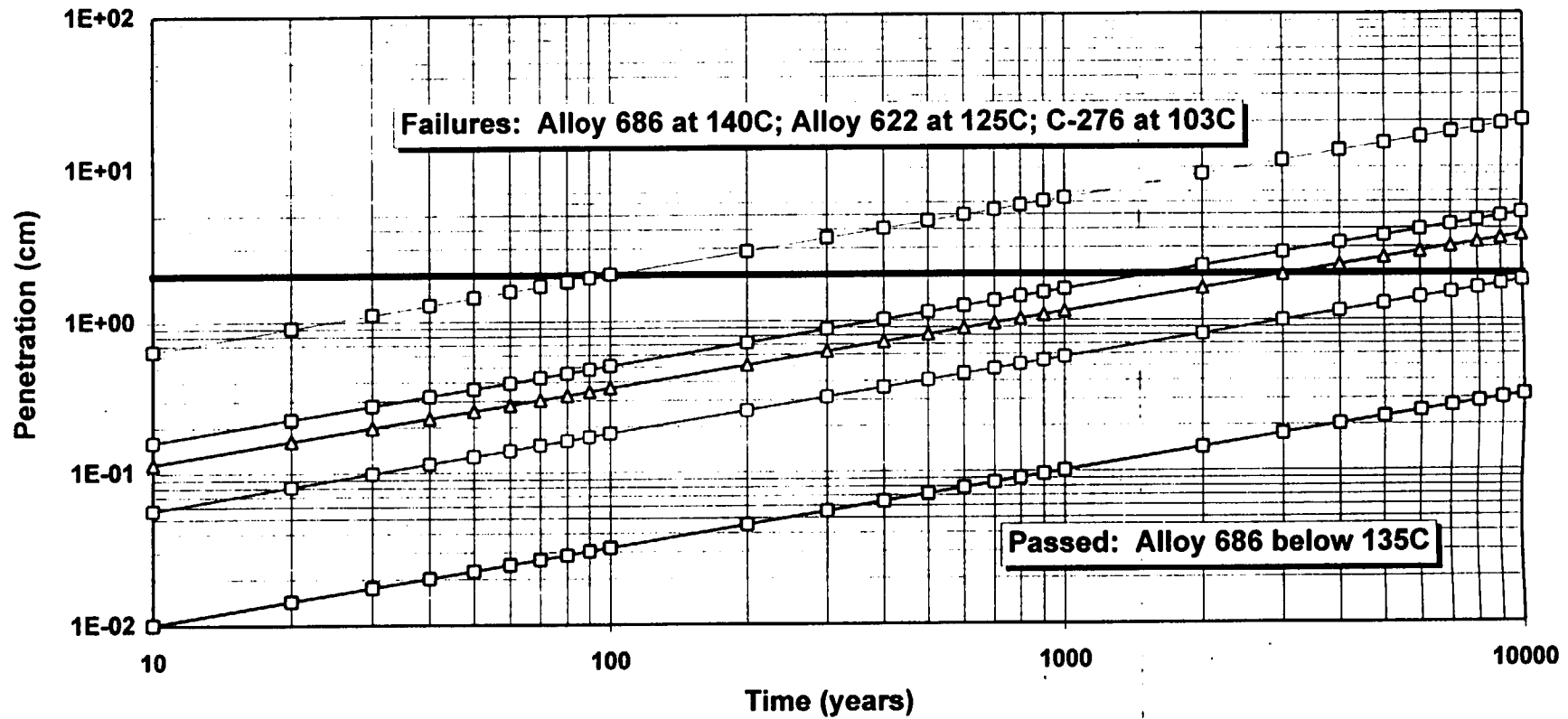
Extrapolation ($t^{1.0}$) of Penetration Rates Observed with Alloy 625 and C-276



- Limiting Value Inner Barrier Wall
- Wide Crevice Data (T20) A-625: 5% FeCl₃ & 25C
- Wide Crevice Data (T20) A-625: 5% FeCl₃ + 5% HCl & 25C
- × Wide Crevice Data (T20) A-625: 5% FeCl₃ & 50C
- ⊗ Wide Crevice Data (T20) A-625: 5% CuCl₂ & 50C
- ◆ Wide Crevice Data (T20) A-625: 5% NaOCl & 50C
- Tight (0.0755 mm) Crevice Data (T20) A-625: 5% FeCl₃ & 50C
- Grooved Block Crevice Data (T22) A-625: 10% FeCl₃ & 25C
- Grooved Block Crevice Data (T22) A-625: 10% FeCl₃ & 50C
- Grooved Block Crevice Data (T22) A-625: 10% FeCl₃ & 75C
- Grooved Block Crevice Data (T22) C-276: 10% FeCl₃ & 25C
- Grooved Block Crevice Data (T22) C-276: 10% FeCl₃ & 50C
- × Grooved Block Crevice Data (T22) C-276: 10% FeCl₃ & 75C
- ⊗ General Corrosion (T23) A-625: 7% H₂SO₄ + 3% HCl + 1% FeCl₃ + 1% CuCl₂ & 25C
- Pitting Attack (T23) A-625: 7% H₂SO₄ + 3% HCl + 1% FeCl₃ + 1% CuCl₂ & 102C
- + General Corrosion (T23) C-276: 7% H₂SO₄ + 3% HCl + 1% FeCl₃ + 1% CuCl₂ & 25C
- General Corrosion (T23) C-276: 7% H₂SO₄ + 3% HCl + 1% FeCl₃ + 1% CuCl₂ & 102C
- Sea Water - Crevice (T36) A-625: 0.61 m/s SW & 25C
- Brine - General Corrosion (T47) A-625: Holtville Brine with 3% TDS & 105C
- × Brine - General Corrosion (T47) C-276: Holtville Brine with 3% TDS & 105C
- ▲ General, Crevice & Pitting Attack (T50) A-625: Brine A with 308,000 ppm TDS & 250C
- ⊗ General, Crevice & Pitting Attack (T50) A-625: SW & 250C
- ▲ General, Crevice & Pitting Attack (T50) C-276: Brine A with 308,000 ppm TDS & 250C
- General, Crevice & Pitting Attack (T50) C-276: SW & 250C

Figure JF-4. Data Taken from UCRL-ID-108330

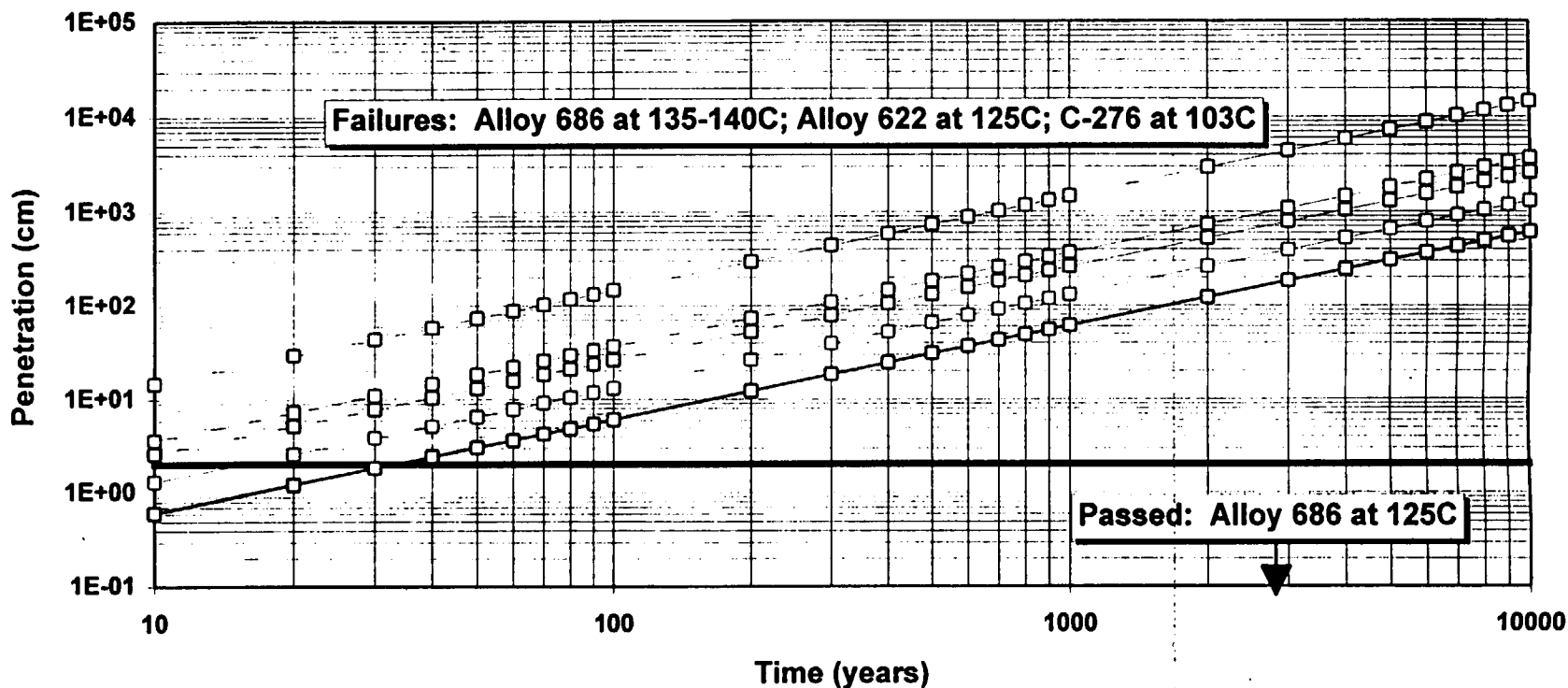
Attack of C-276 & A-686 by Green Death ($t^{1/2}$)



- Limiting Value Inner Barrier Wall
- General Corrosion (LLNL T23) C-276: 7% H₂SO₄ + 3% HCl + 1% FeCl₃ + 1% CuCl₂ & 102C
- △— Crevice Corrosion Data (INCO T14) C-276: Green Death (11.9% H₂SO₄ + 1.3% HCl + 1% FeCl₃ + 1% CuCl₂) & 103C
- Crevice Corrosion Data (INCO T14) A-622: Green Death & 125C
- x Crevice Corrosion Data (INCO T14) A-686: Green Death & 125C
- Crevice Corrosion Data (INCO T14) A-686: Green Death & 135C
- Crevice Corrosion Data (INCO T14) A-686: Green Death & 140C

Figure JF-5. Data from INCO International

Attack of Alloy 686 & C-276 by Green Death ($t^{1.0}$)



- Limiting Value Inner Barrier Wall
- General Corrosion (LLNL T23) C-276: 7% H₂SO₄ + 3% HCl + 1% FeCl₃ + 1% CuCl₂ & 102C
- Crevice Corrosion Data (INCO T14) C-276: Green Death (11.9% H₂SO₄ + 1.3% HCl + 1% FeCl₃ + 1% CuCl₂) & 103C
- Crevice Corrosion Data (INCO T14) A-622: Green Death & 125C
- x Crevice Corrosion Data (INCO T14) A-686: Green Death & 125C
- Crevice Corrosion Data (INCO T14) A-686: Green Death & 135C
- Crevice Corrosion Data (INCO T14) A-686: Green Death & 140C

Figure JF-6. Data from INCO International