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Radioactive Waste Isolation in Salt: Peer Review of the Office of Nuclear Waste Isolation's Reports on Multifactor Life Testing of Waste Package Materials

C. C. McPheeters, W. Harrison, J. C. Ditmars, A. Lerman,
D. M. Rote, D. E. Edgar, and D. F. Hambley

ARGONNE NATIONAL LABORATORY
Energy and Environmental Systems Division

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RADIOACTIVE WASTE ISOLATION IN SALT:
PEER REVIEW OF THE OFFICE OF NUCLEAR WASTE ISOLATION'S REPORTS ON MULTIFACTOR LIFE TESTING OF WASTE PACKAGE MATERIALS

by

C.C. McPheeters,* W. Harrison, J.D. Ditmars, A. Lerman,**
D.M. Rote, D.E. Edgar, and D.F. Hambley

Energy and Environmental Systems Division
Geoscience and Engineering Group

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August 8, 1984

NOTICE TO READERS

At the request of the Salt Repository Project Office (SRPO), Argonne National Laboratory carried out a review of two closely related reports entitled, "Design of a Multifactor Life Test to Investigate Uniform Corrosion of Low-Carbon Cast Steel as a Nuclear Waste Package Overpack Material in a Salt Repository Environment," ONWI O/TM-48,* and "Methodology for Predicting the Life of Waste Package Materials and Components Using Multifactor Accelerated Life Tests," ONWI-501. The two documents provide the approaches in designing a test program to investigate uniform corrosion of low-carbon cast steel in a salt repository environment. The results of the test will provide the characteristics of the reference overpack material and the data base necessary to support design, modeling, and licensing activities associated with the salt repository project.

Specific instructions were provided to the review panel to define the scope of the review. The panel also reviewed the documents from the overall point of view. Valuable comments were provided that should contribute to the quality of the documents and the improvement of the design of our test program.

RCWunderlich

R. C. Wunderlich
Deputy Project Manager
Salt Repository Project Office

SRPO:KKW:max:3228B

ST# 746-84

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*A microfiche copy of this report is attached to the inside back cover of this report.

FOREWORD

Documents are being submitted to the Salt Repository Project Office (SRPO) of the U.S. Department of Energy (DOE) by Battelle Memorial Institute's Office of Nuclear Waste Isolation (ONWI) to satisfy milestones of the Salt Repository Project of the Civilian Radioactive Waste Management Program. Some of these documents are being reviewed by multidisciplinary groups of peers to ensure DOE of their adequacy and credibility. Adequacy of documents refers to their ability to meet the standards of the U.S. Nuclear Regulatory Commission, as enunciated in 10 CFR Part 60, and the requirements of the National Environmental Policy Act and the Nuclear Waste Policy Act of 1982. Credibility of documents refers to the validity of the assumptions, methods, and conclusions, as well as to the completeness of coverage.

Since late 1982, Argonne National Laboratory has been under contract to DOE to conduct multidisciplinary peer reviews of program plans and reports covering research and development activities related to siting and constructing a mined repository in salt for high-level radioactive waste. This report summarizes Argonne's review of two ONWI documents. The first report is an internal technical memorandum that treats the design of a multifactor life test to investigate uniform corrosion of low-carbon cast steel. This steel is being considered for use as an overpack material for nuclear waste packages to be emplaced in a mined repository in salt. The second document is a published report that covers the methodology used by ONWI to predict the life of waste package materials, a methodology used, in part, by the authors of the internal technical memorandum.

Argonne was requested by DOE to review these reports on May 14, 1984 (see App. A). The review procedure involved obtaining written comments on the reports from four members of Argonne's core peer review staff and from two Argonne experts and one extramural expert in related research areas. The peer review panel met at Argonne on June 11, 1984, and reviewer comments were integrated into this report by the review session chairman, with the assistance of Argonne's core peer review staff. All of the peer review panelists concurred in the way in which their comments were represented in this report (see App. B). A draft of this report was sent to SRPO on June 21, 1984.

PREVIOUSLY PUBLISHED REPORTS IN THE SERIES

"RADIOACTIVE WASTE ISOLATION IN SALT"

ANL/EES-TM-242	Peer Review of the Office of Nuclear Waste Isolation's Geochemical Program Plan (Feb. 1984)
ANL/EES-TM-243	Peer Review of the Office of Nuclear Waste Isolation's Socioeconomic Program Plan (Feb. 1984) (revised July 1984)
ANL/EES-TM-246	Peer Review of the Office of Nuclear Waste Isolation's Plans for Repository Performance Assessment (May 1984)
ANL/EES-TM-254	Peer Review of the Office of Nuclear Waste Isolation's Reports on Preferred Repository Sites within the Palo Duro Basin, Texas (June 1984)
ANL/EES-TM-256	Special Advisory Report on the Status of the Office of Nuclear Waste Isolation's Plans for Repository Performance Assessment (Oct. 1983)
ANL/EES-TM-258	Peer Review of the Office of Nuclear Waste Isolation's Plan to Decommission and Reclaim Exploratory Shafts and Related Facilities (July 1984)
ANL/EES-TM-259	Peer Review of the Office of Nuclear Waste Isolation's Final Report on the Organic Geochemistry of Deep Groundwaters from the Palo Duro Basin, Texas (Aug. 1984)
ANL/EES-TM-260	Peer Review of the Texas Bureau of Economic Geology's Report on the Petrographic, Stratigraphic, and Structural Evidence for Dissolution of Upper Permian Bedded Salt, Texas Panhandle (Aug. 1984)
ANL/EES-TM-261	Peer Review of the Office of Nuclear Waste Isolation's Report on Functional Design Criteria for a Repository for High-Level Radioactive Waste (Aug. 1984)
ANL/EES-TM-262	Peer Review of the D'Appolonia Report on Schematic Designs for Penetration Seals for a Repository in the Permian Basin, Texas (Sept. 1984)

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FIGURE

* * *

A microfiche copy of the following unpublished document is attached to the inside back cover of this report: R. Cote and R. Thomas, *Design of a Multifactor Life Test to Investigate Uniform Corrosion of Low-Carbon Cast Steel as a Nuclear Waste Package Overpack Material in a Salt Repository Environment*, Office of Nuclear Waste Isolation internal technical memorandum O/TM-48, Battelle Memorial Institute, Columbus, Ohio (April 1984).

The second report reviewed herein -- R.E. Thomas and R.W. Cote, *Methodology for Predicting the Life of Waste-Package Materials and Components using Multifactor Accelerated Life Tests*, Office of Nuclear Waste Isolation report ONWI-501 (Sept. 1983) -- has been formally published and may be ordered from Battelle Memorial Institute, Columbus, Ohio.

RADIOACTIVE WASTE ISOLATION IN SALT:

PEER REVIEW OF THE OFFICE OF NUCLEAR WASTE ISOLATION'S REPORTS ON MULTIFACTOR LIFE TESTING OF WASTE PACKAGE MATERIALS

by

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SUMMARY OF RECOMMENDATIONS

This Argonne report reviews two related documents prepared by Battelle Memorial Institute's Office of Nuclear Waste Isolation (ONWI): *Design of a Multifactor Life Test to Investigate Uniform Corrosion of Low-Carbon Cast Steel as a Nuclear Waste Package Overpack Material in a Salt Repository Environment*, O/TM-48, an ONWI internal technical memorandum that is relatively preliminary in nature, and *Methodology for Predicting the Life of Waste-Package Materials and Components Using Multifactor Accelerated Life Tests*, ONWI-501, a previously reviewed and published report. The following recommendations for improving the two documents have been abstracted from the body of this review report. In general, the peer review panelists found serious deficiencies in O/TM-48, while ONWI-501 was judged to be generally understandable and useful, although certain amplifications of the methodology were deemed desirable.

O/TM-48: DESIGN OF A MULTIFACTOR MATERIAL-LIFE TEST

This report should be revised and augmented to:

1. Explain the relationship between the methodology for accelerated material-life testing, as described in ONWI-501, and the long-term test design being considered in O/TM-48.

2. Show how the proposed testing relates to other corrosion testing in ONWI's national waste package program, with particular attention to completed and ongoing testing.

3. Document the reasons for selecting uniform corrosion as the basis of the test program and low-carbon steel as the test material.

4. Provide an adequate connection between the body of the report and the recommended, but unsupported, test plan in Table 6.

5. Describe more completely the method of "pruning" used to reduce the complete factorial design shown in Table 2 to the experimental matrix given in Table 6.

6. Follow the guidelines of ONWI-501 more closely, particularly those related to documentation of the essential aspects of test-plan formulation.

7. Describe the types of data to be collected and discuss how these data will be used in demonstrating compliance with U.S. Nuclear Regulatory Commission criteria and guidance.

The manner of presentation in O/TM-48 should be improved by:

1. Providing at the beginning of the report a section on background, objective (or purpose), and scope.

2. Defining upon first use the terms "overpack" and "reference overpack material."

3. Including information on the theoretical or experimental areas covered by the panelists and their duties and responsibilities as participants in the test design group.

4. Giving examples of how the design team attempted to carry out each step of the method given in ONWI-501.

5. Providing complete definitions for each variable or parameter in Table 1, together with the rationale for their selection.

6. Specifying the two types of brine studied by using a notation other than "e" and "1/e."

7. Explaining what is involved in modifying the test matrix "as more data become available from experiments currently underway."

8. Informing the reader of the relationship of App. A to the rest of the document and clarifying many of the bulleted items in that appendix.

9. Relating information on brine composition to published references, wherever possible.

ONWI-501: METHODOLOGY FOR PREDICTING MATERIAL LIFE

The authors of this report should have:

1. Provided stronger and more specific links between two generic concepts, performance degradation and time to failure, and the objectives of uniform corrosion testing, the primary type of life testing being addressed.

2. Expanded the discussions of the test stresses to include consideration of the stress characteristics that may frustrate the appropriate and successful application of the methodology.

3. Provided specific guidance on the method of predicting failure or long-term performance once hypothetical or real test results are available (or deleted the words "methodology for predicting" from the title).

The understandability of ONWI-501 would be improved if it:

1. Explained how the equation on page 42 is related to the original reaction rate model of Eyring. The mathematical form alone is not sufficient to call the equation "the Eyring model."

2. Provided improved descriptions of the procedures given for computing the values used in the factorial tables and hierarchical trees.

3. Addressed the issue of variable uncertainty in the corrosion rate estimates and its potential effect on the analysis.

1 INTRODUCTION

Corrosion-resistant waste package materials are important components of the engineered barriers of a nuclear waste isolation system. A durable container (overpack) for the waste canister should prevent hydrothermal interactions between the canister and the waste form it contains. Battelle Memorial Institute's Office of Nuclear Waste Isolation (ONWI) is under contract to the U.S. Department of Energy's (DOE's) Salt Repository Project Office (SRPO) to design an overpack to isolate commercial high-level radioactive waste in a repository constructed in salt.

Argonne National Laboratory conducted a peer review of ONWI's design of a test to investigate uniform corrosion of low-carbon cast steel overpack materials, as reported in an ONWI internal technical memorandum, O/TM-48: R. Cote and R. Thomas, *Design of a Multifactor Life Test to Investigate Uniform Corrosion of Low-Carbon Cast Steel as a Nuclear Waste Package Overpack Material in a Salt Repository Environment* (1984). The Argonne review also considered an ONWI methodology for predicting the life of waste package materials through use of multifactor accelerated corrosion tests, a methodology detailed in a published ONWI report, ONWI-501: R. Thomas and R. Cote, *Methodology for Predicting the Life of Waste-Package Materials and Components Using Multifactor Accelerated Life Tests* (1983).

Argonne's peer review involved obtaining written critiques of both ONWI documents from four members of Argonne's core peer review staff and from two Argonne experts and one extramural expert in related research areas. The Argonne panelists then reviewed all of the comments, and the review session chairman drafted the present report, with the assistance of Argonne's core peer review staff. Panelists did not contact ONWI personnel, and none of the panelists have been involved in any programs sponsored by DOE or directed by ONWI such that their participation in the review could be construed as a conflict of interest.

Although no specific guidance was provided to Argonne by DOE/SRPO on how the review of the two reports was to be conducted, a set of questions and requests for comments were prepared by DOE/SRPO to assist in the review process (see App. A). These questions and requests for comments form the basis of Sec. 5 of this report. In addition, Secs. 2 and 3 relate the test design report, O/TM-48, to regulatory requirements and recommend improvements in the presentation of material in O/TM-48, respectively. Section 4 considers a variety of technical issues related to both ONWI reports, and Sec. 6 presents a page-by-page commentary.

2 REGULATORY ISSUES AND O/TM-48

Both the U.S. Environmental Protection Agency (EPA) and the U.S. Nuclear Regulatory Commission (NRC) have developed regulations pertinent to the performance of repositories for high-level radioactive waste. Because the EPA standards are not yet in final form, only NRC regulations are considered in the following discussion.

Waste package performance is addressed by NRC in several sections of 10 CFR Part 60 (U.S. Nuclear Regulatory Commission, 1981). Package integrity is of concern relative to Sec. 60.111(b), which requires that the ability to retrieve waste be maintained for up to 50 years after waste emplacement operations begin. More specifically, Sec. 60.113(a)(1)(ii)(A) states that "containment of HLW [high-level waste] within the waste packages will be substantially complete for a period to be determined by the Commission ... provided that such period shall be not less than 300 years nor more than 1000 years after permanent closure of the geologic repository," and Sec. 60.113(a)(1)(ii)(B) stipulates that "the release rate of any radionuclide from the engineered barrier system following the containment period shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1000 years following permanent closure ..." Section 60.135(a)(1) further requires that "packages for HLW shall be designed so that the in situ chemical, physical, and nuclear properties of the waste package and its interactions with the emplacement environment do not compromise the function of the waste packages or the performance of the underground facility or the geologic setting." Finally, Sec. 60.143 presents information on the monitoring and testing program required to evaluate waste package performance before repository closure.

The Nuclear Regulatory Commission has published a draft technical position on waste package performance after repository closure (Davis and Schweitzer, 1983), which presents the major issues and problems associated with evaluating the ability of a waste package to comply with the performance objectives and the criteria and design requirements stipulated in 10 CFR Part 60 in general, and those in Sec. 60.113 in particular. This document notes that several alternatives are available to address the performance criteria. In general, the objectives may be achieved by the whole waste package or by the individual components (waste form[s], container system, and packing). As stated in Davis and Schweitzer (1983, p. 6-7), NRC's preferred approaches for ensuring compliance of a waste package with NRC criteria are, in decreasing order of acceptability:

1. Combinations of independent high-integrity components which, by their individual behavior, can satisfy the NRC criteria (i.e., redundant compliance).

2. A single component which, by itself, can satisfy the NRC criteria, in combination with other barriers that may not individually meet these criteria (single compliance).

3. Combinations of components that cooperatively comply but individually do not completely satisfy the proposed NRC criteria. These components acting together can be assigned, with some level

of assurance, credit for complying with the performance objectives (composite compliance). The package constructed from these components should satisfy the 300- to 1000-year containment requirement.

Each of these options involves different considerations in terms of demonstrating "reasonable assurance" of the necessary compliance with the performance criteria.

Davis and Schweitzer (1983) identified a number of major, generic issues related to reducing the uncertainties in waste package performance after repository closure (i.e., issues that are independent of material and design choices and specific repository site conditions). These generic issues are (1) characterization of repository water and groundwater attributes, including chemistry and flow rates; (2) anticipated repository temperatures; (3) predictability of accelerated testing of waste package materials (i.e., mechanisms responsible for aging and estimated rates of degradation identified under accelerated conditions may not be applicable to normal stress conditions); (4) radiation effects; (5) total package testing, as opposed to testing of only individual components; (6) use of statistics to demonstrate compliance; and (7) use of modeling. Davis and Schweitzer's publication should be consulted for the details of each of these issues and the corresponding NRC positions.

It is difficult to evaluate the test design presented in O/TM-48 in terms of NRC requirements because the testing effort described there is presumably only one portion of DOE's waste package program and because NRC apparently will require that compliance be demonstrated for the entire package and engineered barrier systems. It was assumed during this review that compliance would not be based solely on the performance of this low-carbon cast steel overpack component of the package.

The existing report would benefit from the addition of a section that describes the relationship of this particular testing activity to the larger waste package program and presents the current thinking on how the program will address NRC licensing requirements. This discussion should present the rationale for selecting low-carbon steel as the test material and for evaluating uniform corrosion rather than other modes of chemical failure (such as pitting corrosion, crevice corrosion, galvanic corrosion, stress corrosion, selective leaching, and hydrogen embrittlement) and should provide information on the other materials and degradation mechanisms that are being considered and tested for other package components. The discussion should also recognize that the testing program is to provide the information necessary for licensing and address the issues identified by NRC. Although some information on completed tests is presented in App. A of O/TM-48, it is difficult to determine how these test results are related to proposed tests, to each other, or to the entire waste package program.

One of the regulatory concerns presented by Davis and Schweitzer (1983) is that the anticipated repository environment of the package be accurately characterized and that the testing program be representative of these conditions. The two brines to be used in the proposed tests are identified as Permian Basin Brines 1 and 2, and their ionic concentrations are presented in App. B of O/TM-48. The basis for selecting these compositions and the evidence that such compositions are representative of anticipated repository conditions should be described.

Additional details should be provided on the specifics of the experimental methodology and the types of data to be collected. Although an experimental matrix is presented, details on these two topics are lacking. Two fundamental issues raised by Davis and Schweitzer (1983) are the detailed physical and chemical processes operative at the metal-fluid interface (e.g., do corrosion products remain on the metal or are they removed to expose new material?) and the effect of the package and degradation products on fluid chemistry. The existing discussion provides no information on whether these topics will be evaluated during the course of the experiments.

Some difficulties exist in evaluating the specific information needs for license application. The existing NRC criteria contain terms such as "reasonable assurance" and "substantially complete containment." Because these terms are unclear, additional guidance and clarification by NRC will be required to ensure that information provided by DOE is appropriate. Davis and Schweitzer (1983) correctly note that evaluating whether a waste package complies with regulatory criteria requires judgment. They also note that "reasonable assurance" is the concept to be used to determine whether the data, models, and rationale submitted justify the performance claimed. Here, too, reasonable assurance requires judgment.

In general terms, it appears that the experimental program described in O/TM-48 is intended to collect some of the data required to support the application for a repository license. However, because of the qualitative nature of the criteria and the absence of specific guidelines for obtaining requisite information for their evaluation, the ability of the proposed experimental program to meet anticipated licensing requirements cannot be objectively evaluated with any reasonable degree of certainty.

3 SUGGESTIONS TO IMPROVE PRESENTATION IN O/TM-48

As presently written, O/TM-48 is sometimes difficult to understand and lacking in needed detail. The following suggestions should assist the authors in their next revision.

3.1 INTRODUCTORY MATERIAL

3.1.1 Need for a Section on Background, Objective, and Scope

Strong statements of background, objective, and scope are needed at the beginning of O/TM-48. Although the first paragraph in the Introduction (p. 1)* is a statement of objective and scope, it is so brief as to be frustrating. At a minimum, it raises the following important questions:

- Is this the only corrosion test matrix under test by ONWI?
- Has ONWI prepared a document describing a design-basis scenario that specifies expected repository conditions as a function of time (e.g., oxygen potential, temperature, stress, radiation level, and brine quality)?
- Are the data from this test program expected to provide the entire corrosion "data base necessary to support design, modeling, and licensing activities ..."?

Another statement of objective is found on page 3: "... obtain a statistically sound data base on the performance of low-carbon cast steel in a salt repository environment ..." This statement is too broad. Only one corrosion mechanism is addressed in this document -- uniform corrosion. The term "performance" implies an entire spectrum, not just one performance measure.

Between the title, the introduction, the section on results, and App. A, one can almost form a picture of the overall corrosion program, where this test program fits in, and the scope of the testing activity. However, a separate section that clearly describes these things would be much more helpful, as would a description of the relationship between ongoing and completed tests and the test design.

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*All page, table, and figure numbers, as well as section headings, are from O/TM-48 unless otherwise specified.

3.1.2 Definition of *Overpack* and Explanation of Its Importance

Inasmuch as the term *overpack* is used in the title, it should be defined clearly upon its first use. The following definition would appear adequate: secondary external containment for the waste canister, or the metallic container into which the canister is placed.

The authors should also explain why overpack materials, rather than canister materials, are being addressed. If different lifetimes (corrosion properties) are being contemplated, the authors should explain why. The Introduction mentions "the reference overpack material," but does not explain what is involved. Since the authors state that "the results of this work will be used to characterize the reference overpack material ...," it is extremely important that said reference overpack material be defined.

3.1.3 Areas of Expertise, Roles, and Affiliations of Key Participants

The names and affiliations of 10 key participants of the test design group are given in the Introduction. The credibility of this group may be beyond question, but readers unfamiliar with the individuals cannot make that judgment. At the very least, the theoretical or experimental areas of expertise of these individuals should be indicated. (An appendix containing one-page resumés for each participant would also be desirable.) The roles of the panelists -- such as committee duties and responsibilities -- should also be spelled out.

The composition of the group is likely to raise questions. Why are 9 of the 10 participants affiliated with Battelle's Pacific Northwest Laboratory? Were so many of the participants selected from that laboratory because of travel considerations or for ease of interaction? Other national laboratories are studying the corrosion of waste package materials and could have supplied team members who "represent the various scientific disciplines that are associated with the physics of the degradation process" (ONWI-501, p. 5). Sandia National Laboratories, in particular, could have undoubtedly supplied participants with extensive, useful experience in the corrosion of waste package materials by repository brines.

To summarize, an adequate case must be made for the credibility of the test design group. At present, critical readers would be unconvinced that the "responsibility for the accelerated test designs [has been assigned] to a highly competent team of independent scientists selected to represent an appropriate mix of scientific and statistical disciplines" (ONWI-501, p. 1).

3.2 TEST DESIGN METHODOLOGY

In the Test Design Methodology section of O/TM-48, examples should be given of how the design team attempted to carry out each step of the method given in ONWI-501. Such an approach would provide a needed logical structure for the subsequent explanation under "Results." For example, under the first bullet on page 2, the nature of the multidisciplinary team and how it functioned could be explained. Under the second bullet, an example could be given of how the team's test matrix reflected "both the (statistical) experimental design and the data analysis characteristics that are required to identify magnitudes of different stresses and their interactions." Under the third bullet, details could be presented on how a team member made "quantitative predictions of the experimental outcomes associated with each combination of stresses."

In addition, the authors should explain the relationship between the methodology for accelerated life testing (ONWI-501) and the long-term test design being considered in O/TM-48. Such additional information, presented in a logical step-by-step fashion, would greatly improve the understandability of O/TM-48.

3.3 RESULTS

The first paragraph of the Results section (p. 3) deals with objectives and should be moved to the Introduction or placed under a new heading or subheading, such as "Objectives and Scope."

The second paragraph on the same page indicates that the five bullets that follow cover key results and conclusions from the initial meeting of the test design team. (However, the second bullet on page 4 may be irrelevant to the present program.) It is not clear whether the text that follows the fifth bullet covers additional results of the first meeting. If not, appropriate subheadings are necessary, beginning at the top of page 5.

Also, in the second paragraph on page 3, "the dominant failure mechanism" is identified as uniform corrosion, but no explanation is given for its selection. Because the choice of a dominant failure mechanism is a critical issue, the basis for the choice should be described in detail.

The title of Table 1 (p. 5) is confusing. Are the words "associated with" equivalent to "chosen by the test design team for"? How were values for temperature, radiation, brine composition, and SA/V selected? Is the parameter SA/V a flow rate, as indicated in Table 1, or a surface-area-to-volume ratio (and related flow rate), as defined on page 15? What is implied by "Flowing, Static" opposite SA/V in Table 1? For the document to be understandable, complete definitions are needed for each variable or parameter, as is a statement of the rationale for selecting the values for each.

Specification of the two types of study brines by means of the notation "l/e" and "e" (p. 7) is completely meaningless as far as the chemical characteristics of the brines are concerned. It may be a matter of algebraic expedience, but no one can tell anything about a brine that has been identified as "l/e."

3.4 SUMMARY

The conclusion of the Summary (pp. 15-16) is unclear. A better explanation is needed of how the test matrix will be modified "as more data become available from experiments currently underway." The kinds of data that will be forthcoming should be described, as should the experiments that are underway. The overall relationship between O/TM-48 and the actual testing program should also be explained.

3.5 APPENDIX A

The title to App. A in O/TM-48 does not make sense. What is meant by "matrix of structural barriers tests"? Also, what is the context for this matrix? What relationship does it have to the rest of the document? Which individuals or what groups conducted each test? It is desirable that the tests be related to published references, if any are available.

Many of the bullets describing test conditions need clarification or amplification to make them understandable to readers unfamiliar with the jargon used in the field of corrosion testing. For example, how does one interpret the following?

- Orientations = TL, LT [Test 3]
- Samples = corrosion coupons [Test 2c]
- Orientations = through-thickness, parallel to surface [Test 6]

Finally, although the title of this appendix includes the words "tests completed," the status of Test 2b and parts of Tests 3 and 4 is given as "in progress" and that of Test 6 as "initiated November 1983." This basic confusion should be resolved.

3.6 APPENDIX B

It is generally desirable to relate brine compositions to published references wherever possible. For example, the stratigraphic positions from whence the brines came may prove to be important to performance assessment considerations at some later date. Also, one could question the composition of Brine No. 3, whose listed chemical composition is not well balanced. The concentrations of the cations exceed those of the anions by about 18% (cations: 6.388 equivalents/liter; anions: 5.957 equivalents/liter). There is either too much of something on the positive side or too little on the negative side, or both.

4 TECHNICAL CONSIDERATIONS

4.1 O/TM-48: DESIGN OF A MULTIFACTOR MATERIAL-LIFE TEST

4.1.1 Specification, Description, and Application of Key Stresses

Specification of Key Stresses. The O/TM-48 report deals with the corrosion effects of four stresses: temperature (70°, 150°, and 250°C), radiation (10^3 and 10^5 rad/hour), brine composition (intrusion and inclusion brines), and brine flows (static and flowing).

If the effects of pressure at the in situ conditions of waste-package burial are insignificant (i.e., if lithostatic or hydrostatic pressures do not affect the anticipated corrosion rates), this should be stated clearly in the report. Also, it seems surprising that SA/V (flow) is considered more important than air/no-air conditions. Flow of brine will only occur under accident conditions (repository flooding), while air will certainly be present after emplacement and for a significant fraction of the life of the containers. Is this an experimental convenience or a belief on the part of the team that brine flow is more realistic or a higher stress than the presence of air? Consider that Basham (1984, p. 281) found that for cast steel, oxic conditions resulted in higher corrosion rates than anoxic conditions.

Description and Application of a Key Stress. Brine composition, one of the four key stresses, is not adequately described in terms of the main parameters that can be monitored and those that can affect the corrosion reactions. Appendix B gives the compositions of three brines. Brines 1 and 2 are very similar to each other and are referred to in the text as intrusion brines, while Brine 3 is the inclusion brine. The intrusion brines are close to saturation with respect to NaCl. It is likely that NaCl would either precipitate from the solution or dissolve from the host rock, but whether it did would depend on local changes in temperature and brine composition.

Brines 1 and 2 contain calcium and sulfate, about 4.5 grams $CaSO_4$ per liter in Brine 1 and 2.7 grams $CaSO_4$ per liter in Brine 2. Solubilities of $CaSO_4$ (solid-phase gypsum, $CaSO_4 \cdot 2H_2O$) in pure water and in NaCl aqueous solutions bracket the $CaSO_4$ concentrations in the subject Permian brines:

H_2O, 65°-100°C: solubility 1.9 to 1.6 grams $CaSO_4$ per liter 260-320 grams NaCl per liter, 25°C: solubility 6.5 to 5.7 grams $CaSO_4$ per liter	} Seidell's solubilities of inorganic compounds

From the above solubility values, it is conceivable that gypsum could precipitate locally.

Identification of a key stress, such as brine composition, can be very misleading. The initial brine composition can change greatly during the process of corrosion and irradiation of the brine and the host rock. Evidence for the occurrence of such dissolved species as OCl^-, HOCl, and H_2 in brines of irradiated salt has been given by Jenks et al. (1975). Levy (1983) reported that when rock salt is irradiated for variable periods at 150°C, significant quantities of Na-gel are formed, accompanied by evolution of chlorine gas. Such a rock salt, if it were in contact with water, would be likely to react and produce NaOH and H_2, making the brine highly alkaline. The stress intensity of the brine would be determined by the extent to which this hypothetically high concentration of OH^- ions could be neutralized by acidic species.

Such brine composition parameters as Cl^-, HS^-, H_2S, HCO_3^-, and CO_2 are listed in Table 1 (p. 5) in the category of "brine dictated." Although this designation takes into account the possibility that their concentrations will vary during the time of corrosion, it tells nothing about which of these chemical species may be more stressful than the others. The distinction between the two kinds of brines -- Brines 2 and 3 -- is based on the magnesium concentration. However, other important chemical parameters must be considered to be among the "stressful characteristics" of a brine, such as:

- Oxidation and reduction of sulfur-containing species.
- Precipitation or dissolution of minerals in the host rock (primarily NaCl and $CaSO_4$).
- Formation of exotic chemical species caused by prolonged irradiation of the host rock, including the ionic species and dissolved gases.
- Possible roles of the electrical potentials at the steel-brine and brine-salt interfaces.
- Development of variably acidic or alkaline conditions in the course of active corrosion.

4.1.2 Applicability of Eyring Model to Data

The mathematical formulation of the rate of corrosion is given on page 7 in the following form:

$$CR = Ae^{B/T}(R)^{C+D/T}\,(BR)^{E+F/T} \qquad (1)$$

where:

CR = corrosion rate (length/time),

R = radiation,

T = temperature, and

BR = brine.

Parameters A through F can be obtained statistically from the "consensus data" on the corrosion rate CR. Equation 1 can be simplified to:

$$CR = K e^{a/T} \tag{2}$$

by making the following substitutions:

$K = A(R)^C(BR)^E$,

$\ln(R) = r$,

$\ln(BR) = b$, and

$a = B + rD + bF$.

Although Eq. 2 does not distinguish between the effects of individual stress factors, it gives an identical dependence of the corrosion rate on temperature and other parameters. Thus, if the corrosion rate CR were determined at different temperatures, keeping all the other parameters at their constant values (i.e., presumably independent of temperature), then the graphs of ln(CR) plotted against 1/T would be identical. The data in Tables 4 and 5 give consensus estimates of the corrosion rates at three temperatures for two brines and two levels of radiation, for a total of $3 \cdot 2^2 = 12$ corrosion rate values. These data are shown plotted in Fig. 1 and consist of two curves for a low-magnesium brine (brine "1/e") and two curves for a high-magnesium brine (brine "e"), for low and high radiation levels, respectively.

If the Eyring model held for the results, the three data points (three temperatures) for each consensus experiment would fall on a straight line. As Fig. 1 shows, however, considerable departures from linearity are clearly visible to the eye, with no need for statistical analysis of the data. Thus, a conclusion that the Eyring model does not apply to the data should be drawn for the entire set of the consensus estimates, not only for the high-temperature portion of the set.

To determine whether the Eyring model is appropriate to corrosion of iron in a radiation field in saline brines at elevated temperatures, the behavior of the individual stress factors and their interactions must be examined. Obtaining a statistically good fit of the consensus estimates to the Eyring model cannot be meaningful if the individual estimates are based on different corrosion-mechanism models.

For the three temperature data points (see Fig. 1), either the Eyring (or Arrhenius) model does not fit or the power exponents (B, D, F, and a) in Eqs. 1 and 2 are temperature dependent. Such a conclusion is obviously unsatisfactory.

One of the problems seems to lie in the definition of the stress factors. Brine composition is not a sufficiently precise stress factor, as explained earlier, and the

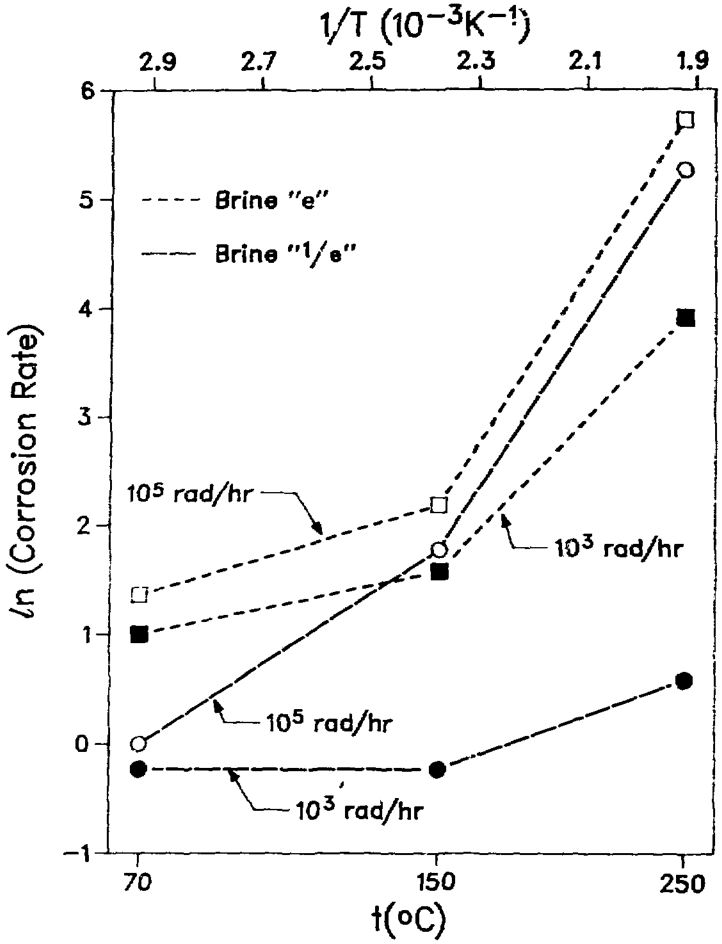

FIGURE 1 Natural Log of Corrosion Rate versus Inverse of Temperature for Data of Tables 4 and 5

additional stresses originating from the irradiated host rock have not been explicitly included in the model. To test the applicability of the Eyring model, one must know more about the corrosion mechanism, which requires a better understanding of the chemical changes taking place in a system comprised of an iron alloy, salt brine, and a host rock. A departure from the simple Arrhenius, or Eyring, plot -- such as that shown in Fig. 1 -- may also indicate that the mechanism of the chemical reaction changes with temperature. If this is the case, understanding the relevant mechanisms is indispensable to successful modeling.

4.2 ONWI-501: METHODOLOGY FOR PREDICTING MATERIAL LIFE

The technical purpose of the ONWI document is clear. However, the scope and objective of the technical discussion and the depth to which some topics are covered are not always well defined. The report title, *Methodology for Predicting the Life of Waste-Package Materials and Components Using Multifactor Accelerated Life Tests,* is probably the best statement of objective in the document.

With a few specific exceptions, the technical aspects of the administrative approach (Sec. 2) and the mechanical aspects of the technical approach (Sec. 3 and Apps. A, B, and C) are relatively clear and understandable. While the discussion of the mechanics of factorial tables and hierarchical trees is quite complete, the discussion of the two aspects of multifactor accelerated life tests that logically follow that topic are incomplete, or at least confusing. These important aspects are (1) technical definition of the objectives of the tests and related definitions of the stresses and (2) extrapolation of test results to predict behavior, or time to failure, at end-use conditions. Both items receive somewhat scant attention, as in Secs. 4.2.1-4.2.3, yet appear to be essential to successful application of the subject methodology to evaluation of waste package materials and components.

4.2.1 Test Objectives

The introductory sections of Sec. 3 (Technical Approach) should provide the rationale for the technical approach. However, the generic description of performance is not well linked to the specific problem of uniform corrosion testing. The use of the term "degradation curve" leads to some confusion. For example, Sec. 3.1 is entitled "Degradation Curves" and Secs. 3.1.1 and 3.1.2 are entitled "Hypothetical Degradation Curves" and "Desired Graphical Output." The latter two topics are quite distinct and probably should not appear under the same heading unless the relationship between them is spelled out more clearly. As the heading implies, Sec. 3.1.1 addresses the dependence of some measure of performance P on the time t during which a sample is exposed to a constant level of stress. The form

$$\frac{P(t/t_F)}{P(o)} = [1 - (t/t_F)]^{1/n}$$

is suggested as a way to express the degree of nonlinearity of this relationship, where t_F is the time required for the sample to fail.

Section 3.1.2, on the other hand, addresses a type of graphical display that can serve as a guide to the analysts of accelerated material-life test programs. In this display (Fig. 3-2), the corrosion rate relative to a reference corrosion rate (center point value) is plotted against the time to failure divided by the reference time to failure (center point value). This graph is constructed so that all of the points fall on a single straight line with a slope of -1. This construction assumes that the time to failure (t) is inversely proportional to the corrosion rate (CR). In other words $(CR/CR_o) = (t_o/t)$.

What is the relationship between Secs. 3.1.1 and 3.1.2? In particular, what is the relationship between performance measure P and corrosion rate CR? Or, is the linearity or lack thereof between P and t relevant? What are the implications of the relationship between P and t with respect to the applicability of a corrosion rate model such as the

Eyring model, which does not have any explicit time dependence? The authors note that failure of performance need not be defined initially. However, if there are critical underlying relationships between some measures of performance of the waste package and the corrosion rate, then perhaps the question deserves more attention. Furthermore, if the relationship between P and t is to be determined experimentally, additional requirements may be placed on the design of the accelerated life test, especially if destructive testing is required.

4.2.2 Definition of Stresses

The introductory portions of Sec. 3 include little discussion of the characteristics of the stresses that may frustrate the successful application of the methodology. Section 3.1.1 begins with these statements: "It is assumed that the system (waste package material or component) has a long life under the stress conditions associated with end-use exposure ... Reduced lifetimes can sometimes be achieved by operating the component under higher-than-normal stress." However, no specific example is given to illustrate how one takes the time-varying stress conditions expected in the repository environment and arrives at a set of constant end-use stress conditions for use with this methodology. Likewise, determination of "higher-than-normal stress" values from transient stress conditions of an actual repository needs fuller explanation.

It would seem that the nature of the stresses deemed important for testing may impose limitations on the methodology. A discussion of such "theoretical" limitations would be helpful. For example, simple quantification to represent brine composition for use in the proposed methodology can be a daunting problem, as demonstrated in the specific application of the methodology given in O/TM-48. Yet, the limitations that such stresses place on the methodology are not covered in ONWI-501.

Another fundamental problem associated with definition of the stress is that the choice of a low and a high value of a stress factor in each model test explicitly assumes that the effects due to such a stress vary monotonically with the value of the stress factor. However, in the case of the stress factor pH, it may be that the effects on iron alloys (and possibly other materials as well) show a different type of behavior. For example, the solubility of iron and aluminum oxides and oxy-hydroxides in aqueous solutions goes through a minimum as the pH is allowed to vary from low to high. Such behavior may be missed if too wide a range of pH values is chosen for the model. The use of pH as a stress factor leads to strange results. Given the definition of pH ($pH = -\log a_{H^+}$), the outcome of a reaction is determined in part by the activity of the hydrogen or hydronium ion in solution. If the negative logarithm of the activity is used, it becomes difficult to understand the complicated chemical mechanisms of the reactions that are involved in corrosion processes and to predict the long-term effects of corrosion processes. Thus, the use of pH raised to a power in Eq. 1 on page 27 looks like a computational convenience divorced from any chemically meaningful reaction mechanisms.

While the purpose of ONWI-501 is to describe a test methodology, concrete examples of the relationships between the stresses imposed in the test situation and those expected in the repository situation would bolster arguments supporting the utility of this approach.

4.2.3 Extrapolation to End-Use Conditions

The concept of extrapolation is introduced in Sec. 3.1 (pp. 16-17), which states that the plot shown in Fig. 3.2, which includes the straight-line extrapolation, may be *helpful for assessing final experimental design but is not to be construed as a method of data analysis.* The authors also note that "more appropriate methods for analysis of accelerated aging data are considered later" (p. 17). Although references to specific sections are not given, App. C and portions of Sec. 4 are probably the most relevant. However, these later parts of the text still leave some questions unresolved.

First, how are the times to failure and their mean values and, hence, the corresponding rates of corrosion or performance degradation, to be experimentally determined? Second, given this information, how should the extrapolation to meaningful real-world stress levels be carried out? Section 4.2 conveys how the test specimens should be allocated to maximize the extrapolation precision and concludes with a numerical example that indicates that accelerated life testing may be undesirable. Section 4.3.1 addresses the problem of experimentally determining the times to failure, but concludes that there are a number of serious problems, not to mention possible nonlinearities, in the time dependence. The authors do say that a method is proposed in App. C that avoids some of these problems. Finally, Sec. 4.3.2 briefly summarizes several corrosion models, all of the same general exponential form, that may be suitable for extrapolation to the end-use stress levels.

Considering all of the above, no justification is given, other than previous applications to electronic components, for the use of any of these models in corrosion testing. In particular, no reason is given for not using a general multiple regression analysis. Granted, the specific models do provide suggestions for particular functions of the stresses to be used in a regression analysis.

As a result of trying to assimilate these related portions of the text, the reader is given the distinct feeling that the methodology is not yet complete and that more specific guidance would be very helpful in answering the questions raised above.

4.2.4 Use of the Eyring Model

Use of the Eyring model for corrosion studies is discussed explicitly in Sec. 4.3.2 of ONWI-501 but is implicit in much of the earlier discussion. It is far from clear how the equation cited on page 42 is related to the original reaction rate model of Henry Eyring and his associates. In general, the Eyring theory of rate processes allows one to compute the forward and backward reaction-rate parameters as functions of the state of an activated complex. In a nutshell, the reaction rate as applied in O/TM-48 depends on an exponential factor of the form $\exp[(X + Y + \ldots)/RT]$, where X, Y, ... are thermodynamic functions, R is the gas constant, and T is the absolute temperature. The mathematical form alone is not sufficient to call the model "the Eyring model." From the text of the two reports, it is not clear whether the parameters X and Y can be identified with the thermodynamic functions. It seems that the authors of the two reports treat parameters like X and Y as if they were freely adjustable, without any clear connection to Eyring's reaction rate model. While the particular name associated with a clearly defined model may not be significant in practice, the association of Eyring's name with the model without noting modifications or limitations leads to confusion of the type indicated above.

4.2.5 *Use of Hierarchical Trees*

Developing hierarchical trees for presenting corrosion data is a valuable technique for evaluating interactions between parameters important to the corrosion process. Furthermore, the exercise would be very helpful for a team responsible for designing a test matrix. However, the document does not clearly express how one goes from the hierarchical tree to the life prediction. Several alternatives are suggested in Sec. 4.3 of ONWI-501, but the connection between the hierarchical tree process and the life-prediction process is weak or poorly explained.

4.2.6 Mechanics of Computations

The explanations of the computations made in developing a hierarchical tree (e.g., App. A, pp. 49-51) are rather mechanical, and they lack much explicit generality to other factorial layouts. Although the specific numerical example is very helpful, a more general description of the procedure, or a more fundamental formulation of the computations, should be added.

An example follows of the type of confusion that a "mechanical" explanation of a computation can lead to. Computation of values used in the factorial tables and hierarchical trees (Apps. A and B) is straightforward and makes use of simple arithmetic or geometric means. However, in a numerical example in App. B, the authors compute the corrosion rate at the "center point" stress conditions using the geometric mean of the corrosion rates obtained from each of the eight possible combinations of the three stresses, rather than by simply evaluating the fitted Eyring model at the center point stress condition. The text does not mention the fact that the two methods of computing CR_0 are equivalent under the assumed form of the Eyring model and the corresponding special definitions of the mean temperature and stress. It might prove misleading if some alternative model were used.

In modeling the relationship between stress levels and corrosion rates to permit extrapolation to the corrosion rate under the normal stress condition, the authors point out that the Eyring model, or various special cases of it, can be considered a default model when the dependence of corrosion rate on the various stresses is not known. This model and its use is satisfactorily described by the authors. However, in one numerical example, a total of five parameters in an Eyring model are fitted to eight points using a regression analysis. No estimates of the standard errors of these five parameters are given. When one has almost as many points as parameters, the quality of the fit is generally very poor.

Another issue related to the methodology, which may become important in a computational sense, is the matter of handling the variability of the uncertainties associated with hypothetical corrosion rates. As the computational procedures for hierarchical trees stand in App. A, all estimated corrosion rates would appear to have identical levels of uncertainty. However, one can imagine in practice that even consensus estimates for corrosion rates might have varying degrees of uncertainty associated with them because of the variability in the knowledge and predictive capabilities available for the ranges of stress conditions encountered. Should the levels of uncertainty vary widely among the estimates, the hierarchical tree methodology could lead to biased, and thus misleading, results. The issue of variable uncertainty in the estimates and its potential effects on the analysis should be addressed.

4.2.7 Other Technical Issues

Assessment of the confounding effects of "pruning" the hierarchical tree (Sec. 4.1) involves the straightforward use of algebra to solve a system of simultaneous linear equations and is quite satisfactory. The objective is to retain the ability to distinguish the effect of each individual stress. However, the physics of the situation and experience may indicate that it is not worthwhile to separate out individual stress effects. Allowance is made in the administrative structure for such a contingency, but it might be reemphasized in the technical portion of both reports.

Determination of the average lifetime τ under constant stress conditions (Sec. 4.3.1) is one of the more interesting and challenging aspects of the accelerated material-life test problem. It is clearly pointed out that one has to make compromises when the process of determining an average time to failure requires that one conduct tests leading to a number of failures. (Some confusion exists between the topic of failure of some performance measure and the topic of corrosion rate. The two are never clearly connected.) In particular, the report points out that if a one-parameter exponential distribution function is used to describe the distribution of the time-to-failure random variable, the standard deviation and therefore the expected error of the mean lifetime $\bar{\tau}$ is inversely proportional to the square root of the number of failures. In other words, for no or few failures, the expected error in $\bar{\tau}$ is unacceptably large.

The authors suggest an interesting and potentially very useful (but untested) alternative approach that can be used with few or no failures (App. C). It involves assuming that the times to failure are distributed according to a two-parameter Weibull distribution. Using the assumption that the Weibull parameters are invariant under changes in stress level, they develop a relationship between the number of samples required under normal conditions and the number required under overstress conditions to make the same statistical inferences regarding sample survival. This alternative procedure should be investigated further and validated with test data.

Allocation of test samples (Sec. 4.2.1) involves the following problem. Given a total of N tests, at which stress levels should the tests be conducted and what fraction of the tests should be conducted at each stress condition to maximize the precision at the extrapolated corrosion rate under normal stress conditions? This problem was solved, as noted by the authors of ONWI-501, by Hoel and Levine (1964) for only one independent variable (i.e., one stress). The authors of ONWI-501 assumed without formal proof that Hoel and Levine's solution could be generalized to the case of several stresses. Although the generalization was straightforward, it is not clear under what conditions Hoel and

Levine's results remain valid. Of particular concern is the case where some of the stresses may not be entirely independent of one another. This problem needs to be investigated more fully, because specifying the number of replications of tests at given stress conditions and the spacing between stress levels is critical to the design of a corrosion test program.

5 ANSWERS TO DOE/SRPO QUESTIONS AND REQUESTS FOR COMMENTS

5.1 O/TM-48: DESIGN OF A MULTIFACTOR MATERIAL-LIFE TEST

Will the resulting test matrix generate a statistically sound data base on the performance of low-carbon cast steel in a salt repository environment to support design, modeling, and licensing activities?

The test matrix reported in O/TM-48 is not final. Although the final test matrix developed using this approach may prove to be acceptable, the present test result (Table 6) is not supported by the document. The statistical soundness of the present form of the data base cannot be judged.

The offered test matrix does not provide a complete data base. Other corrosion mechanisms must be, and apparently are being, addressed. The authors need to explain how they selected uniform corrosion as the dominant degradation mechanism. The method of selection is not described or referenced.

Are there other key stresses, besides those mentioned in the report, that should be considered in the design of the test matrix to meet the stated objectives?

The preclosure environment of the repository includes an air environment, which is not addressed in O/TM-48. Lithostatic and induced pressure stresses are not addressed, nor are sulfide and carbonate concentrations and chemical reactive stresses individually identified in the report. The reasons for excluding these stresses are not given. Also, the chosen stresses are neither well referenced nor well justified.

Are there better approaches for the nominal variables?

One could argue that a better approach to the nominal variables would be to analyze them mechanistically and not necessarily statistically. Guidance must be given as to which variables will be used to accelerate the life tests. This guidance would allow clearer identification of the physically and chemically meaningful variables within the artificially lumped category of a nominal variable.

Comment on the dominant type of degradation for the overpack material.

Selection of the dominant degradation mechanism underlies the document, yet it is neither described nor referenced. Therefore, we cannot evaluate the selection process. Actually, the assumption that uniform corrosion dominates the degradation process is not adequately justified in either O/TM-48 or ONWI-501.

Are the interpretation[s] of the results presented correct?

One cannot tell, because Table 6 has not been interpreted.

Comment on the Eyring model used in the curve fitting. Are there other better models?

The Eyring model may be appropriate, but refer to the answer to the next question. However, the report seems to conclude that the model is not adequate and states that a model presently under development to address the problem will be relied upon.

What happens when radiation approaches zero?

Since zero radiation levels will not be achieved within the lifetime of the package, this issue should not be of concern. The zero-radiation case may be an important experimental link to existing data on low-carbon cast steel.

If this question refers to the fact that in O/TM-48 the radiation level (R) enters the Eyring model in such a way that when R approaches zero so does the corrosion rate (CR), then the following answer applies: Since one does not expect CR to go to zero when R does, it follows that the form of the Eyring model being used is inadequate. A better choice of corrosion rate model would allow the corrosion rate to remain finite even when the radiation level is zero. In general, if the corrosion rate remains finite when a particular stress is turned off, that stress should be represented by an additive term rather than a multiplicative factor.

5.2 ONWI-501: METHODOLOGY FOR PREDICTING MATERIAL LIFE

Comment on the technical approaches for the designing of the test matrix.

The basic approach seems good. It highlights the important parameters and allows the design team to visualize the interactions of the parameters. However, the method has two weaknesses. First, the importance of selecting the dominant degradation mechanism is underemphasized. If the wrong mechanism is selected, the whole process is worthless. Second, the method for extrapolating supporting data to end-use conditions is not well defined. Each user must devise a mechanistic model to make a meaningful extrapolation.

Comment on the 2^n factor approaches.

The 2^n factor approaches seem appropriate and justifiable, although individual stresses may be difficult to quantify and interactions between nonthermal stresses are not accommodated. Some distinction should be made between the variables that are suitable for accelerating corrosion rates and those that are not. In addition, using only a high and a low value of a variable may be helpful in the preliminary design phase, but such a limited choice of values is not consistent with the need to allocate test specimens to maximize the precision of the extrapolation at normal stress conditions.

Comment on the mathematical approaches to the accelerated life testing.

See Sec. 4.2 of this review report, especially Secs. 4.2.3-4.2.6.

6 PAGE-BY-PAGE COMMENTARY

6.1 O/TM-48: DESIGN OF A MULTIFACTOR MATERIAL-LIFE TEST

Page(s)	Line(s)	Comment
6	5	What were the bases for the "predicted" corrosion rates? Were they quantitative predictions? If so, how were these predictions made, given the "undefined" nature of the steel, specimen orientation, salt solid phase, and oxide film thickness?
9		The right-hand column in Table 3 should be labeled "LOG(EST CR)," not "LOG(CR)."
10	19	The Eyring model does not account for nonthermal stress interactions. What the model is proposed to quantitatively describe is interactions between, say, brine composition and radiation level. Is there any guarantee that the mechanistic models under development can account for these interactions? Will this same type of analysis be used to refine the test design once those models are available? These conclusions should be stated somewhere, as should plans for revising the test matrix.
13	4	"Rows 1 and 4" should be changed to "rows 1 and 5."
13, 14		The right-hand columns in Tables 4 and 5 should be labeled "LOG(EST CR)," not "LOG(CR)."
14	14-16	A bit of confusion has gradually crept into the discussion. In the second paragraph on page 7, it is clear that the corrosion rates are "hypothetical predicted corrosion rates that represent the consensus of the members of the team." On page 8, these hypothetical data are fitted to the Eyring model. Then, on page 13, the hypothetical consensus values are called "data," and the fitted values are called "estimated corrosion rates." Now, on page 14, we have "estimated CR" and "actual CR." The terminology needs to be consistent throughout to make it clear that actual experimental data are not being introduced on pages 13 and 14.
15	7	In this discussion, "actual data" presumably means actual experimental data, and "hypothetical data" means the "hypothetical consensus values" referred to earlier. This distinction should be clarified through the use of appropriate, consistent language throughout.

Page(s)	Line(s)	Comment
16		In Table 6, only one test condition involves high radiation. Radiation is estimated (hypothetical consensus values) to be an important splitting parameter, so at least two or three high-stress cases should be tested. Why is only one case being tested?
16	21-23	This concluding sentence should be in the Introduction. One has to read the entire document before finding out that it does not describe the entire ONWI corrosion testing program.

6.2 ONWI-501: METHODOLOGY FOR PREDICTING MATERIAL LIFE

Page(s)	Line(s)	Comment
3	25-30	The ideas expressed here should be presented near the beginning of Sec. 1, and the references especially should be cited there. Also, a clearer statement of the scope and objectives of the document would be helpful.
6-7	13-31; 1-9	While identification of failure mechanisms and selection of the dominant failure mechanism are discussed here, the importance of these steps is not placed in proper perspective. At least half the effort should be placed on this item, or it will be necessary to take all reasonable failure mechanisms through the same design procedure.
		The first paragraph of Sec. 2.2.2 implies that more than one failure mechanism will be examined. The second bullet refers to the "first iteration of the design procedure." However, the point should be highlighted. Selection of the dominant failure mechanism is critical. Corrosion testing programs have been known to spend millions of dollars studying a particular mechanism only to have the material fail in service as a result of some other cause.
		The importance of identifying all reasonable failure mechanisms and selecting the dominant mechanism cannot be overemphasized. ONWI-501 treats the issue entirely too lightly. The reader is then lulled into a false sense of security by the mathematics and statistics in the rest of the report. The idea of iterating through several possible failure mechanisms seems to get lost in the mathematical details.

Page(s)	Line(s)	Comment
11	8-25	Further iterations on other failure mechanisms are not mentioned. Only one failure mechanism is analyzed. For the case of metal corrosion, at least three mechanisms should be examined by this process: uniform corrosion, stress corrosion cracking or environmentally enhanced crack growth mechanisms, and localized corrosion (pitting and crevice corrosion). In addition, at least two environments should be evaluated: the preclosure environment, including air-saturated (perhaps steam) dry or moist salt, and the postclosure environment, including anoxic inclusion brine. The preclosure environment obtains over a significant fraction of the total life requirement, that is, over more than 50 years out of a total of 300 years.
24	15	The phrase "... first iteration ..." occurs again. What does this refer to? It implies more than one iteration. Do the iterations include the mechanism determination step?
36	23	"$L_6 = 0.5682$" should be "$L_6 = 0.0568$."
36	24	"$L_7 = 0.5682$" should be "$L_7 = 0.0568$."
37	8	"$p_8 = 0.001$" should be "$p_8 = 0.003$."
49	7	The citation for "Davies, 1977" is not given in the references.
50		In the caption to Table A-1, "rotation" should be changed to "radiation." Also, the mechanical description of the analysis (e.g., add successive pairs) is not very general or appealing. Finally, the description of column (5) is very weak.

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The credentials of the panel members are summarized in App. C.

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*Member of core peer review staff.

**Review panel and review session chairman, and member of core peer review staff.

APPENDIX A

U.S. DEPARTMENT OF ENERGY LETTER REQUESTING PEER REVIEW

Department of Energy
Chicago Operations Office
Salt Repository Project Office
505 King Avenue
Columbus, Ohio 43201-2693

May 14, 1984

Wyman Harrison
EES-362
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

Dear Dr. Harrison:

SUBJECT: REVIEW OF REPORTS ENTITLED, "DESIGN OF A MULTIFACTOR LIFE TEST TO INVESTIGATE UNIFORM CORROSION OF LOW-CARBON CAST STEEL AS A NUCLEAR WASTE PACKAGE OVERPACK MATERIAL IN A SALT REPOSITORY ENVIRONMENT," ONWI O/TM-48, AND "METHODOLOGY FOR PREDICTING THE LIFE OF WASTE-PACKAGE MATERIALS AND COMPONENTS USING MULTIFACTOR ACCELERATED LIFE TESTS," ONWI-501

We would appreciate your forming a panel to review the attached subject reports. Since these two reports are closely related, we feel it is appropriate to review both reports simultaneously. The review should include, but need not be limited to, the following points:

ONWI O/TM-48

1. Will the resulting test matrix generate a statistically sound data base on the performance of low-carbon cast steel in a salt repository environment to support design, modeling, and licensing activities?

2. Are there other key stresses, besides those mentioned in the report, that should be considered in the design of the test matrix to meet the stated objectives?

3. Are there better approaches for the nominal variables?

4. Comment on the dominant type of degradation for the overpack material.

5. Are the interpretation of the results presented correct?

6. Comment on the Eyring model used in the curve fitting. Are there other better models?

7. What happens when radiation approaches zero?

8. Other comments.

1. Comment on the technical appproaches for the designing of the test matrix.

2. Comment on the 2^n factor approaches.

3. Comment on the mathematical approaches to the accelerated life testing

4. Other comments.

Please complete the review and submit the final report to SRPO by June 18, 1984. If you have any questions, please contact Roger Wu at FTS 976-5916.

Sincerely,

Leslie A. Casey

for Robert C. Wunderlich
Acting Chief
Engineering and Technology
Salt Repository Project Office

SRPO:KKW:2367B

ST# 519-84

Enclosures:
1. ONWI-501, "Methodology for Predicting the Life of Waste-Package Materials and Components using Multifactor Accelerated Life Tests" (September 1983)
2. ONWI 0-TM/48, "Design of a Multifactor Life Test to Investigate Uniform Corrosion of Low-Carbon Cast Steel as a Nuclear Waste Package Overpack Material in a Salt Repository Environment." (April 1984)

cc: T. Baillieul, SRPO
R. Wu, SRPO
J. Sherwin, SRPO

APPENDIX B

CONCURRENCE SHEET

CONCURRENCE SHEET

I concur that the Argonne National Laboratory report on ONWI's internal technical memorandum O/TM-48 and on ONWI-501 fairly represents my comments, where incorporated, to the peer review panel.

John D. Ditmars
John D. Ditmars

Abraham Lerman

Dorland Edgar
Dorland E. Edgar

Charles C. McPheeters
Charles C. McPheeters

Douglas F. Hambley

Donald M. Rote
Donald M. Rote

Wyman Harrison
Wyman Harrison

John D. Ditmars

Princeton University: B.S.E., Civil Engineering (1965)
California Institute of Technology: M.S., Civil Engineering (1966)
California Institute of Technology: Ph.D., Civil Engineering (1971)

Dr. Ditmars is leader of the Geophysics and Engineering Section of the Geoscience and Engineering Group of the Energy and Environmental Systems Division at Argonne National Laboratory. Measuring and modeling portions of the hydrosphere impacted by energy technologies and natural resource development has been the main research area of this section. Particular attention has been given to evaluations of model performance and to experimental designs for the acquisition of data at prototype scales for performance evaluation. Dr. Ditmars has extensive experience in modeling and measurement of transport and mixing processes in the hydrologic environment. He was for several years responsible for the annual literature review in the area of "Mixing and Transport" for the *Journal of the Water Pollution Control Federation* and is presently the Chairman of the Paper Awards Committee of the Hydraulics Division of the American Society of Civil Engineers. He is also the Chairman of the Task Committee on Verification of Models of Hydrologic Transport and Dispersion for the Hydraulics Division of the same society and, as such, has been concerned with the generic aspects of verification and validation as well as with those aspects of particular models.

Before joining Argonne in 1977, Dr. Ditmars was Assistant Professor of Civil Engineering at the University of Delaware. From 1970 to 1972 he was Visiting Assistant Professor in the Water Resources and Hydrodynamics Division of the Civil Engineering Department at MIT. His teaching and research activities at the University of Delaware and MIT focused on hydraulic engineering and fluid mechanical processes in the natural hydrologic environment, and involved analytical and numerical modeling as well as laboratory and field experiments. He is author of more than 45 technical publications in these areas.

Dorland E. Edgar

Central Missouri State University: B.S., Geology (1968)
Colorado State University: M.S., Geology (1973)
Purdue University: Ph.D., Geology (1976)

Dr. Edgar joined the Geoscience and Engineering Group of the Energy and Environmental Systems Division of Argonne National Laboratory in 1978. Since that time he has worked as a geologist and hydrologist on programs related to waste management and energy and mineral resources development. From 1981 through 1983, he participated in studies of the geologic setting of crystalline rocks of the northeastern and Lake Superior regions of the United States for the purpose of assessing their suitability as sites for a high-level radioactive waste repository. His primary areas of responsibility on this project were surface-water and groundwater hydrology, geomorphology, and surficial geology.

From 1978 to 1981, Dr. Edgar was affiliated with Argonne's Land Reclamation Program and Environmental Control Technology Program, where he studied the relationships between surface mining and reclamation activities, and geomorphic processes, hydrology, water quality, and erosion and sedimentation. Dr. Edgar also served as a U.S. Department of Energy representative to an interagency group that reviewed comments and drafted revised regulatory guidelines for the U.S. Office of Surface Mining.

Before coming to Argonne, Dr. Edgar was employed at Oak Ridge National Laboratory, where he conducted research on surface and subsurface hydrologic and geologic conditions, and their relationship to the shallow land disposal of low-level radioactive waste. One project involved the study of the hydrologic and geomorphic processes involved in transporting radionuclides from burial sites through an instrumented watershed. Dr. Edgar's graduate research was directed primarily toward the relationships between hydrology and the geomorphic processes operating within alluvial stream channels and drainage basins.

Dr. Edgar has authored approximately 25 scientific and technical publications, and is a member of two professional societies.

Douglas F. Hambley

Queen's University at Kingston: B.Sc., Mining Engineering (1972)
Lewis University: MBA candidate
Registered Professional Engineer, No. 18026014, Province of Ontario, and
No. 062-039201, State of Illinois

Mr. Hambley has more than 10 years experience in mining, tunneling, and underground construction. He joined the staff of the Geoscience and Engineering Group of the Energy and Environmental Systems Division of Argonne National Laboratory in 1984. Prior to working at Argonne, Mr. Hambley was employed as a Senior Mining Engineer for nearly four years by Engineers International, Inc., a mining/tunneling consulting firm located in Westmont, Ill. In addition to designing several large tunnels for various purposes, he spent over two years as Project Engineer on U.S. Nuclear Regulatory Commission contracts to assess retrievability from repositories for high-level radioactive waste and to provide technical assistance for repository design reviews.

Between 1972 and 1980, Mr. Hambley held various technical positions with major Canadian mining companies, including Denison Mines Ltd. and Falconbridge Nickel Mines Ltd. During his employment at Denison (1977-1980), he was responsible for several major projects, including (1) a tripartite (Denison/Rio Algom/CANMET) regional stability study; (2) investigation, specification preparation, and tender evaluation for Stanrock Mine dewatering and shaft rehabilitation; (3) design of the backfill system for a pillar recovery scheme; and (4) design of the underground garage and supply station for diesel fuel at No. 1 shaft.

Mr. Hambley has published on retrievability of high-level nuclear waste, design of shafts and tunnels, computer modeling of mine openings, and raise boring cost estimation. He is active in several technical societies.

Wyman Harrison

University of Chicago: S.B., Geology (1953), after three years of undergraduate work at Stanford University
University of Chicago: S.M., Geology (1954)
University of Chicago: Ph.D., Geology (1956)
Registered Geologist, No. 2476, State of California
Certified Professional Geologist, No. 134, American Institute of Professional Geologists, and No. 487, State of Virginia

Dr. Harrison is Associate Director for Geoscience and Engineering for Argonne National Laboratory's Energy and Environmental Systems Division. He directs a 25-person group that performs analytical and experimental studies related to management of energy and mineral resources and to development and deployment of related technologies. Major activities of the group include (1) acquisition of geophysical and geotechnical data bases, (2) analysis of the data of geoscience to support design and deployment of energy technologies, and (3) development of physical and mathematical models of geophysical/geotechnical systems.

Dr. Harrison's group recently completed comprehensive surveys of the geoscience data pertaining to crystalline rock complexes in the northeastern and Lake Superior regions of the United States to help assess their potential as possible sites for repositories for high-level radioactive waste. Dr. Harrison has conducted numerous other geological and geotechnical studies at Argonne, ranging from estimating the petroleum resources of selected basins in the Soviet Union to determining near-shore circulation in Lake Michigan.

From 1971 to 1975, Dr. Harrison was Professor of Geography (Associate Department Chairman) at the University of Toronto, where he specialized in geophysical studies related to slope stability in sedimentary terrains and the siting of supertanker ports. Prior to that, he was Associate Director for Physical, Chemical, and Geological Oceanography at the Virginia Institute of Marine Science and a Professor of Marine Science at the University of Virginia. Dr. Harrison was Director of Environmental/Science Services Administration's (now National Oceanic and Atmospheric Administration's) Land and Sea Interaction Laboratory from 1964 to 1968. Before that he was on the faculty of Dartmouth College's Department of Geology and a geologist with the Indiana Geological Survey.

An author of over 100 papers, reports, reviews, and books, Dr. Harrison was made Senior Scientist at Argonne in 1976.

Abraham Lerman

The Hebrew University: M.Sc., Geology (1960)
Harvard University: Ph.D., Geology (1964)

Dr. Lerman joined the Department of Geological Sciences at Northwestern University in 1971 as Associate Professor and has been Professor since 1975. Dr. Lerman has extensive experience in aqueous geochemistry, geochemistry of brines, isotope geochemistry, and radionuclide migration. He is a resource consultant on waste packaging and geochemistry for the Basalt Waste Isolation Project Overview Committee. During 1980 Dr. Lerman was a member of the Backfill Evaluation Panel for Battelle's Pacific Northwest Laboratory.

While associated with Northwestern University, Dr. Lerman has served, at various times, as a visiting professor at several European universities. Prior to joining the faculty at Northwestern, he was a Research Scientist in Chemical Limnology at the Canada Centre for Inland Waters (1969-1971), a Visiting Investigator and Senior Scientist in Isotope Research at Weizman Institute of Science (1966-1969), an Assistant Professor of Geology at the University of Illinois at Chicago Circle Campus (1965-1968), a Visiting Investigator (geochemistry) at Lamont-Doherty Geological Observatory of Columbia University (Summer, 1965), and a Lecturer and Assistant Professor of Geology at the Johns Hopkins University (1964-1965).

Dr. Lerman has published extensively in the areas of geochemical processes in water and sediments, halite and brines, chemical limnology, geochemical cycles, and radionuclides in sediments. He is a member of five professional societies and a Fellow of the Geological Society of America.

Charles C. McPheeters

University of Missouri: B.S., Metallurgical Engineering (1963)
University of New Mexico: M.S., Engineering Science of Materials (1968)

Mr. McPheeters joined the Chemical Technology Division of Argonne National Laboratory in 1970 and currently provides technical support to the Materials Integration Office of the U.S. Department of Energy's Chicago Operations Office. He has helped coordinate the development and review of test methods and data used to support nuclear waste repository licensing and acceptance of waste for disposal in repositories. In previous work at Argonne, Mr. McPheeters developed a computer model for a sodium impurity precipitation process, various sodium processing systems, and instrumentation for monitoring impurities. Other areas of research have included lithium/sulfur batteries, liquid-metal fast breeder reactor safety experiments in TREAT, and detection and location systems for failures of fuel elements.

Prior to joining Argonne, Mr. McPheeters was employed by Atomics International, Rockwell International, where he designed equipment for sodium purification and removal of dissolved gases from sodium in liquid metal fast breeder reactors. Between 1963 and 1968, at Los Alamos Scientific Laboratory, he developed a solid-electrolyte electrochemical cell for determining oxygen activity in sodium and studied the corrosion of containment materials in liquid Pu-Co-Ce alloys. During this time he supervised and operated a metallography laboratory where the effects of Pu-alloy corrosion of containment materials were studied.

Mr. McPheeters has authored approximately 25 publications and has three patents.

APPENDIX C

CREDENTIALS OF PEER REVIEW PANEL MEMBERS

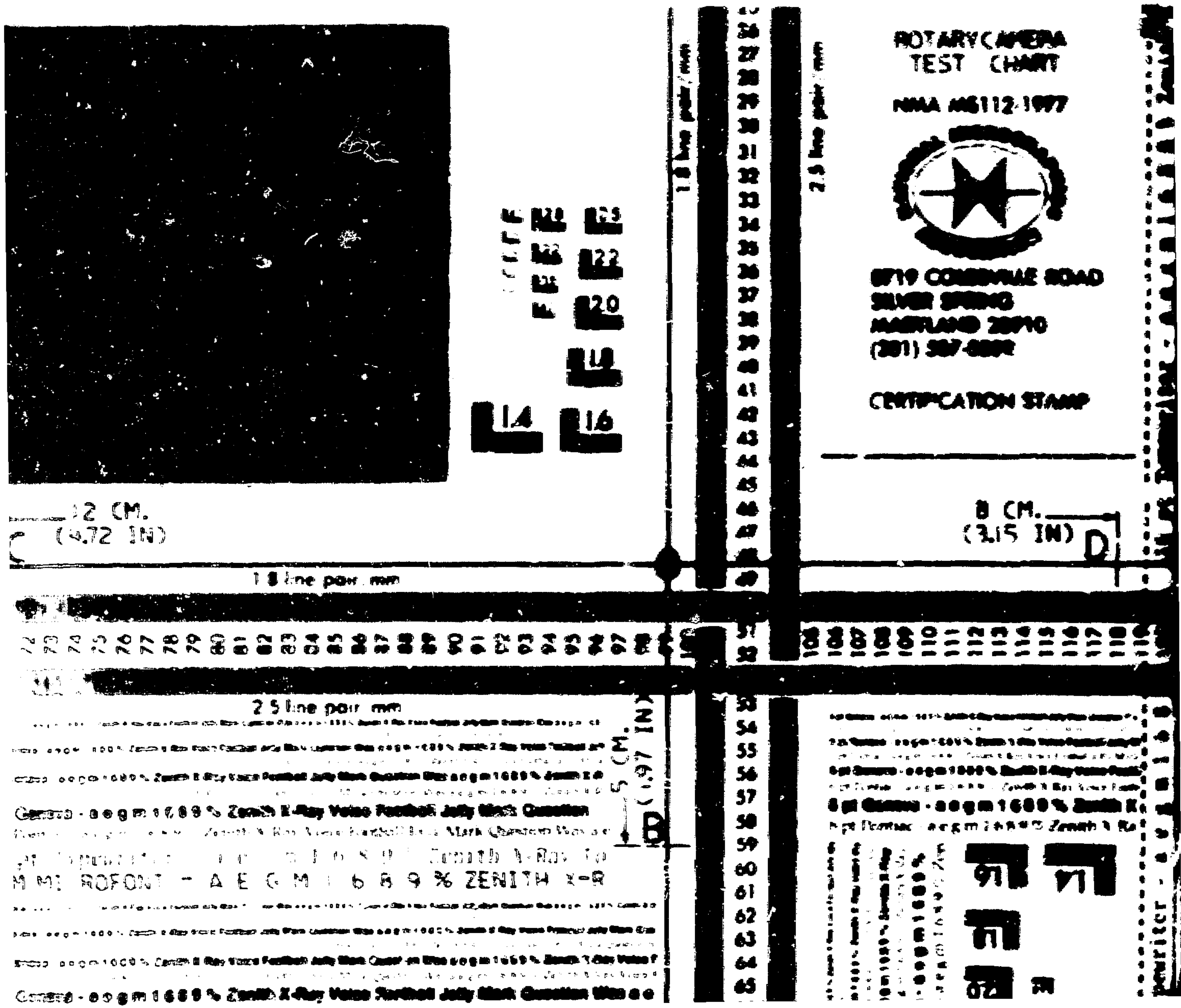
Donald M. Rote

Cleveland State University: B.E.S., Engineering Science (1960)
Case Western Reserve: M.A., Theoretical Physics (1963)
Case Western Reserve: Ph.D., Theoretical Nuclear Physics (1967)

Dr. Rote is a geophysicist in the Geoscience and Engineering Group of the Energy and Environmental Systems Division of Argonne National Laboratory. He has served as principal investigator since 1970 on numerous projects sponsored by the U.S. Environmental Protection Agency, U.S. Air Force, and Federal Aviation Administration concerned with development, verification, validation, and documentation of models used for air pollution assessment. He has also directed a number of field programs that required the acquisition, analysis, and interpretation of air-quality, meteorological, and source data.

Dr. Rote has concurrently served as an advisor on model validation, model applications, monitoring, and data analysis techniques to the above institutions. In addition, he has given series of lectures on these subjects at both the Majorana School of Physics of the Planetary Boundary Layer held at Erice, Sicily, and the Korean Institute for Science and Technology at Seoul, Korea.

Dr. Rote has published over 60 reports, book chapters, and journal articles.



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This report has not undergone patent or policy review. It is not to be referenced in public documents, nor is it to be disseminated or published without prior written approval by management.

DESIGN OF A MULTIFACTOR LIFE TEST TO INVESTIGATE UNIFORM CORROSION OF LOW-CARBON CAST STEEL AS A NUCLEAR WASTE PACKAGE OVERPACK MATERIAL IN A SALT REPOSITORY ENVIRONMENT

Internal Technical Memorandum

April 1984

Prepared by: ______________ and ______________
Roger Cote , Ralph Thomas

Approved by: ______________
S. C. Matthews, Manager

Engineering Function
Office of Nuclear Waste Isolation
Battelle Project Management Division
505 King Avenue
Columbus, Ohio 43201-2693

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Design of a Multifactor Life Test to Investigate Uniform Corrosion of Low-Carbon Cast Steel As a Nuclear Waste Package Overpack Material in a Salt Repository Environment

Introduction

In February, 1983, a group comprised of key technical personnel connecte with the Waste Package Program (WPP) at PNL was formed to assist the WPP program managers in designing an experimental program to investigate uniform corrosion of low-carbon cast steel in a salt repository environment. The product of this group effort is the framework of the experimental design and test matrix of laboratory work to be carried out over the next few years. Th results of this work will be used to characterize the reference overpack material and to develop the data base necessary to support design, modeling, and licensing activities associated with the salt repository project.

During the period February, 1983 through December, 1983, the test design group held a series of seven meetings in which the methodology described in ONWI-901 was applied in designing this experimental test program. The key participants in this task are listed below:

RE Westerman, PNL
WL Kuhn, PNL
KD Merz, PNL/ACC
SG Pitman, PNL
JL Nelson, PNL
SA Simonson, PNL
FN Hodges, PNL
DE Shannon, PNL
DJ Bradley, PNL
RW Cote, ONWI

This report presents the results of this team effort.

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Test Design Methodology

The approach used in designing the test matrix which is the subject of this report is described in detail in the ORNL Technical Report (ORNL-501), "Methodology for Predicting the Life of Waste Package Materials and Components Using Multifactor Accelerated Life Tests". The key elements of this methodology are:

- The test design is the result of the composite effort of a multidisciplinary team.
- The resulting test matrix must reflect both the (statistical) experimental design and the data analysis characteristics that are required to identify magnitudes of different stresses and their interactions. That is, strong use is made of statistical concepts.
- The individual team members are required to make quantitative predictions of the experimental outcomes associated with each combination of stresses.
- Predictive models are fit to the hypothetical data generated by the quantitative predictions mentioned above.
- A consensus design that represents compromise and agreement among the team members is generated. At this point the test matrix usually is in the form of a 2^n complete factorial design.
- An initial "engineering" design is determined by deleting unneeded or experimentally intractable portions of the complete factorial matrix. The accomplishment of this step is aided by analyzing the hypothetical data generated earlier and plotting the results of this analysis in the form of a hierarchical tree.
- This engineering design is then augmented to recover sufficient statistical stucture in the test matrix so that with optimal allocations of test specimens, statistically valid and optimal estimations/predictions/extrapolations can be obtained.

The remainder of this report will emphasize the results of this team effort and not the details of the methodology. As stated above, the methodology is described in ORNL-501.

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Results

The objective of this team effort was to develop a test matrix that woul be the framework of a multi-year experimental and modeling program. The objective of this multi-year experimental program is to carry out the laboratory experiments needed to obtain a statistically sound data base on th performance of low-carbon cast steel in a salt repository environment so that engineering design, modeling, and licensing activities can be supported.

The initial meeting of the team focused on clarifying the specific objectives of the team effort to be undertaken. In addressing this issue the potential types and mechanisms of degradation that would need to be investigated were considered. In designing a multi-factor long-term test matrix a dominant failure mechanism must be selected from the list of relevan failure mechanisms and then the process of designing the test protocol focuse on that mechanism. In the case of low-carbon cast steel as a container (overpack) material in a salt repository, the dominant type of degradation expected is uniform corrosion. The key results and conclusions of this initial meeting are given below:

- Careful consideration needs to be given to the various corrosion products formed under different environmental conditions. An Eh-pH diagram can be of some assistance in making such predictions, however such thermodynamic predictions are not always valid under the non-equilibrium conditions that prevail when metal is corroding rapidly. The importance of the nature of these corrosion products and their influence on corrosion rates were stressed several times during team discussions. For example, magnetite (Fe_3O_4) is the most protective corrosion product film formed on iron. The presence of carbonates or sulfides, even at low concentrations, can cause the preferential formation of iron carbonate or iron sulfide corrosion products, which being less protective, can cause significant increase in the corrosio rates observed.

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- Since sulfurous species are so common in Permian Basin ground waters and since the presence of sulfides can have significant effects on metals degradation, it is important that these species at least be monitored during experimental work. It was noted that the presence sulfur can promote the hydrogen charging of steels by inhibiting the recombination of corrosion-product nascent hydrogen into gaseous molecular hydrogen that could readily escape into the atmosphere. I general, hydrogen embrittlement is not a severe problem in near-neutral pH environments and if the ferrous alloy involved is not hardened.

- Low pH brines at elevated temperatures, especially those containing some sulfurous species, are extremely corrosive. It was noted that recently there has been much interest in steels containing large amounts of Cr and Mo, e.g., 37% Cr and 4% Mo.

- Considerable discussion revolved around the formation of very thick corrosion product films, and the types of environments that might be formed in such films under conditions of irradiation-corrosion. The team generally agreed that heavily-oxidized specimens should be investigated. Heavy oxidation can be brought about by imposition of high fugacity oxidizing species on the specimen, either by electrolysis or a high gaseous oxygen overpressure, during hydrothermal exposure.

- The mechanism of pH control, both in the repository and in the laboratory, was discussed extensively. High magnesium (inclusion type) brines are believed to drop in pH due to the formation of an insoluble oxy-sulfate. Such a condition could be artificially simulated by adding HCl, however, such a pH adjustment would not be sustained in a test autoclave as the HCl addition would be rapidly consumed. The team generally agreed that the best way to "adjust" p for accelerated testing or otherwise, would be to select the appropriate brine formulation, and permit the elevated temperature conditions to dictate the test pH level.

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A listing of the key stress parameters to be considered in forming a test matrix for long term testing is given in Table 1.

Table 1. Stress Parameters Associated With Uniform Corrosion Testing of Low-Carbon Cast Steel

Temperature	250, 150, 70 C
Radiation	10^5 rad/hr, 10^3 rad/hr
Brine Composition	Inclusion, Intrusion
SA/V (Flow Rate)	Flowing, Static
O_2	anoxic feed brine
Fe in solution	monitor - no control
Cl^-	brine dictated
HS^-, H_2S	brine dictated
HCO_3^-, CO_2	brine dictated
Metallurgical condition	unstressed cast material
Specimen orientation	not yet defined
Salt solid phase	not yet defined
Oxide film thickness	not yet defined

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The first four stresses (shown above the line in Table 1) are used to define a $3 \cdot 2^3$ complete factorial design. With three levels of temperature it is convenient to regard the overall design as being comprised of three 2^3 designs. At the conclusion of the first meeting, each team member was asked to specify a "predicted" corrosion rate for each of the 24 combinations of temperature, radiations, brine compositions, and flow rate, and record them i a table such as shown in Table 2.

Table 2. $3 \cdot 2^3$ Complete Factorial Design for Uniform Corrosion Testing of Low-Carbon Cast Steel

Radiation	Brine	SA/V	Corrosion Rate - mils/yr 200 C	150 C	70 C
0	0	0	2.0	0.8	0.8
0	0	1	2.5	1.0	1.0
0	1	0	90	5.0	2.0
0	1	1	95	5.5	3.0
1	0	0	200	5.6	1.0
1	0	1	200	6.0	1.1
1	1	0	300	9.0	4.0
1	1	1	300	10.0	4.2

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In Table 2 the low and high stress levels are denoted by 0 and 1, respectively, for the three non-thermal stresses (radiation, brine compositions, and flow rate). For radiation, the two stress levels are 10^3 rad/hour and 10^5 rad/hour. For brine composition the low stress level corresponds to an intrusion brine, represented by Permian Basin Brine No. 2, and the high stress level corresponds to an inclusion (high Mg concentration) brine, designated as Permian Basin Brine No. 3. Compositions for these two brine formulations are shown in Appendix B. For the flow rate stress parameter, the low stress corresponds to a static test, and the high stress corresponds to a low flow rate of approximately 35 ml/hour.

The values given in the three right most columns of Table 2 are the hypothetical predicted corrosion rates that represent the consensus of the members of the team. These hypothetical data were "analyzed" as if they we actual observed data for the complete factorial design. The results of this analysis are indicated graphically in the hierarchical tree that is shown in Figure 1. The data are further "analyzed" by attempting to fit an Eyring model to these consensus hypothetical predictions. The Eyring model used has the following form:

$$\begin{aligned} &CR=A*EXP(B/T)\\ &*(R)**(C+D/T)\\ &*(BR)**(E+F/T) \end{aligned}$$

where * and ** denote multiplication and exponentiation, respectively; CR denotes corrosion rate, R denotes radiation, BR denotes brine, and T denotes temperature. The letters A through F denote constants that are computed usi a least squares procedure to fit the model to the consensus data.

Because brine is a nominal variable, it is necessary to assign distinct numerical values to represent the intrusion brine and high magnesium brine. The assigned values are arbitrarily taken to be 1/e and e, respectively. Thi choice is guided by the fact that the fitting procedures involve geometric means and logarithmic transformations. The geometric mean of 1/e and e is unity, and the logarithm of unity is zero. This assignment permits the least

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square computations to be made without numerical difficulty. It should be stressed at this point that the exercise of fitting an Eyring model is carried out as a mechanism for exploring the structure of the consensus of the group as reflected in these hypothetical data. It is not intended to be regarded as an appropriate mathematical model that could be used for purposes of prediction and extrapolation. Indeed the discussion that follows points out instances in which the fitted Eyring model is inadequate even within the range of the hypothetical data, not to mention the problems that could be expected upon extrapolations. Nevertheless, the fitting exercise is useful for the purposes stated.

The fitted Eyring model is given as follows:

CR=7.[illegible]*([illegible])
*EXP([illegible]/T)
*(R)**(1.[illegible]-[illegible].[illegible]/T)
*(BR)**(1.[illegible]-[illegible].[illegible]/T)

Table 3 shows the results for the case of static flow. The first three columns show the levels for temperature in degrees C, radiation in rads/hr, and type of brine in arbitrary units. Column 4 shows the consensus estimates for the corrosion rate CR in mils/yr. The values obtained from the fitted Eyring model are shown in column 5 together with their base 10 logarithms in the last column.

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Table 3. Eyring Model Fitted to Consensus Estimates
for the Corrosion of Iron
Static Case, 70 C and 200 C

T	R	[illegible]	CR	FIT CR	[illegible]
70	1000	1/e	0.8	0.77	-0.111
	1000	e	2.0	2.[illegible]	0.4[illegible]
	100000	1/e	1.0	1.[illegible]	[illegible]
	100000	e	4.0	3.[illegible]	[illegible]
200	1000	1/e	2.0	4.[illegible]	[illegible]
	1000	e	[illegible]	[illegible]	1.[illegible]
	100000	1/e	[illegible]	[illegible]	1.[illegible]
	100000	e	[illegible]	[illegible]	2.[illegible]

A comparison between the consensus and fitted values shows agreement within 4 percent at a temperature of 70 C. However, at 200 C large percentage errors are involved. In general the fitted values are either twice as large or half as large as the consensus values, with the result that their ratios have a geometric mean that is approximately equal to 1.0.

The relatively poor fit suggests that the Eyring model may not be a suitable form to represent the corrosion process. Alternatively, the consensus values may need some revision. Each of these possibilities is briefly examined below.

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The fit provided by the Eyring model may be deficient because of the need to assign arbitrary values to the nominal levels of brine. Typically, such models are not intended to involve nominal variables. However, of more importance may be the fact that the consensus values show that the interaction between radiation and brine is an order of magnitude larger at 250 C than it is at 70 C. This may be seen in the hierarchical tree representation of the consensus values (Figure 1). The bottom portion of the right branch of the tree shows that the main effect of brine at the low radiation level is much larger than the main effect of brine at the high level of radiation. Graphically this is indicated by the fact that the horizontal distances for the brine splits are greatly different in magnitude. In contrast, the splits at the terminal branches at the left side of the tree involve horizontal distances that are approximately equal. These observations suggest that the large main effect, equivalent to the large horizontal distance, for brine at 250 C may be an anomaly in the structure of the consensus values. If it is, then the consensus values should be suitably modified. If the large main effect is not an anomaly, then the Eyring model may be an inappropriate model for representing the relations among temperature, radiation, and brine for the corrosion of iron. Although the Eyring model permits each nonthermal stress to interact with temperature, no other interactions are accommodated. This may be seen by taking logarithms of Equation (1). The resulting form is a linear form in the logarithms of the stresses, with coefficients that are temperature dependent. Because products of nonthermal stresses, such as radiation and brine, cannot be obtained in this way, the model cannot accommodate the kind of interaction shown in the hierarchical tree.

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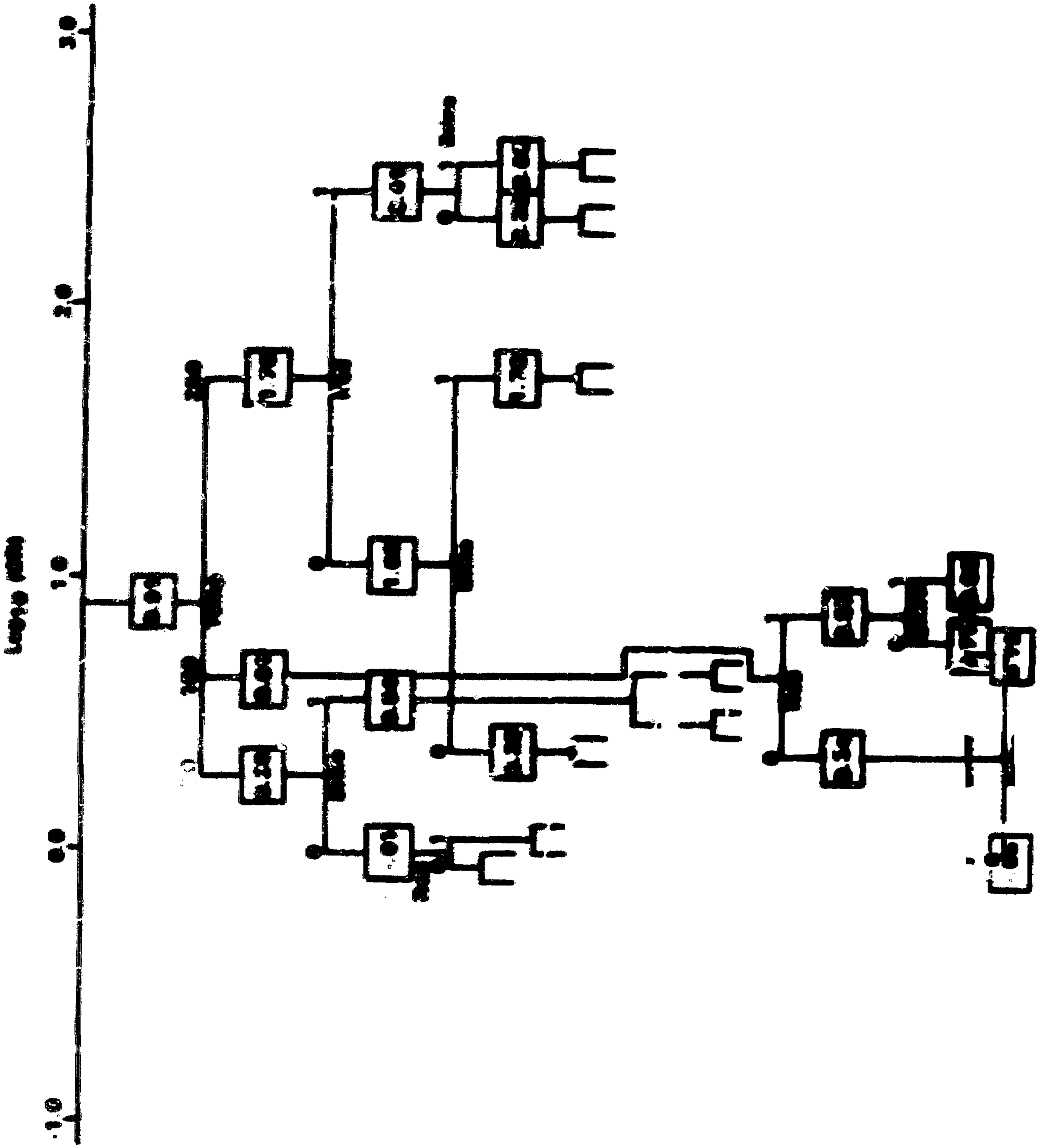

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It may also be noted that the initial factors of the Eyring model represent the Arrhenius model:

CR=A*EXP(B/T)

When written in this way it is usually assumed that B is negative so that increases in temperature result in increases in the corrosion rate. In contrast, it is noted that the fitted B-coefficient is positive in the Eyring model fitted to the consensus values. This does not mean that increases in temperature yield decreases in the corrosion rate because the effects of temperature are also reflected in the exponents of the other factors in the Eyring model.

In a similar manner Eyring models were also fitted to the consensus data for temperatures 70 C and 150 C, and for temperatures 150 C and 250 C. The fitted equations for these two cases are given below:

CR=1.[illegible]*(E-3)
*EXP(21[illegible]/T)
*(R)**(1.[illegible]-3[illegible].[illegible]/T) (2)
*(BR)**(0.17[illegible]-1[illegible].[illegible]/T)

for the values at 70 C and 150 C; and

CR=3.[illegible]*(E-4)
*EXP(27[illegible]/T)
*(R)**(2.4633-9[illegible].136/T) (3)
*(BR)**(2.3367-7[illegible].[illegible]/T)

for the values at 150 C and 250 C.

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Tables 4 and 5 show the results for these two cases. Again the overall fit is not impressive, indicating possible problems with either the model or the data. As an instance of a potential problem with the data it can be noted that in Table 4 the same corrosion value of 0.8 is assigned to rows 1 and 4, even though the temperatures associated with these two rows are 70 C and 150 C, respectively. The conditions on radiation and brine for these two rows are matched. It seems unlikely that such a change in temperature would leave the corrosion rate unchanged.

Table 4. Eyring Model Fitted to Consensus Estimates
for the Corrosion of Iron
Static Case, 70 C and 150 C

T	R	BR	CR	EST CR	LOG(CR)
70	1000	1/e	0.8	0.77	-0.312
	1000	e	2.8	2.88	0.461
	100000	1/e	1.0	1.03	0.014
	100000	e	4.0	3.86	0.986
150	1000	1/e	0.8	1.13	0.084
	1000	e	5.0	3.57	0.347
	100000	1/e	5.8	4.06	0.612
	100000	e	9.0	12.73	1.105

Table 5. Eyring Model Fitted to Consensus Estimates for the Corrosion of Iron
Static Case, 150 C and 250 C

T	R	[illegible]	CR	EST CR	LOG(CR)
150	1000	1/e	0.8	1.13	0.[illegible]
	1000	e	5.0	3.58	0.[illegible]
	100000	1/e	5.8	4.[illegible]	0.[illegible]
	100000	e	9.0	12.74	1.[illegible]
250	1000	1/e	2.0	4.04	0.[illegible]
	1000	e	50.0	24.73	1.[illegible]
	100000	1/e	200.0	98.98	1.[illegible]
	100000	e	300.0	[illegible].72	2.[illegible]

Some additional insight into the fitting process used in these applications may be gained by examining pairs of rows. For rows 1 and 2, fo example, the ratio of the estimated CR to the actual CR in Table 5 is seen t be 1.13/0.8 = 1.4. The corresponding ratio for row 2 is given by 3.58/5.0 = 0.71. The geometric mean of these two ratios is given by SQR(1.41[illegible]*0.70[illegible] = 0.999. The ideal value for this geometric mean is unity. A geometric mea of unity on a logarithmic scale corresponds to a zero sum of deviations on a arithmetic scale that is typically produced by a least squares fitting procedure. Because the Eyring model is fitted using a logarithmic scale, ratios of fitted to actual values, rather than differences between these values, should be examined. When the results given in Tables 3, 4 and 5 are examined in terms of ratios, the results are seen to give geometric means th are approximately equal to unity as desired.

These calculations show that to obtain an adequate representation of the consensus values, either the Eyring model or the consensus values or both must be modified. Work is currently in progress within the modeling task of the PNL Waste Package Program to develop a corrosion model. A preliminary version of this model was submitted to ONWI in August, 1983. An update version of this model along with a documented computer code is scheduled for August, 1984. At that time it will be appropriate to fit both actual and hypothetical data to the model. Where possible, this model will be used to predict results to be compared to the hypothetical predictions contained in this report. It is anticipated that the corrosion model being developed will provide a more satisfactory model.

Summary

The basic test matrix for long-term corrosion testing of low-carbon cast steel is the following:

Temperatures: 70 C, 150 C, 250 C
Radiation: 10^5 rad/hr, 10^3 rad/hr
Brine: Intrusion (low Mg), Inclusion (high Mg)
Flow Rate: Flowing, Static

The temperatures indicated are representative of the range of temperatures that appears to be important for these tests. As interim results are obtained, the need for additional data within this range (at values other than the three listed above) may be indicated. The same situation could hold for the other stresses; i.e., additional radiation levels, brine chemistry parameters, surface area-to-volume ratios (and related flow rates). The particular combinations of stresses included within the engineering - experimental design are indicated by +'s in Table 6.

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Table 6. Experimental Matrix For Long-Term Corrosion Testing of Low-Carbon Cast Steel

Radiation	Brine	SA/V	Corrosion Rate - mils/yr 200C	 150C	 70C
0	0	0	◆	◆	◆
0	0	1	◆	◆	
0	1	0	◆	◆	◆
0	1	1	◆	◆	
1	0	0			
1	0	1		◆	
1	1	0			
1	1	1			

The test matrix as indicated in Table 6 represents the initial framework of a statistically designed experiment to develop a sound data base on corrosion behavior of low-carbon cast steels in a salt repository environment. It does not represent the final version that has a desired statistical structure. The process of modifying this test matrix will be revisited late in FY 84 as more data become available from experiments currently underway. At that time a documented Corrosion Model I will also be available to assist in defining future data requirements.

To assist in evaluating the test matrix proposed here for long term tests, a matrix of all structural barrier tests already completed is presented in Appendix A.

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APPENDIX A

Matrix of Structural Barriers Tests Completed

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Matrix of Structural Barriers
Tests Completed

1. Ceramic Screening Studies - (Static Leach Tests)
   - Materials tested = alumina (99% and 99.8%), mullite, basalt, $BaTiO_3$, $CaTiO_3$, $CaTiSiO_5$, $CaZrO_3$, vitreous silica, TiO_2, ZrO_2, $ZrSiO_4$, graphite, Pyroceram 9617, Macor glass-ceramic
   - Temperature = 150 C and 250 C
   - Sample form = monolithic, hot pressed in a graphite die: 2.5 cm di x 2.5 cm high. Samples were cut to fit inside gold ampules
   - Time = 43 days total exposure
   - Environment = WIPP B brine
   - Analysis = metallographic examination for alteration depth, solution analysis for matrix elements
   - Status = tests completed October 1980

2. General Corrosion Studies
   a. Preliminary Screening Studies at 250 C
      - Materials tested = 300 and 400 series stainless steels, cast irons, Zircaloy-2, nickel base alloys, titanium base alloys and copper base alloys
      - Sample form = U-bend with simulated weld bead used both as a stress corrosion cracking indicator and as a weight loss sample
      - Environment = a NaCl-$MgCl_2$ brine, at 800 psi with a flow of 30 mL/h for three month exposures
      - Analysis = weight loss, visual analysis for cracking
      - Status = preliminary screening tests completed October 1980

   b. General Corrosion Studies of Ferrous Materials
      - Alloys tested = 2-1/4 Cr-1 Mo, 1-1/4 Cr-1/2 Mo, ductile iron, ca low-carbon steel, high purity iron
      - Samples = flat coupons and U-bends
      - Temperature = 150 C

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- Environment = Permian Basin brine No. 2, oxic (1.5 ppm O_2) and anoxic (0.5 ppm O_2)
- Analysis = weight loss, visual analysis for cracking, SEM, and some surface analysis by ESCA
- Status = tests are in progress

c. Limited Reactant (Moist Salt) Test

- Alloys tested = cast and wrought low carbon steels, ductile cast iron, high-purity iron
- Samples = corrosion coupons
- Temperature = 100 C
- Environment = dehydrated WIPP A brine with water levels of 2%, 10%, 15%, and 32%
- Analysis = visual, weight change
- Time = 3 months
- Status = test completed summer of 1983

3. Environmental Fatigue Crack Growth Rate

- Material = Titanium grades 2 and 12, wrought 1018 steel
- Product form = sheet, mill annealed
- Environment = WIPP A brine (titanium), Permian Basin brine No. 2 (steel)
- Temperature = 90 C (titanium), 100 C (steel)
- Orientations = TL, LT
- Specimens = center-cracked tension
- Frequency = 5, 1, 0.1, 0.01 Hz
- Analysis = visual examination of crack length
- Status = tests completed October 1982 (titanium), steel tests began November 1983

4. Slow Strain Rate Testing

- Material = Titanium grades 2 and 12, wrought and cast ferrous materials

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- Product form = sheet, mill-annealed (titanium alloys); plate and cast material (iron alloys), normalized and as-cast
- Environment = WIPP A brine, and Permian Basin brine No. 2
- Temperature = 150 C and 200 C
- Orientations = TL, LT (wrought materials), through-thickness (cast materials)
- Specimens = tensile specimens cut from sheet material or castings
- Strain rates = 2 x 10^{-7}, 10^{-6}, 10^{-5}, 10^{-4} in/in-sec
- Analysis = determine elongation and reduction of sample area, fractography, and energy absorbed during deformation
- Status = original titanium test matrix completed September 1982; wrought and cast ferrous materials in Permian Basin brine are in progress; cast materials testing in WIPP A brine completed September 1982. Testing of reference cast mild steel in progress

5. Irradiation-Corrosion Testing
   - Material = Titanium grades 2 and 12, wrought and cast ferrous materials
   - Product Form = sheet and plate, mill annealed (titanium alloys); sheet or cast material (iron alloys)
   - Environment = Permian Basin brine No. 2, for ferrous materials; WIPP A brine, for titanium alloys
   - Temperature = 150 C
   - Specimens = titanium; 32 corrosion coupons, 8 U-bends, 12 Charpy V-notch, 2 bolt-loaded fracture toughness specimens; iron based alloys: corrosion coupon specimens only
   - Radiation field = to 2 x 10^6 rad/hr for titanium alloys, 2 x 10^3 and 1 x 10^5 rad/hr for ferrous materials
   - Analysis = visual examination, U-bends and fracture toughness specimens; weight loss (corrosion coupons) and impact energy absorption (Charpy V-notch)

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- Status = titanium; 3 months exposure upon test termination by summer 1983

  = iron-based alloys; 10 months exposure by 1/84

6. Irradiated Slow Strain Rate Testing
   - Material = reference cast mild steel
   - Product Form = castings
   - Environment = Permian Basin brine No. 2
   - Temperature = 90 C, 150 C
   - Orientations = through-thickness, parallel to surface
   - Specimens = tensile specimens machined from casting
   - Strain Rates = 2 x 10^{-7}, 10^{-6}, 10^{-5}, 10^{-4} in/in sec
   - Analysis = reduction of area and elongation at fracture, yield and ultimate strengths, fractography, energy absorbed during deformation
   - Status = initiated November 1982

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APPENDIX B

Price Compositions

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Brine Compositions

	Concentration, mg/l Permian Basin Brines		
Ion	**No. 1**	**No. 2**	**No. 3***
Na^+	123,000	[illegible]	22,200
Ca^{2+}	1,000	1,130	14,200
Mg^{2+}	134	122	80,000
K^+	30	28	10,000
Sr^{2+}	35	35	—
Zn^{2+}	7.8	7.9	—
Cl^-	191,000	165,000	200,000
SO_4^{2-}	3,200	1,000	100
HCO_3^-	30	[illegible]	—
Br^-	32	24	2,400
F^-	1.1	1.0	—
I^-	—	—	—
BO_3^{3-}	—	—	—

*20.5 C Equilibration with undissolved solids