NIST

UNITED STATES DEPARTMENT OF COMMERCE
National Institute of Standards and Technology
Gaithersburg, Maryland 20899

December 18, 1990

Dr. Charles Interrante
Materials Engineering Section
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Washington, DC 20555

Dear Dr. Interrante:

Enclosed is the draft biannual report for the project "Evaluation and Compilation of DOE Waste Package Test Data," NUREG/CR-4735, Volume 8 (FIN-A4171). If you have any questions, please call me.

Sincerely,

Anna C. Fraker

Anna C. Fraker
Metallurgist
Corrosion Group
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Enclosure

Distribution:
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DRAFT

NUREG/CR-4735
Volume 8

EVALUATION AND COMPILATION OF DOE WASTE PACKAGE TEST DATA

BIANNUAL REPORT
Covering the Period August 1989 - January 1990

C. G. Interrate, A. C. Fraker, and E. Escalante, Editors

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August 1989 - January 1990

Prepared for:

U.S. Nuclear Regulatory Commission
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PREVIOUS REPORTS IN SERIES

NUREG/CR-4735, Volume 1: Interrante, C. G. (editor), "Evaluation and Compilation of DOE Waste Package Test Data: Biannual Report December 1985-July 1986," National Bureau of Standards, March 1987.

NUREG/CR-4735, Volume 2: Interrante, C. G. (editor), "Evaluation and Compilation of DOE Waste Package Test Data: Biannual Report August 1986-January 1987," National Bureau of Standards, May 1987.

NUREG/CR-4735, Volume 3: Interrante, C. G. (editor), "Evaluation and Compilation of DOE Waste Package Test Data: Biannual Report February 1987-July 1987," National Bureau of Standards, August 1987.

NUREG/CR-4735, Volume 4: Interrante, C. G. (editor), "Evaluation and Compilation of DOE Waste Package Test Data: Biannual Report August 1987-January 1988," National Bureau of Standards, August 1988.

NUREG/CR-4735, Volume 5: Interrante, C. G. (editor), "Evaluation and Compilation of DOE Waste Package Test Data: Biannual Report February 1988-July 1988," National Institute of Standards and Technology, August 1988.

NUREG/CR-4735, Volume 6: Interrante, C. G., Fraker, A. C., and Escalante, E. (editors), "Evaluation and Compilation of DOE Waste Package Test Data: Biannual Report February," August 1988-January 1989," National Institute of Standards and Technology, August 1988.

NUREG/CR-4735, Volume 7: Interrante, C. G., Fraker, A. C., and Escalante, E. (editors) , "Evaluation and Compilation of DOE Waste Package Test Data: Biannual Report February," February 1989-July 1989," National Institute of Standards and Technology, August 1988.

ABSTRACT

This report summarizes evaluations by the National Institute of Standards and Technology (NIST) of Department of Energy (DOE) activities on waste packages designed for containment of radioactive high-level nuclear waste (HLW) for the six month period, August 1989 - January 1990. This includes reviews of related materials research and plans, information on the Yucca Mountain, Nevada disposal site activities, and other information regarding supporting research and special assistance. Short discussions are given relating to the publications reviewed and complete reviews and evaluations are included. Reports of other work are included in the Appendices.

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EXECUTIVE SUMMARY

This is the eighth biannual progress report of the Inational Institute of Standards and Technology (NIST), that deals with assessments of some of the Department of Energy (DOE) activities related to the waste package for disposal of radioactive high-level waste (HLW). This report contains NIST reviews conducted over the period, August 1989 through January 1990 of DOE reports related to activities of the Yucca Mountain Program. Also included in this report are other reports of work conducted in support of this assessment activity. One one these is a report of laboratory research on the corrosion behavior of zirconium alloy nuclear fuel cladding. The second report is one that discusses some mechanisms of acqueous localized corrosion of copper and its alloys.

The laboratory study is present in two parts; one is a literature review of the corrosion behavior of zirconium and Zircaloy and the other part presents data from laboratory studies conducted in an environment and conditions simulating those that could occur at the Yucca Mountain site. Results showed that Zircaloy nuclear fuel cladding passivates and has good general corrosion resistance to the aqueous environment and temperatures used in these tests. Some tests did not show evidence that localized corrosion could occur, and other tests showed localized corrosion could occur, but in these cases, the protection potential was considerably more noble than the corrosion potential. It is not clear whether localized would or would not be a problem, and this area needs further study.

Seven reviews of technical reports are included in this report. Three of these reports deal with the waste package and its design. One of these reports indicates that the number of components in the engineered barrier system to be used for claiming containment will be kept to a minimum for simplifying the assessment and testing process. This same report also emphasizes the importance of modeling due to the involved long time periods of 1,000 to 10,000 years. Another of these papers discusses repository temperatures and the monitored retrievable storage system. The third paper is an earlier paper that discusses design constraints and early considerations involved in the design of the high level waste containers. The historical sequence of events from 1981 to 1988 and the selection of six candidate materials is discussed in another paper. Another paper discusses a program for corrosion studies and electrochemical measurements of the six candidate materials that would be useful for assessing their behavior after long term exposures in the repository. Another paper deals with modeling of radionuclide release, and little difference is found in the radionuclide release with and without backfill. The second paper along this same line dealing with radionuclide transport also uses modeling to show that in the case of radionuclide transport, the rate of transport of the radionuclide out of the breached canister can be increased by the presence of the backfill, but the rate of transport also will be dependent on the isotope that in the final analysis could result in hindering or enhancing transport.

There are now 1181 papers in the NIST/NRC database. 100 of the papers have been reviewed. The database is based on advanced Revelation and is designed for ease and convenience of use. The content of the NIST/NRC data base, periodically, is transferred to the Center for Nuclear Waste Regulatory Analysis, Southwest Research Institute, San Antonio, Texas.

Acknowledgements

The editor wishes to thank the following contributors to the production of this report:

The following contributing reviewers authored the reviews and evaluations given in Appendix B -- Dr. T. Ahn, Dr. Kevin Coakley, Mr. E. Escalante, Dr. A. Fraker, and Dr. C. Interrante.

Ms. Joyce F. Harris who typed and coordinated this report and coordinated production of the reviews included in this report.

Ms. Carla Messina who has continued to develop applications software for the NIST/NRC Database for Reviews and Evaluations on High-Level Waste (HLW) Data.

1.0 INTRODUCTION

1.1 Background

This is the eighth biannual progress report to the Nuclear Regulatory Commission (NRC) from the National Institute for Standards and Technology (NIST). These reports deal with the NIST assessments of some of the Department of Energy (DOE) activities related to the waste package for disposal of radioactive high-level waste (HLW). The NIST provides the NRC with critical reviews and evaluations of selected research, reports and publications and has established a database for the reviews. The NIST also provides the NRC with data from laboratory measurements designed to verify or establish some failure mechanisms of materials being considered for use in nuclear waste storage.

This report covers NIST activities under FIN A4171 for the period from August 1989 through January 1990. Material and activities reported deal only with NNWSI reports or other material pertinent to disposal of high-level waste at Yucca Mountain. The Yucca Mountain Project (YMP) deals with the storage site at Yucca Mountain, Nevada. This site was selected in December 1987 as the primary site in the United States for the first nuclear waste repository.

1.2 Reviews and Evaluations

Reviews are created using guidelines that are modified periodically. The guidelines describe for reviewers the types of information to be contained in each section of a review. The current version of the guidelines for reviewers is included in Appendix A (pp. A-1 to A-6).

The reviews and evaluations conducted by the NIST during the period August 1989 through January 1990 are found on pages B-3 through B-29 of Appendix B.

1.3 Database Activities

The NIST/NRC database is composed of 1181 entries and uses the database management system (DBMS), Advanced Revelation®. The database includes 100 reviews and evaluations at this reporting period.

Development of a new program called key.list sit, which generates keyword list followed by a list of all citations that contain that keyword.

A paper titled, "Advanced Revelation, Scientific Notation, and Nuclear Waste," by C. Messina, C. Interrante, and J. Ruspi (see Appendix D) has been approved by our Washington Editorial Review Board (WERB). This will be published in the future.

1.4 Related Laboratory Testing

Studies involving laboratory testing at the NIST were continued in three areas. The results of one of these studies, "Corrosion Behavior of Zircaloy Nuclear Fuel Cladding", appears in this report (see Appendix D).

1.5 Interpretive Reports

There is a need to have various scientific and technical aspects clarified relating to specific materials and problems that could occur during storage. Interpretative papers are being prepared on several subjects. Three pertinent topics that are being studied and papers written

1. Mechanisms of Localized Aqueous Corrosion of Copper and Its Alloys
2. Mechanisms of Stress Corrosion Cracking
3. Mechanisms of Internal Corrosion of Spent Fuel Rods

2.0 DOE Activities

The location and environment at Yucca Mountain are discussed briefly in this section. Other topics covered are DOE activities, waste package materials, vitrification activities.

2.1 Yucca Mountain -- Location and Environment

The lack of characterization data from the Yucca Mountain site continues to be a major deficiency in the information needed for design and modeling of a nuclear waste container. Without this information, studies must rely on data that is assumed to represent the Yucca Mountain tuff environment. Thus, while reading the results of the many Yucca Mountain project studies, it must be kept in mind that their results are based on these assumptions.

The necessity for burial of high level waste containers for thousands of years places a burden on the modeling capabilities of the scientific community. This challenge, however, is being answered in part, by the many researchers working to develop an understanding of the mechanisms involved in all phases of the problem. The results of these modeling efforts, however, can be no better than the data entered into the models. Information on the characterization of Yucca Mountain continues to be a major deficiency in our knowledge.

The assumptions on the environment of the repository being used today may be correct, but only direct measurements at the site will verify their validity.

3.0 NIST Activities

3.1 Reviews and Summaries

Technical reviews completed during the reporting period are presented in Appendice B. All reviews included in this Appendix been approved by the NIST Washington Editorial Review Board (WERB).

Seven reviews have been completed, and five deal with the container design, materials or performance. The remaining two reports are on modeling the thermal/hydrological environment and radionuclide transport. A brief description of these reviews follows.

3.1.1 Waste Package

O'Neal: 1984

The final design for the high level waste container is not yet developed, since pertinent information about the environment and materials selection is still needed. This report describes the conceptual design of the container based on information available as of its writing. At least three container designs are being considered, based on the expected thermal energy generated by the three types of high level waste. The design constraints include containment of waste for 300 to 1000 years, Thermal limits, contamination of the environment, transportability, and cost-effectiveness. Use of a packing material is still under consideration.

Ramspott: 1988

Presently, the Department of Energy (DOE) defines the Engineered Barrier System as all components within the wall of the borehole, with the major components being a borehole liner, the air gap, a container, and the waste form. This report describes an overview of the approach being taken by the DOE to assure compliance with the requirements of the Nuclear Regulatory Commissions' 10 CFR 60 regulations. The number of components for which "credit" is claimed is kept to a minimum, thereby, simplifying the assessment and testing process. Because of the unprecedented time periods considered, 1,000 to 10,000 years, computer modeling is essential.

Nelson: 1989

This document, developed by Lawrence Livermore National Laboratory, is a report to the Office of Civilian Radioactive Waste Management, describing the waste package design, alternatives, and heat-tailoring of the repository as applied to the Monitored Retrievable storage System [Nelson]. Consideration is given to a one-canister design, a canister within a canister design, and options in packing of the waste form in a canister. Maintaining the repository temperature above 97 C for as long as possible is dependent on the distribution of waste in the containers and the distribution of the containers in the repository, and is an important part of this evaluation. The assumptions used in making this study are identified.

At the early stages of the selection process, only iron-based materials were chosen for consideration for the container, but in 1984, a high nickel alloy and three copper-based metals were included.

3.1.2 Candidate Materials

McCright: 1988

The historical sequence of events from 1981 to 1988, leading up to the present choice of candidate materials being considered for the waste form canister, is described. Status reports, letters, memos, and other pertinent documents are reproduced in the appendix. At the early stages of the selection process, only iron-based materials were chosen from consideration for the container, but in 1984, a high nickel alloy and three copper-based metals were included.

3.1.3 Modeling Radionuclides

Nitao: 1988

The presence of backfill against a container opening will significantly increase the rate of transport out of the container. Preliminary calculations of release rates for certain radionuclides based on a simplified model of diffusive transport in rock indicate that some isotopes, with long half lives, show little difference in release rates between backfilled and non-backfilled cases. Others are significantly reduced or are not affected over a long term period.

3.1.4 Radionuclide Transport

Nitao 1988

Earlier work indicated that a continuous moisture bridge between the fuel and the surrounding rock is necessary for the aqueous transport of radionuclides [Nitao]. Using a mathematical model, the effect of a bentonite emplacement backfill on radionuclide transport, was examined. The results indicate that the presence of a backfill will significantly increase the rate of transport out of the breached canister, but depending on the isotope, the rate of diffusion through the backfill may be hindered or enhanced.

3.1.5 Container Corrosion

Beavers: 1989

This is a report on an ongoing program made up of seven tasks directed at developing independent experimental data to assist the NRC in evaluating the uncertainties in DOE's claims concerning waste container corrosion [Beavers]. The DOE position has been that corrosion rates of the metallic waste canisters can be quantified and extrapolated to long term exposures (300-1000 years). The study includes electrochemical measurements and slow strain rate testing of materials in simulated repository environments. This is the first report of the second year of the study.

Appendix A. Waste Package Data Review Form Guidelines

Appendix A

Waste Package Data Review Form Guidelines

DATA SOURCE

Full document reference. This section may be completed for the reviewer before he/she receives the document. If completing this section yourself, use the following format:

TECHNICAL REPORT:

Pitman, S. G., "Slow-Strain-Rate Testing of Steel," Rockwell Hanford Operations, SD-BWI-TS-008, August 1984.

CONFERENCE PAPER:

Abrajano, T. A., Jr. and Bates, J. L., "Transport and Reaction Kinetics at the Glass: Solution Interface Region: Results of Repository-Oriented Leaching Experiments," in Materials Research Society, 1983 Symposia Proceedings, Vol. 26, Scientific Basis for Nuclear Waste Management, McVay, G. L. (editor), North-Holland, 1984, p. 533-542.

DATE REVIEWED

Give the date the document review was completed. Add an additional date each time that the review is revised, e.g. 11/25/86; Revised 12/01/86.

PURPOSE

If the author states the purpose, give that; if not, give your perception of what the purpose must have been.

KEY WORDS

These are to be checked off on the key word checklist. In general, these keywords should reflect the information given in the above categories discussed above. Additional keywords, which are truly different from terms on this list, should be added to the list under the category "other" which appears at the end of each key word list.

CONTENTS

List the number of pages, figures and tables, and some breakdown (as appropriate) of subsections, e.g. literature survey 15 p, test methods 2 p, discussion 1 p.

TYPE OF DATA

(1) Scope of the Report, e.g. Experimental, Theoretical, Literature Review, Data Analysis.

(2) Failure Mode or Phenomenon Studied, e.g. Corrosion, Creep, Fatigue, Leaching, Pitting, Hydrogen Embrittlement, Debonding, Dealloying

MATERIALS/COMPONENTS

Description of the material studied, e.g., 304L stainless steel, brass, zircaloy cladding, welds in 316 stainless steel, packing material, basalt. Also describe, if specifically addressed, component parts, e.g. the screw-type cap on a waste cylinder.

TEST CONDITIONS

(1) State of the material being tested -- cold worked or annealed 304L stainless steel, thermo-mechanical history of the material (or component) studied.

(2) Specimen Preparation -- prestressed, precracked, size, type of specimen.

(3) Environment, pressures, and other test parameters of the material being tested, e.g. aqueous environment, radioactive surrounding, electrolytes or corrosive agents present, temperature and pressure (externally applied or not) during the test.

METHODS OF DATA COLLECTION/ANALYSIS

This section includes data measurement methods and types of data measured, as well as data analysis techniques, e.g. electron microscopy, weight loss vs time, slow strain rate tensile test, x-ray diffraction, differential thermal analysis, A.C. electrical resistivity using a Wheatstone bridge, mass spectroscopic chemical analysis of the corrosive environment, Latin Hypercube method, Monte Carlo techniques.

AMOUNT OF DATA

This section includes the number of tables and graphs together with their titles and axes (including the range in values). If a listing of figure and table titles is provided, the reviewer should add the limits given on each axis, i.e. for temperature, or other explanatory information as appropriate.

Sometimes a synthesis is preferable to a listing of table and figure titles:

Five tables of temperature and time data for five molten-glass pouring operations, each table including the data from ten sensor locations. The temperatures ranged from 1100°C to 0°C over a time period of 24 hours.

<u>UNCERTAINTIES IN DATA</u>

Included here are error bars and uncertainties in the data as <u>stated by the author</u>. This also includes qualitative statements by the author on the <u>reliability</u> of the data:

The author states that, "Temperatures carry an accuracy of +5°C while the times are reported to within +15 sec. It was felt that under real glass pouring operations (without well controlled crucible cooling) the temperature-time curves will be shifted to somewhat higher temperatures than shown here."

<u>DEFICIENCIES/LIMITATIONS IN DATABASE</u>

Statements <u>by the author</u> on the <u>applicability</u> of the data are given here:

The author states "Extrapolation of the temperature-time (time < 24 hrs) data presented here to times in excess of 100 years should not be performed." The data presented here is useful only for indicating trends and qualitative parameter relationships, not for the purpose of presenting absolute values.

<u>CONCLUSIONS</u>

Put the conclusions of the author in quotes whenever the author's words are used without interpretation or paraphrasing.

<u>COMMENTS OF REVIEWER</u>

The reviewer's general comments on the document. This category is wide open as far as content. It contains information the reviewer did not enter into any of the above categories, but which is considered important for the reader to know. It is also in this section that the reviewer would put any of his/her comments on the deficiencies and uncertainties in the data and analysis:

This is a very comprehensive review of the literature on the temperature sensitization of stainless steels. Even though it neglects the definitive work of Bertocci, Shull, Kaufman, and Escalante [Phys. Rev. J13, (1979), pp. 15-358] in this area (presumably because of the difficulty in locating this document), this review still considers a sufficiently large number of other investigations to provide a good understanding of the present status of the field. The one discordant note here, however, is that it would have been a much more useful review if stainless steel types 301, 303, 304, 316, and 440°C had also been addressed.

Statements such as, "Further tests in this area are needed," or "More data is required," require an explanation. To state the need is valuable; such statements, however, do not provide enough information.

Abstracts taken from the document to be reviewed will be attached to the review. The abstract is also available in the database. Therefore, references to the abstract may be made.

<u>RELATED HLW REPORTS</u>

The report number(s) of any report(s) known to be directly related to the report being reviewed should be entered here so that these reports may be cross-referenced in the database.

The reviewer might also indicate any other reports taken from the reference list (in the report being reviewed) that should be acquired and included in the database.

<u>APPLICABILITY OF DATA TO LICENSING</u> -- READ, BUT DO NOT COMPLETE THIS SECTION, NOT TO BE FILLED IN BY THE REVIEWER

Indicated here is the licensing issue addressed by this paper. It is either (a) a specific <u>Listed</u> licensing <u>Issue</u> in an NRC Site Characterization Plan (ISTP) or (b) a new issue not yet identified in an ISTP.

The ranking of the paper is determined as follows: The "Key Data" box is marked if the paper contains data that is of sufficient quality that it must be considered by NRC in an evaluation of a license application. Such a paper must meet at least one of the following criteria: (1) it is an in-depth review of the pertinent literature, (2) it contains data that is found to be especially significant after being assessed for scientific merit and quality, or

(3) it contains data with such a small uncertainty that it must be considered in a performance evaluation of a license application. If the paper does not meet any of the above three criteria, it is indicated as "Supporting Data".

Reviewer's comments on the listing of the document may be included with the appropriate Issue Listing in subcategory (a) or (b).

AUTHOR'S ABSTRACT

The author's abstract is given whenever available. Usually, it presents key numerical data. Whenever it does not, the reviewer is asked to furnish key numerical data within the review. These key data may be placed in any appropriate section of the review.

Appendix B. NIST Reviews of Documents Concerning the Durability of Proposed Packages for High-Level Radioactive Waste

Appendix B

NIST Document Reviews Concerning the Durability of Proposed Packages for High-Level Radioactive Waste

Page

Waste Package

Ramspott, L. D., UCRL-98029
"Assessment of Engineered Barrier System and Design of Waste Packages" B-4

Nelson, T, Russell, E., Johnson, G. L., Morisette, R., Stahl, D., LaMonica, L., Hertel, G., UCID-21700
"Yucca Mountain Project Waste Package Design for MRS System Studies" B-6

O'Neal, W. C., Ballou, L. B., Gregg, D. W., and Russell, E. W., UCRL-89830
"Nuclear Waste Package Design for the Vadose Zone in Tuff" B-11

Candidate Materials

McCright, R. D., UCID-21472
"An Annotated History of Container Candidate Material Selection" B-14

Modeling Radionuclides

Nitao, J. J., UCID-21444
"Numerical Modeling of the Thermal and Hydrological Environment Around a Nuclear Waste Package Using the Equivalent Continuum Approximation: Horizontal Emplacement" B-17

Radionuclide Transport

Nitao, J., UCID-21466
"Simulations of the Near-Field Transport of Radionuclides by Liquid Diffusion at Yucca Mountain -- Comparisons With and Without Emplacement Backfill" B-22

Page

Container Corrosion

Beavers, J. A. and Thompson, N. G.
"Container Corrosion in High Level Nuclear Waste Repositories", First Semi-Annual Report/Year 2, September 1988 to February 1989 . . . . B-26

Container Material

Kass, J. N., UCRL-101097
"Evaluation of Copper, Aluminum Bronze, and Copper-Nickel for YMP Container Material" B-34

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Author(s), Reference, Reference Availability

Ramspott, L. D.
"Assessment of Engineered Barrier System and Design of Waste Packages"
UCRL-98029, June 1988.

(b) Organization Producing Data

Lawrence Livermore National Laboratory for the
U.S. Department of Energy

DATE REVIEWED: 2/26/90

PURPOSE

To explain the general concept of "performance allocation" as it applies to the Yucca Mountain waste package.

KEY WORDS

Design, simulated field, Yucca Mountain, tuff, gamma radiation field, copper base, stainless steel, commercial high-level waste (CHLW), defense high-level waste (DHLW).

CONTENTS

13 pages of text, 1 table of Engineered Barrier System elements, 7 references.

AMOUNT OF DATA

None given.

TEST CONDITIONS

None given.

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

CONCLUSIONS OF AUTHOR

To meet the post-closure objectives for the waste disposal system established by the NRC in 10 CFR 60, computer modeling is required, and performance assessment is and will remain a key element of the waste package program through licensing.

COMMENTS OF REVIEWER

This report is a description of the "performance allocation" process, whereby elements of the Engineered Barrier System are evaluated on their contribution to containment, credit, of the nuclear waste.

APPLICABILITY OF DATA TO LICENSING
[Ranking: key data ( ), supporting (x)]

(a) Relationship to Waste Package Performance Issues Already Identified

2.2.8 How will the design of the waste package container accommodate all potential natural and waste package-induced conditions?

(b) New Licensing Issues

(c) General Comments

AUTHOR'S ABSTRACT

The U.S. Nuclear Regulatory Commission has established two post-closure performance objectives for the Engineered Barrier System (EBS) in a geologic repository. These require containment of the waste followed by controlled release. The EBS for a repository in unsaturated tuff at Yucca Mountain is designed to meet these performance objectives. The major components are the waste form, container, air gap, and borehole liner. Assessment of post-closure performance of the EBS is based on allocating performance for various components toward meeting overall design objectives. Because of the unprecedented time periods considered, 1000 to 10,000 years, computer modeling is essential and will be used in conjunction with testing to assess whether the performance allocations are met.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Author(s), References, Reference Availability

Nelson, T, Russell, E., Johnson, G. L., Morisette, R., Stahl, D., LaMonica, L., Hertel, G.
"Yucca Mountain Project Waste Package Design for MRS System Studies"
UCID-21700, April 1989

(b) Organization Producing Data

Lawrence Livermore National Laboratory for the U.S. Department of Energy
Contract No. W-7048-Eng-48.

DATE REVIEWED: 2-29-90

PURPOSE

"This report, prepared by the Yucca Mountain Project, is the report for Task E. 'Waste Package Design' of the MRS (Monitored Retrievable Storage) system study." "Task E. Waste Package Design, defined a scope of work that involves developing information on current and alternative waste package designs, developing a canister usable at the MRS for either intact or consolidated fuel, and providing a discussion of the potential for developing a 'heat-tailored' repository."

The primary aim of the MRS system studies is to develop cost and schedule information relative to the application of current designs and technology."

"This section (5.0 subtask E-2) is intended to provide a summary description of waste package concepts being investigated under the Alternate Barriers Task. The objective of this task is twofold. First, the task is to meet the requirements of 10 CFR Part 60 for consideration and comparison of alternates. Second, the task is to select one or two alternates which can be carried through ACD (Advanced Conceptual Design). The latter is to provide a fall-back position in the event that results from site characterization render the reference metal container unacceptable."

"The objective (7.0 Subtask E-4) is to enhance the unsaturated nature of the emplacement horizon such that the mean time for liquid water reaching the waste-emplacement borehole can be maximized and the presence of liquid water on the waste container can be minimized."

KEY WORDS

Literature review, scoping test, field, Yucca Mountain, tuff composition, tuff, bronze, copper base, nickel base, stainless steel, titanium base, iron-base, aluminum, lead, zinc, 304L stainless steel, 316L stainless steel, Alloy 825, CDA 613, CDA 952, CDA 715, CDA 102, CDA 122, intact assemblies of fuel rods, glass (West Valley reference glass), glass (defense waste reference glass), commercial high-level waste (CHLW), defense high-level waste (DHLW), spent fuel, spent fuel (BWR), spent fuel (LWR), spent fuel (PWR),

CONTENTS

This 140-page report consists of an introduction and summary, 14 figures, 10 tables, and the following content:

CONTENT	NUMBER OF PAGES
General Assumptions	19
General Sensitivity Considerations	2
Subtask E-1: Metal Barrier Waste Package Concepts	12
Subtask E-2: Alternate Waste Package Concepts	6
Subtask E-3: MRS Canister Concept	5
Subtask E-4: "Heat-Tailored" Repository	8
References (5)	1
Appendix. Documentation of Bases and Assumptions	87

TEST CONDITIONS

Materials:

- light water reactor (LWR) spent fuel: either pressurized water reactor (PWR) or boiling water reactor (BWR) spent fuel.
- defense high-level waste (DHLW).
- commercial high-level waste (CHLW).
- borosilicate glass inside a stainless steel canister for CHLW.
- six alloys as candidates for container materials: 304L stainless steel, 316L stainless steel, alloy 825, Aluminum Bronze (CDA 613 or CDA 952), Copper-Nickel Alloy (CDA 715), and High Purity Copper (CDA 102 and CDA 122).
- alternative container materials: single metals (titanium alloys, high nickel alloys), bi-metallics (nickel and iron-base alloys and copper alloys for the outer and inner liners respectively), coatings

(aluminides, nickel-chrome-aluminum alloys, oxides, nitrides), fillers (magnetites, glass, aluminum, lead and zinc), alumina, and graphite.

Specimen Preparation:

- Intact assemblies of fuel rods or consolidated fuel rods. The consolidated fuel rods may be contained in a canister. Ninety-five percent of the spent fuel would be consolidated. (Combinations are in Tables 2-3, 4-1, and 4-2.)

- A fixed spent fuel loading in each waste package type with a maximum thermal output at the time of emplacement of 3.5 KW/package. -Table 2-2. Waste Form Assumptions. Essentially a right cylinder of 310-480 cm height, 50-75 cm diameter, and 1.0-2.5 cm thickness, with a lid containing a handling pintler (Table 4-2).
- Fabrication and welding for metal containers: back extrusion, roll-and-welding, centrifugal casting, deep drawing, electron beam welding, plasma arc welding, and friction welding.
- Alumina containers: similar sizes to those of metal containers: an alumina shell and a thin stainless steel jacket (Table 5-1). Hot isostatic pressing and active metal brazing are used for processing.
- NDE: ultrasonic inspection, radiography and dye penetrating testing.
- Canister: 304L stainless steels (or alloy 825 if not closed well) 6~9 in. side and 175 in. long of square cross sections of 55 gallon.

Environment:

- Yucca Mountain Repository, with its unsaturated "dry" environment.
- Dry spent fuel.
- A maximum fuel cladding temperature limit of 350°C.
- The nominal thermal output at emplacement is 3300 W per package for the spent fuel and 470 W per package for the high-level waste. APD (The Areal Power Density) limit is 57 KW/acre.
- Model-calculated temperatures:
  - Model 1 - borehole wall (56~113°C), interior of panel (>97°C), panel center (25-50°C).
  - Model 2 - borehole wall (22°C), at below 97°C (15% by not heat- tailoring, 7.5% by heat-tailoring).

UNCERTAINTIES IN DATA

LLNL MRS canister design (tolerance limits in figures 10 and 14).

The metal containers will have the wall thickness of <u>about</u> 1 cm, except for high purity copper, where a <u>2.5-3 cm</u> thickness is required, and will be of a right cylinder of <u>310-480 cm</u> height, <u>50-75 cm</u> diameter, and a <u>1.0-2.5 cm</u> thickness.

DEFICIENCIES/LIMITATIONS IN DATABASE

"In order to perform a system study such as the MRS system study, it is necessary that a number of assumptions be made to fix some of the variables still under consideration. These assumptions may not represent an optimum set, however, and it should not be assumed that they represent a preferred set. They should be viewed simply for what they are: a set of reference conditions for the purpose of the MRS system study." "These assumptions do not represent the total variations anticipated in the variables listed."

"No one concept would work for all scenarios because of the different functions being performed by the MRS and the repository."

CONCLUSIONS OF AUTHOR

"A number of assumptions were necessary prior to initiation of this system study." "Existing concepts were utilized because of schedule constraints."

"With the exception of rod consolidation considerations, the system study should not be sensitive to the parameters assumed for the waste package."

"Although stainless steel is assumed for this study, a container material has not been selected for Advanced Conceptual Design from the six candidates currently under study."

"The alternate waste packages and materials" are "being considered in the event that the waste package emplacement environment is more severe than is currently anticipated."

"A concept is provided "for an MRS canister to contain consolidated fuel for storage at the MRS and eventual shipment to the repository."

Heat-tailoring is not necessary to achieve the required performance of the waste package. Although no performance has been allocated to the potential benefits of 'heat tailoring' because of the many uncertainties involved, this benefit is being considered in the design of the repository."

COMMENTS OF REVIEWER

The content of this report is based heavily on many assumptions made for Monitored Retrievable Storage (MRS). However, the list of those assumptions does not seem to be complete. The cost of rod consolidation consideration in the sensitivity analysis is not mentioned. Such assumptions should be justified by tabulating existing data from many on-going projects such as vitrification data in the West Valley demonstration project, or from seismic behavior.

The site for the MRS is not clearly indicated and may be confused with that for the permanent storage. The location of the candidate sites for the MRS are not given. Also, it is not clear whether retrievability procedures for the MRS can be used for the permanent storage as well.

The candidate container materials are based heavily on the corrosion performance of those materials. The selection of the candidate materials should include consideration of other factors such as fabricability, nondestructive evaluation (NDE), and cost. In this sense, alternative container materials appear to be very important.

The importance of the canister was described quite precisely. However, it is not clear to the reviewers whether the metal canister, holding waste glass, is taking any credit for corrosion protection.

It would be helpful to have the guidelines of heat-tailoring explained in a more illustrative manner. Also, it is not clear whether or not this heat-tailoring is applicable to both the MRS and the permanent storage.

APPLICABILITY OF DATA TO LICENSING
[Ranking: key data ( ), supporting data (x)]

(a) Relationship to Waste Package Performance Issues Already Identified

2.2.8 How will the design of the waste package container accommodate all potential natural and waste package induced conditions?

(b) New Licensing Issues

(c) General Comments on Licensing

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Author(s), Reference, Reference Availability

O'Neal, W. C., Ballou, L. B., Gregg, D. W., and Russell, E. W.
"Nuclear Waste Package Design for the Vadose Zone in Tuff"
UCRL-89830, February 1984

(b) Organization Producing Data

Lawrence Livermore National Laboratory for the
U.S. Department of Energy

DATE REVIEWED:

PURPOSE

"The objective is to develop and analyze waste package designs which incorporate qualified materials and which are fully compatible with the repository design." "The basic design philosophy for waste package conceptual designs is to meet NRC design criteria with flexibility in technical performance and cost."

KEY WORDS

Design, simulated field, nickel base, stainless steel, 304L stainless steel, 316L stainless steel.

CONTENTS

15 pages, 2 figures (container designs), and 2 tables.

AMOUNT OF DATA

Some data on costs of various package designs.

TEST CONDITIONS

None given.

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

CONCLUSIONS OF AUTHOR

"The conceptual design ensemble provides a group of designs from which a set can be chosen for eventual detailed design of waste packages. Within the variations in materials and configurations available, detailed designs should meet all requirements, barring unexpected results from long-term materials testing or packaging environment characterization activities."

COMMENTS OF REVIEWER

This report is a brief overview of the process used in arriving at the present canister design for containment of high level nuclear waste, and includes a brief description of the various mechanical tests performed on the container, simulating possible scenarios in the repository. An economic analysis compares the cost of vertically emplaced canisters with and without packing.

APPLICABILITY OF DATA TO LICENSING
[Ranking: key data ( ), supporting (x)]

(a) Relationship to Waste Package Performance Issues Already Identified

2.3.7 How will the design of the waste form accommodate all potential natural and waste package induced conditions?

(b) New Licensing Issues

(c) General Comments

AUTHOR'S ABSTRACT

This report presents an overview of the selection and analysis of conceptual waste package designs that will be used by the Nevada Nuclear Waste Storage Investigation (NNWSI) project for disposal of high level nuclear waste (HLW) at the proposed Yucca Mountain, Nevada Site.

The design requirements that the waste packages are required to meet are listed. Concept drawings for the reference designs and one alternative package design are shown. Four metal alloys; 304L SS, 321 SS, 316L SS and Incoloy alloy 825 have been selected for candidate canister/overpack materials, and 1020 carbon steel has been selected as the reference metal for the borehole liners.

A summary of the results of technical and economic analysis supporting the selection of the conceptual waste package designs is included. Post-closure containment and release rates are not discussed in this paper.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Author(s), Reference, Reference Availability

McCright, R. D.
"An Annotated History of Container Candidate Material Selection".
UCID-21472, July 1988.

(b) Organization Producing Data

Lawrence Livermore National Laboratory for the U.S. Department of Energy

DATE REVIEWED: 6/27/89

PURPOSE

"The purpose of this paper is to document the history of the part of the Metal Barrier Selection and Testing Task that concerns selection of candidate materials for the waste package container."

KEY WORDS

Design, literature review, Yucca Mountain, tuff composition.

CONTENTS

Text - 17 pgs., 24 references, 7 Attachments.

AMOUNT OF DATA

None given.

TEST CONDITIONS

None given.

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

CONCLUSIONS OF AUTHOR

None given.

COMMENTS OF REVIEWER

This is an historical review of the events leading to selection of canister materials from 1981 to 1988 by an individual that has been closely involved with these events at Lawrence Livermore National Laboratories since before 1981. The events are well documented by an extensive list of references and pertinent letters.

The author starts with the period when there were three possible sites at Hanford, WA, Deaf Smith, TX, and Yucca Mountain, AZ. The review includes the changing container requirements as the site selection was narrowed to Yucca Mountain, and the horizon was changed from the saturated zone to the unsaturated zone. At the early stages of the selection process, only iron-based materials were chosen for consideration for the container, but in 1984, a high nickel alloy and three copper-based metals were included.

RELATED HLW REPORTS

1) Halsey, H.G. and McCright, R. D., "Metal Barrier Selection and Testing Task Scientific Investigation Plan," UCID-21262, November 1987.

2) Conceptual Waste Package Designs for Disposal of Nuclear Waste in Tuff," Westinghouse Electric Corporation Report AESD-Tme-3138, September 1982.

3) McCright, R. D., Van Konynenburg, R. A., and Ballou, L. B., "Corrosion Test Plan to Guide Canister Materials Selection and Design for a Tuff Repository, UCRL-89476, November 1983.

4) McCright, R. D., Weiss, H., Juhas, M. and Logan, R. W., "Selection of Candidate of Canister Materials for High-Level Nuclear Waste Containment in a Tuff Repository," UCRL-89988, April 1984.

APPLICABILITY OF DATA TO LICENSING
[Ranking: key data ( ), supporting (x)]

(a) Relationship to Waste Package Performance Issues Already Identified

Does not apply.

(b) New Licensing Issues

(c) General Comments

AUTHOR'S ABSTRACT

This paper documents events in the Nevada Nuclear Storage Investigations (NNWSI) Project that have influenced the selection of metals and alloys proposed for fabrication of waste package containers for permanent disposal of high-level nuclear waste in a repository at Yucca Mountain, Nevada. The time period from 1981 to 1988 is covered in this annotated history. The history traces the candidate materials that have been considered at different stages of site characterization planning activities. At present, six candidate materials are considered and described in the 1988 Consultation Draft of the NNWSI Site Characterization Plan (SCP). The six materials are grouped into two alloy families, copper-base materials and iron to nickel-based materials with an austenitic structure. The three austenitic candidates resulted from a 1983 survey of a longer list of candidate materials; the other three candidates resulted from a special request from DOE in 1984 to evaluate copper and copper-base alloys.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Author(s), Reference, Reference Availability

Nitao, J. J.
"Numerical Modeling of the Thermal and Hydrological Environment Around a Nuclear Waste Package Using the Equivalent Continuum Approximation: Horizontal Emplacement" UCID-21444, May 1988.

(b) Organization Producing Data

Lawrence Livermore National Laboratory for the
U.S. Department of Energy
Contract No. W-7405-48 Eng.

DATE REVIEWED: 1/31/90.

PURPOSE

The author has "performed computer simulations of the immediate thermal and hydrological environment around a nuclear waste package". "Fluid behavior in the rock was modeled using the equivalent continuum approximation." A computer code called TOUGH (Pruess, 1985) was modified to model the flow of water, water vapor and air through the rock.

KEY WORDS

Theory, modeling, computer modeling, TOUGH, simulated field, Yucca Mountain, air, water vapor, aerated water, high-level, heat capacity, thermal conductivity, hydrology.

CONTENTS

There are 72 pages of text, 59 figures and 3 tables. In the text, there are: 2 pages of introduction, 14 pages which describe the model assumptions, 2 pages concerning the computer code used, 7 pages which describe model results for different input parameters, 2 pages of concluding remarks and 3 pages of references.

UNCERTAINTIES IN DATA

The author's work is theoretical; there is no experimental data to validate the equivalent continuum approximation for flow. Further, there is no data to verify the values of the input parameters used in the model.

DEFICIENCIES/LIMITATIONS IN DATABASE

Because of so many simplifying assumptions about the rock matrix, fractures and flow, how well the model describes reality is an open question. The author states that, "considerable work needs to be done to develop better models of fluid behavior in partially fractured rock and more experimental data is needed to accurately model the waste package environment." The author remarks that "our results should be viewed as preliminary at this time because many of the physical input parameters to the model as well as the exact conditions in Yucca Mountain are either not known or have a high degree of uncertainty and many idealizations and approximations of complicated physical and chemical behavior have been made. "The author recommended research on the following issues."

1. "The accuracy and applicability of the equivalent continuum model... "

2. "...comparisons need to be made with heat conduction models that use variable specific heats... and the effect of using periodic boundary conditions needs to be considered."

3. "The effect on container spacings and the placement of containers with different heat outputs..."

4. "Experimental data for the matrix and fracture characteristic curves at different temperatures, and under both drainage and imbibition conditions."

5. "Discrete fracture modelling is needed to study the effect of gravity flow in fractures, fracture orientation, fracture cross flow, and highly permeable rubbilized shear zones."

6. "The effect of thermally stressed fracture closings on the near field hydrology is not known."

7. The possible effect of film flow ... should be investigated..."

8. "Depending on suction potential curves, there may be significant amounts of surface absorbed water in matrix rock... the diffusive transport properties of this water may have to be determined experimentally."

Further, the author states that, "chemical effects, such as possible increased concentration of silica by dissolution in hot water moving toward waste package via "heat pipes" and deposition where water evaporates, are not taken into account."

CONCLUSIONS OF THE AUTHOR

The author notes that "the predictions reported in this paper are highly preliminary due to the current uncertainty in the model input parameters and the sub-models used in our simulations." Given this caveat, his conclusions are:

1. "At the surface recharge rates studied and during the 2600 year time span of our simulations the liquid saturation at the borehole wall next to the container did not return to the initial native saturation after drying from the waste package waste heat began. Liquid pore pressures remain below the borehole pressure so that no liquid flow into the borehole is predicted."

2. "Small amounts of water due to capillary condensation first reach the borehole wall at about 200 years. This time is very sensitive to the capillary curves used at the low saturation range. Based upon the conservative recharge rate estimate of 0.5 mm/year [Montazer and Wilson, 1984], bulk water first reaches the borehole wall at about 1000 years from emplacement due primarily to capillary imbibition."

3. "Predictions of temperatures near the waste package are significantly lower when flow is included as compared to the case when only thermal conduction and constant specific heat are considered."

4. "Significant amounts of fracture water are predicted to occur due to the movement and condensation of water vapor in the fractures during the heating period. However, there is no water in the fractures in the vicinity of the waste package due the drying effects of the waste package heat."

COMMENTS OF REVIEWER

Nitao uses an equivalent medium approximation to numerically compute the multiphase flow of air and water through the rock matrix and fractures. In the equivalent medium approach, bulk averages of hydrological parameters such as saturation, porosity and hydraulic conductivity are approximated in terms of hydrological parameters of the rock matrix and rock fractures. The bulk conductivity of the overall medium which consists of both the matrix and fractures, is expressed as a weighted average of the conductivities of the rock matrix and the fractures. It is assumed that "there are enough fractures of varied orientation to ensure isotropic behavior." Nitao remarks that the validity of the effective medium approximation must be checked. To get numerical solutions, Nitao used a modified version of the computer code TOUGH (Pruess, 1985).

The author states that his results depend on a model which greatly simplifies the physics and chemistry that govern the thermal and hydrological environment around the waste canister. The greatest weakness of the work is the lack of experimental data. For instance, the author assumes an equivalent continuum medium approximation for modeling flow through both the fractures and rock matrix. However, no data on fractures is presented. Without experimental data, it is not possible to verify the equivalent medium approximation. Rather than an equivalent medium continuum approximation, it may be necessary to solve for flow through discrete fractures. Thus, as the author recognizes, his conclusions depend on many simplifying assumptions that may not be valid.

Nitao does not remark on the possible benefit of designs that would channel water away from the waste package.

APPLICABILITY OF DATA TO LICENSING
[Ranking: key data ( ), supporting data (x)]

(a) Relationship to Waste Package Performance Issues Already Identified

2.1 When, how, and at what rate will groundwater penetrate the packing around waste package containers.

(b) New Licensing Issues

(c) General Comments

AUTHOR'S ABSTRACT

In support of the investigations for an underground high-level nuclear waste repository at Yucca Mountain, Nevada, we have performed computer simulations of the immediate thermal and hydrological environment around a nuclear waste package. Calculations of this type will be needed for waste package design, performance assessment, and radionuclide transport analyses. Two dimensional computer simulations using a modified version of the TOUGH code were run for an idealized configuration derived from the COVE3 benchmarking effort consisting of a single spent fuel waste package with laterally periodic boundary conditions. The model domain extended downward to the water table and upward to the ground level. Fluid behavior in the rock was modeled using the equivalent continuum approximation. Runs were made with surface water in flux rates at the surface set to 0.1, 0.5, and 1.0 mm/yr. A significant amount of code modification and development was needed in order to develop the capability to run these types of problems out to the long time spans required.

Since any significant transport of non-gaseous radionuclides will involve liquid water as a main vehicle of movement, and since liquid water, if present, will also contribute to the waste package corrosion, its presence is of vital concern. Initial heating from the radioactive decay will vaporize the liquid pore water around the waste package. Of major interest to waste container design is the time at which possible wetting of the package occurs during the subsequent cooldown period. Our simulations showed that vapor transport and capillary condensation are the major mechanisms of water movement early in the cool-down period. However, the amount of liquid water in the rock next to the waste package during this time is very small and will have very low mobility, although the diffusive transport properties of this water are not exactly known. In our simulations the main front of water returns to the borehole wall at approximately 1000 years from emplacement as it is drawn in by capillary imbibition. At no time during the 2600 year time span of our simulation does the water saturation of the rock next to the borehole wall increase above initial native saturation. The values of these two time periods as well as the other predictions reported in this paper are highly preliminary due to the current uncertainty in the model input parameters and the sub-models used in our simulations. However, it is seen that the effect of the hydrological fluid flow on the thermal history may be significant. Considerable work needs to be done to develop better models of fluid behavior in partially fractured rock and more experimental data is needed to accurately model the waste package environment.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Author(s), Reference, Reference Availability

Nitao, J.
"Simulations of the Near-Field Transport of Radionuclides by Liquid Diffusion at Yucca Mountain -- Comparisons With and Without Emplacement Backfill"
UCID-21466, July 1988.

(b) Organization Producing Data

Lawrence Livermore National Laboratory for the
U.S. Department of Energy
Contract No. W-7405-Eng-48.

DATE REVIEWED: 2/14/90

PURPOSE

"We consider in this report simplified simulations of one-dimensional transport of radionuclides in the rock due to liquid molecular diffusion in order to determine the effects of an emplacement backfill."

"The radionuclide species that are considered are I-129, Sr-240, Pu-240 and U-234."

KEY WORDS

Theory, computer simulation of diffusion, one-dimensional molecular diffusion, simulated field, Yucca Mountain, tuff, backfill, ^{90}Sr, ^{240}Pu, ^{234}U, ^{129}I, ambient temperature, molecular diffusion, bentonite, ^{234}U, ^{90}Sr, groundwater

CONTENTS

24 pages, 13 figures, 1 table
The text includes 2 pages of introduction,
1 page which describes the mathematical model,
2 pages which describe how the model is solved numerically,
3 pages of applications and a 2 page conclusion.

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

1. "In this report we perform some preliminary calculations on the release rates for certain radionuclides based on a simplified model of diffusive transport in the rock. Convective transport is neglected..."

2. "Due to the lack of experimental data we have used a value of one for the tortuosity factor which is a conservative value from the standpoint of overestimating diffusive release rates. But in the future, simulations using lower values of the tortuosity factor should be made, in which case, convective transport will become important relative to diffusion."

3. "The effect of spatial variations in tortuosity and sorption in the rock have not been considered."

4. "The simplified mathematical models used in our simulations are based on solving the one-dimensional diffusion-decay equation in spherical coordinates for molecular diffusion, sorption, and radioactive decay of a single aqueous specie... More sophisticated mathematical models may have to be developed in the future to take into account the complex hydrological and geochemical processes that may exist in the field."

5. "Our simulations of the no-backfill case are pertinent only to the, perhaps unlikely, scenario that a contiguous bridge of liquid water is sustained from the waste to the tuff. For the backfill case, it is assumed that such a bridge exists from the waste form to the backfill... our simulations and the resulting release rates do not take account the lower probability of a contiguous diffusion path occurring in the no-backfill case..."

CONCLUSIONS OF AUTHOR

1. "As expected, isotopes such as those of iodine, that have long half-lives and are not significantly sorbed by the tuff or Bentonite backfill, will show little difference in release rates between the backfill and no-backfill cases."

2. "Some isotopes such as Pu-240 have their release rates significantly reduced by a Bentonite backfill."

3. "Some isotopes such as U-234 will have an initial reduction in the release rate due to the backfill but will settle down to a steady state rate that is about the same as for the case without a backfill."

4. "For isotopes that are more sorbed by the backfill than by the tuff, the presence of a backfill against a container will significantly increase the rate of transport out of the container as compared to the case where the tuff is against the opening. However, subsequent diffusive transport from the backfill to the tuff is less or about the same in some cases. Steady-state concentration profiles in the tuff for species that escape the backfill barrier before decaying are in some cases significantly lower with a backfill and in other cases are higher but not by more than 20 percent in the cases considered."

COMMENT OF REVIEWER

Nitao has modeled the diffusive transport of radionuclides in the nearby vicinity of a waste package by solving a one-dimensional diffusion equation. In his simplifying model, neither heat convection nor heterogeneities in tortuosity and absorption are considered. Nitao considers the case where conditions for diffusive transport exist. He does not consider the case where an air gap between the container and the borehole would prohibit aqueous diffusive transport.

Because of all the simplifications made concerning the hydrology and geochemistry, the results of the model should be viewed as preliminary. The hydrological and geochemical environment for a real waste form at Yucca Mountain will be more complex than assumed by Nitao.
Hence, it is not possible to determine how well the model describes realistic situations.

APPLICABILITY OF DATA TO LICENSING
[Ranking: key data ( ), supporting data (x)]

(a) Relationship to Waste Package Performance Issues Already Identified

2.3.5 How will packing, container materials (including overpacks, canisters, and any special corrosion-resistant alloys or spent fuel rod cladding, if applicable) and/or their alteration products interact with the waste form to cause its alteration and/or effect release of radionuclides?

(b) New Licensing Issues

(c) General Comments on Licensing

AUTHOR'S ABSTRACT

In support of the investigations for an underground high-level nuclear waste repository at Yucca Mountain, Nevada, we have performed computer simulations of the immediate thermal and hydrological environment around a nuclear waste package. Calculations of this type will be needed for waste package design, performance assessment, and radionuclide transport analyses. Two dimensional computer simulations using a modified version of the TOUGH code were run for an idealized configuration derived from the COVE3 benchmarking effort consisting of a single spent fuel waste package with laterally periodic boundary conditions. The model domain extended downward to the water table and upward to the ground level. Fluid behavior in the rock was modeled using the equivalent continuum approximation. Runs were made with surface water influx rates at the surface set to 0.1, 0.5, and 1.0 mm/yr. A significant amount of code modification and development was needed in order to develop the capability to run these types of problems out to the long time spans required.

Since any significant transport of non-gaseous radionuclides will involve liquid water as a main vehicle of movement, and since liquid water, if present, will also contribute to waste package corrosion, its presence is of vital concern. Initial heating from the radioactive decay will vaporize the liquid pore water around the waste package. Of major interest to waste container design is the time at which possible wetting of the package occurs during the subsequent cool-down period. Our simulations showed that vapor transport and capillary condensation are the major mechanisms of water movement early in the cool-down period. However, the amount of liquid water in the rock next to the waste package during this time is very small and has very low mobility, although the diffusive transport properties of this water are not exactly known. In our simulations the main front of water returns to the boreholes wall at approximately 1000 years from emplacement as it is drawn in by capillary imbibition. At no time during the 2600 year time span of our simulation does the water saturation of the rock next to the borehole wall increase above initial native saturation. The values of these two time periods as well as the other predictions reported in this paper are highly preliminary due to the current uncertainty in the model input parameters and the sub-models used in our simulations. However, it is seen that the effect of the hydrological fluid flow on the thermal history may be significant. Considerable work needs to be done to develop better models of fluid behavior in partially fractured rock and more experimental data is needed to accurately model the waste package environment.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Author(s), Reference, Reference Availability

Beavers, J. A. and Thompson, N. G.
"Container Corrosion in High Level Nuclear Waste Repositories"
First Semi-Annual Report/Year 2, September 1988 to February 1989.

(b) Organization Producing Data

Cortest Columbus, Inc., Columbus, OH.

DATE REVIEWED: 6/5/89; Revised 8/8/89

PURPOSE

"The overall objective of the proposed program is to develop independent experimental data to assist the NRC in evaluating the uncertainties in DOE's claims concerning waste container corrosion. DOE has claimed in the environmental assessments, and is expected to claim in the license application, that corrosion rates can be so quantified and extrapolated as to make it possible to obtain credit for the container in meeting the containment requirement of 10CFR60."

"The purpose of task 1 is (1) to compile repository site specific data which are necessary to develop and update the work plan, (2) to provide continuity between the individual tasks of the program, and (3) to coordinate the program with other NRC projects."

"The purpose of task 2 is to examine the effects of environmental and metallurgical variables on the electrochemical behavior of the candidate container materials."

"The purpose of task 3 is to evaluate the corrosion behavior of the candidate container materials in the vapor phase and under alternate-immersion conditions."

"The purposes of task 4 are (1) to study the relationships between the pitting parameters E_{pit} and E_{prot} and long-term pit initiation studies, and (2) to evaluate pit-propagation behavior."

"The purpose of task 5 is to identify the environmental conditions under which the candidate alloys will undergo stress-corrosion cracking (SCC)."

"The purpose of task 6 is to explore failure modes that are likely, according to current knowledge, to produce accelerated attack and may lead to premature failure of the waste container."

"The purpose of task 7 is to provide long-term exposure data for evaluating the various modes of corrosion identified in tasks 2 through 6".

KEY WORDS

Experimental data, corrosion, electrochemical, slow-strain-rate, weight change, microscopy, laboratory, J-13 water, Cl, Yucca Mountain, high temperature, copper base, copper alloys, pitting, stress corrosion cracking.

CONTENTS

The report has sections of ABSTRACT, EXECUTIVE SUMMARY, INTRODUCTION, OBJECTIVE AND SCOPE OF WORK, 38 figures, 10 tables and the following contents:

CONTENTS	NUMBER OF PAGES
Task 1 - Review of Problems in Repositories	2
Task 2 - Cyclic Potentiodynamic Polarization	21
Task 3 - Vapor-Phase Corrosion Studies	17
Task 4 - Pitting Studies	20
Task 5 - Stress Corrosion Cracking	4
Task 6 - Other Failure Modes	1
Task 7 - Long-Term Exposure	1
Work Next Period	1
7 References	1
Appendix A. Matrix of CPP curves for Alloy 304L	38
Appendix B. Matrix of CPP curves for Alloy 825	37

AMOUNT OF DATA

There are 38 figures, mostly showing cyclic polarization curves with a few polarization resistance curves, a few scanning electron micrographs, a schematic showing weight loss change as a function of descaling, and a schematic of a slow strain rate specimen. There are ten tables showing test solutions, test parameters, and summaries of results.

TEST CONDITIONS

Tasks 1, 6 and 7 are not applicable to test conditions.

Task 2 -- Materials - alloy 304L stainless steel, Incoloy Alloy 825, Copper CDA 102 alloy, Copper-30 Nickel alloy CDA 715
Specimen Preparation - typically 1.3 cm in length with the diameter depending on the metal being tested and polished with successively finer grades of silicon carbide paper, finishing with a 600-grit grade
Environments - attached table 3 and 75°C tests in simulated J-13 well water for temperature-effects studies

Task 3 -- Materials - Copper alloys CDA 102 and CDA 715
Specimen Preparation - creviced and uncreviced specimens as well as u-bends
Environments - simulated J-13 well water and its vapor at 90°C for periods up to 2000 hours

Task 4 -- Materials - CDA 102 Cu and alloy CDA 715
Specimen Preparation - the same as task 2 and additional creviced specimens
Environments - attached table 3

Task 5 --
Materials - solution annealed alloy 304L
Specimen Preparation - cylindrical specimen without precrack at strain rate of $1x10^{-6}$ sec^{-1} (additional $5x10^{-7}$ s-1 for oil test)
Environment - oil, J-13, J-13 + CO_2 (purge rate of about 10 ml/min), all at 90°C

UNCERTAINTIES IN DATA

"Cyclic potentiostatic polarization (CPP) tests I33-I36 were performed in the same solution and provide an indication of the reproducibility of the polarization behavior; figures 8 and 9."

In the slow strain rate experiments of Task 5, the authors reported that "in the SCC of Task 5, "there was considerable scatter in the data which is not uncommon for slow strain rate (SSR) tests."

DEFICIENCIES/LIMITATIONS IN DATABASE

Not stated.

CONCLUSIONS OF AUTHOR

During this reporting period:

Task 1 -- "a minor addition was made to Task 4 of the work plan."

Task 2 -- "matrices of potentiodynamic polarization experiments were completed on Type 304L stainless steel and Incoloy Alloy 825 in simulated Tuff repository environments. While both alloys performed well in the simulated J-13 well water, pitting and crevice corrosion were observed under some of the simulated repository conditions."

Task 3 -- "2000-hour exposure tests were completed on CDA 102 Copper and CDA 715 Copper-Nickel in simulated J-13 well water at 90°C. Surprisingly, significant pitting was observed on vapor-phase specimens of CDA 715 after 2000 hours exposure."

Task 4 -- "potentiostatic pit-initiation studies were performed on Type 304L stainless steel, Incoloy Alloy 825, CDA 102 Copper and CDA 715 Copper-Nickel in simulated Tuff repository environments. The most significant finding was the confirmation that the cyclic-potentiodynamic- polarization (CPP) technique provided relatively poor prediction of the long-term pitting behavior of the copper-based alloys."

Task 5 -- "SSR tests were completed on Type 304L stainless steel in the control environment (oil), in simulated J-13 well water and in J-13 well water with added CO_2. No SCC was observed in any of the test environments, but there was considerable scatter in the mechanical property data for the test specimens. This scatter is typical for SSR tests and indicates the variability in the mechanical properties of the small diameter gauge sections of the specimens."

Task 6 -- "set up of the thermogalvanic couples experimental apparatus was started."

Task 7 -- "Set up of the initial long-term exposure tests were started."

<u>COMMENTS OF REVIEWER</u>

This progress report summarizes the research results obtained in the first semi-annual period of year two of this contract. The scope of the present review is extended to the overall program without being restricted to the particular results obtained during this period, because (1) the related previous reports have not been reviewed extensively and (2) the program is being modified as the research progresses.

1. General Comments

   This work applies electrochemical and other measurements to determine parameters responsible for container failures by various corrosion modes. The study includes the present candidate materials for HLW containers in expected corrosion environments derived from the Tuffaceous solution. The results certainly would be useful in screening various candidate materials and in identifying key environmental conditions responsible for the container failure. There is a need for obtaining long-term data and identifying new failure modes, such as steam corrosion, that could be active in repository conditions.

In deriving the matrix of environmental conditions, it is recommended that, where possible, the statistics be based on the available generic information. There maybe corrosion data available for the candidate material in various solutions which include the species present in the Tuffaceous solution. The knowledge from those, though not having been obtained at exactly the same repository conditions, will help the author to derive the optimum matrix, avoiding many time-consuming runs which may not be necessary. Likewise, in the interpretation of data obtained by the author from the selected matrix, it is recommended that efforts be directed toward interpreting them in comparison with (1) the results from J-13 well water and (2) the generic data. These interpretations should (1) identify species responsible for the specific mode of corrosion and (2) specify the roles of those species in the corrosion processes. Finally, it is highly recommended to include gamma-pool tests as variables in the experimental matrix. Short-lived radicals or hydrogen build-up may be important. For instance, the higher-order interaction term may become important in the synergistic effects of solution species in the presence of such radicals.

The cyclic potentiostatic polarization (CPP) or slow strain rate (SSR) tests may be acceptable as screening tests. However, in the prediction of "long-term" behavior, other techniques also should be used. The efforts for long-term prediction of HLW containers may prevent any serious mistakes in designing the HLW packages, but may not allow for predicting the performance of the HLW packages precisely for 300-1000 years. In light of this concern, it is unclear how the present data provide us with information on the long-term behavior of the containers. The plan for the use of these data in the long-term prediction should be more specific. A couple of such examples are: (1) SSR tests with notched samples of passive materials can be performed to measure the crack initiation time at various strain (or extension) rates. Because the crack propagation time is normally short with respect to the design life of the container, measurement of it is of limited value. The measured crack initiation time can be extrapolated to zero strain rate and to very low values of stress intensity; (2) likewise, time to pit initiation of passive materials may be monitored by recording the current response at various potentials above and below the pitting potential to determine the potential limit by time-extrapolation to avoid pit initiation for an extended period of time.

The studies on hydrodynamics and mass-transport are largely ignored. Clarification is needed regarding (1) how the system goes up above the pitting potential, (2) how severe the crevice (expected to form between the package and bore-hole wall or fallen rocks) solution would be, and (3) how the accumulated corrosion products, such as hydration products, affect the in-situ electrochemical monitoring of corrosion. This clarification may lead to the inclusion hydrogen embrittlement since the large amount of radiolytic hydrogen molecules can be dissociated on the surface of the containers upon passivity break-down. Eventually, these studies should also include the thermodynamic considerations of the stability of passivity and of the solubility limit of dissolved (or hydrated) corrosion products and these should be related to long-term predictions. It is important to understand the discrepancy between the data of weight measurement and electrochemical measurement and also, the time dependence of corrosion rates.

The authors should have justified the use of the Stern-Geary equation for corrosion in the vapor phase. It is not clear how the measured data are interpreted with a partial exposure of specimens to vapor. The equation may not be valid in the absence of liquid solution or in the presence of corrosion products for both passive and non-passive materials. Also, the author do not address the vapor corrosion of alloy 304L or 825.

RELATED HLW REPORTS

1. "The Literature Review in Subtask 1.1 (Draft), August, 1988"
   "The First Semi-Annual Report for Year 1 (9/87-2/88)"

2. R. S. Glass, G. E. Overturf, R. D. McCright and R. A. Van Konynenburg, Lawrence Livermore Laboratory, Livermore, CA, UCRL-92311, February, 1985.

APPLICABILITY OF DATA TO LICENSING
[Ranking: key data ( ), supporting data (x)

(a) Relationship to Waste Package Performance Issues Already Identified

2.2.4 What are the potential corrosion failure modes for the waste package container?

(b) New Licensing Issues

(c) Comments Related to Licensing

AUTHOR'S ABSTRACT

Cortest Columbus is investigating the long-term performance of container materials used for high-level waste packages as part of the information needed by the Nuclear Regulatory Commission to assess the Department of Energy's application to construct a geologic repository for high-level radioactive waste. The scope of work consists of employing short-term electrochemical techniques to examine a wide range of possible failure modes. In addition, the susceptibility of candidate container materials to stress-corrosion cracking is being studied utilizing slow-strain-rate testing. Long-term tests are being used to verify and further examine specific failure modes identified as important by the short-term studies. The original focus of the program was on the salt repository but the emphasis was shifted to the Tuff repository.

During the reporting period, matrices of potentiodynamic-polarizatio experiments were completed on Type 304L stainless steel and Incoloy Alloy 825 in simulated Tuff repository environments. Vapor-phase corrosion experiments were completed on CDA 102 Copper and CDA 715 Copper-Nickel in simulated J-13 well water. Potentiostatic pit-initiation tests were completed on all four of the above alloys in simulated repository environments. Slow-strain-rate stress-corrosion-cracking tests were started on Type 304L stainless steel.

Table 3. Series Of Tests Included In The Resolution IV Matrix.

Test Number	Si	HCO_3	F	Cl	NO_3	NO_2	H_2O_2	Ca	Mg	Al	P	Oxalic	O_2	Temp	pH
1	1.0	10	200	1000	1000	200	200	20	0.1	0.01	0.1	0	5	90	5
2	1.0	2000	200	1000	1000	0	0	0.1	0.1	20	20	200	5	50	5
3	100	10	1.0	5.0	1000	200	0	20	0.1	20	20	0	30	50	5
4	100	2000	1.0	5.0	1000	0	200	0.1	0.1	0.01	0.1	200	30	90	5
5	1.0	10	200	5.0	5.0	0	200	20	20	20	0.1	200	30	50	5
6	1.0	2000	200	5.0	5.0	200	0	0.1	20	0.01	20	0	30	90	5
7	100	10	1.0	1000	5.0	0	0	20	20	0.01	20	200	5	90	5
8	100	2000	1.0	1000	5.0	200	200	0.1	20	20	0.1	0	5	50	5
9	1.0	10	1.0	1000	5.0	200	200	0.1	0.1	0.01	20	200	30	50	10
10	1.0	2000	1.0	1000	5.0	0	0	20	0.1	20	0.1	0	30	90	10
11	100	10	200	5.0	5.0	200	0	0.1	0.1	20	0.1	200	5	90	10
12	100	2000	200	5.0	5.0	0	200	20	0.1	0.01	20	0	5	50	10
13	1.0	10	1.0	5.0	1000	0	200	0.1	20	20	20	0	5	90	10
14	1.0	2000	1.0	5.0	1000	200	0	20	20	0.01	0.1	200	5	50	10
15	100	10	200	1000	1000	0	0	0.1	20	0.01	0.1	0	30	50	10
16	100	2000	200	1000	1000	200	200	20	20	20	20	200	30	90	10
17	100	2000	1.0	5.0	5.0	0	0	0.1	20	20	20	200	30	50	10
18	100	10	1.0	5.0	5.0	200	200	20	20	0.01	0.1	0	30	90	10
19	1.0	2000	200	1000	5.0	0	200	0.1	20	0.01	0.1	200	5	90	10
20	1.0	10	200	1000	5.0	200	0	20	20	20	20	0	5	50	10
21	100	2000	1.0	1000	1000	200	0	0.1	0.1	0.01	20	0	5	90	10
22	100	10	1.0	1000	1000	0	200	20	0.1	20	0.1	200	5	50	10
23	1.0	2000	200	5.0	1000	200	200	0.1	0.1	20	0.1	0	30	50	10
24	1.0	10	200	5.0	1000	0	0	20	0.1	0.01	20	200	30	90	10
25	100	2000	200	5.0	1000	0	0	20	20	20	0.1	0	5	90	5
26	100	10	200	5.0	1000	200	200	0.1	20	0.01	20	200	5	50	5
27	1.0	2000	1.0	1000	1000	0	200	20	20	0.01	20	0	30	50	5
28	1.0	10	1.0	1000	1000	200	0	0.1	20	20	0.1	200	30	90	5
29	100	2000	200	1000	5.0	200	0	20	0.1	0.01	0.1	200	30	50	5
30	100	10	200	1000	5.0	0	200	0.1	0.1	20	20	0	30	90	5
31	1.0	2000	1.0	5.0	5.0	200	200	20	0.1	20	20	200	5	90	5
32	1.0	10	1.0	5.0	5.0	0	0	0.1	0.1	0.01	0.1	0	5	50	5
33	50	500	50	250	250	50	50	5.0	5.0	0.5	5.0	50	15	70	7.5
34	50	500	50	250	250	50	50	5.0	5.0	0.5	5.0	50	15	70	7.5
35	50	500	50	250	250	50	50	5.0	5.0	0.5	5.0	50	15	70	7.5
36	50	500	50	250	250	50	50	5.0	5.0	0.5	5.0	50	15	70	7.5
37	J-13 well water at 90°C														
38	J-13 well water + 1000 ppm Cl at 90°C														

WASTE PACKAGE DATA REVIEW

DATA SOURCE

(a) Author(s), Reference, Reference Availability

Kass, J. N.
"Evaluation of Copper, Aluminum Bronze, and Copper-Nickel for YMP Container Material"
UCRL-101097, May 1989

(b) Organization Producing Data

Lawrence Livermore National Laboratory for the U.S. Department of Energy

PURPOSES

"I will discuss our evaluation of the materials copper, 7% aluminum bronze, and 70/30 copper-nickel. These are three of the six materials currently under consideration as potential waste-package materials." "We are also considering alternatives to these six materials. This work is part of the Yucca Mountain Project (YMP), formerly known as the Nevada Nuclear Waste Storage Investigations (NNWSI) Project."

KEY WORDS

Experimental data, general corrosion, laboratory, Yucca Mountain, air, tuff composition, Cl, gamma radiation, ambient pressure, ambient temperature, lithostatic pressure, neutral solution, static (no flow), copper base, groundwater, stress or strain, corrosion (general), corrosion,(intergranular), corrosion (local), cracking, fracture, hydrogen embrittlement.

CONTENTS

This 33-page report consists of 8 tables and 9 figures and is written narratively without subtopics. Eight references were quoted.

TEST CONDITIONS

Materials: copper (CDA102), aluminum bronze (CDA613), and 70/30 copper-nickel (CDA715)

Specimen Preparation:

- waste package size: ~2 feet in diameter and ~14 feet high
- package: PWR bundles, BWR bundles or mixtures

- thickness: ~1 cm (aluminum bronze, copper-nickel)
  ~3 to 4 cm (pure copper)

Environment:

- repository: 700 feet above the water table and 300 to 1200 feet below the surface of the mountain
- temperature: Nominal - 250 to 97°C (some packages 250°C to <97°C)
- water composition and infiltration rate: 5 liters/year per container, neutral pH, ~10 ppm Cl-, NO_3-, O_2, ~20 ppm SO_4^{2-}, ~120 ppm HCO_3^-
- gamma flux: 10^4 to <10^2 rad/h, radiolysis products - Hydrogen peroxide and nitrogen-bearing species
- lithostatic and hydrostatic pressure: normally none
- Infiltration water rate: 5 liters/year per container

UNCERTAINTIES IN DATA

- approximated water chemistry
- approximated waste package size

DEFICIENCIES/LIMITATIONS IN DATABASE

- "A miscibility gap has been postulated (CDA715), but no phase separation has actually been reported." "Our research will have to justify that phase separation, indeed, does not occur."
- "The gamma fluxes used in these tests were about 10 times as high as expected in an actual repository."
- "These results (SCC for Cu/Al and Cu/Ni) are from constant-load tests."
- "The use of U-bend specimens makes the test very mild since the stresses will relax with time."
- We remain concerned about the possibility of alloy segregation with the Al bronzes."
- "Copper-based materials are not used in irradiated environments."
- "The performance of copper-based materials has not been established under repository-relevant conditions of temperature and oxidizing environment and gamma irradiation. This is particularly important to the early containment period."
- "High purity copper is very soft. Hence, we would need increased wall thicknesses for this material."
- "We need to determine the cause of ductility minimum around 250°C to 300°C."
- "We have to show that the fuel-cladding temperature will not exceed 350°C."
- "We need to guarantee that we can make the closure weld."

- "There are many inspection techniques available for the austenitic alloys, but not for the copper alloys."
- "We need to investigate the embrittlement of the weld metal over long periods of time."
- "We need to prepare weld materials samples and heat-treat them in various ways to simulate these long exposure periods."
- "We need to evaluate the possibility of alloy separation."
- "We need to know whether these threshold levels (ammonia for SCC) are lower in the presence of other species."
- "It is difficult to be convinced that what doesn't happen in a short test will not happen over a few hundred years."
- "There will be cost limitations."
- "We have not performed the key experiments yet" (copper-based materials).

CONCLUSIONS OF AUTHOR

- "Since the exposure environment is relatively benign, both general and localized corrosion performance will almost certainly be acceptable."
- "I am similarly optimistic about the mechanical properties," but "we need to determine the cause of the ductility minimum and how it will be influenced over many years at our temperatures."
- "Thermal problems are also very unlikely."
- "We do have fabrication techniques developed," "but we still need to guarantee that we can make the closure weld."
- "We haven't done much in the area of inspection."
- "We must show that the metallurgical structures are stable for 300 years at temperatures in the range of 250°C to 100°C."
- "The ability of NH_3 to cause SCC is a further concern."

COMMENTS OF REVIEWER

The text of this report is, apparently, a transcription of a talk given at a workshop, and includes questions posed by the attendees with answers by the author. The report lacks a summary statement, but the general tone of the report is that copper and its alloys will not develop serious problems as container materials. This is in spite of the potential problems posed throughout the text by the author, which included:

1) embrittlement of pure copper (hydrogen sickness) through the hydrogen reduction of oxides and the formation of bubbles in the metal,
2) phase separation of the alloys (possible miscibility gap in Cu-Ni alloy),
3) iron segregation in the alloys,

4) formation of NH_3 in the presence of irradiation that may result in stress corrosion cracking of copper and its alloys, especially the Al-Cu alloy,
5) a decrease in ductility at 250° to 300°C,
6) selective leaching in the Al-Cu alloy.
7) creep of copper at elevated temperatures,
8) rate of crack growth in the weld over long times and high temperatures,
9) the corrosion rate of the Cu-Ni alloy increases with irradiation in all cases tested up to 5,000 h exposure.

<u>APPLICABILITY OF DATA TO LICENSING</u>
[Ranking: key data ( ), supporting data (x)

(a) Relationship to Waste Package Performance Issues Already Identified

2.2.4 what are the potential corrosion failure modes for the waste package containers?

(b) New Licensing Issues

(c) Comments Related to Licensing

Appendix C. Corrosion of Zirconium and Zirconium Alloys

Corrosion of Zirconium and Zirconium Alloys

I. INTRODUCTION

Zircaloy's corrosion behavior is of particular interest in applications such as nuclear fuel cladding and in subsequent long term nuclear waste storage are of particular interest. The zirconium alloys termed Zircaloys were developed for use in the nuclear industry. Zircaloy cladding, which is tubing with a wall thickness of less than 1 mm, is a container for UO_2 nuclear fuel pellets during the time when the fuel is in reactor service, in temporary storage and in long term nuclear waste storage.

The Environmental Protection Agency (EPA) has promulgated environmental radiation protection standards for management and disposal of spent nuclear fuel high-level and transuranic waste[1]. The Nuclear Regulatory Commission (NRC) requires that nuclear waste containment shall be substantially complete for a period of 300 to 1000 years[2]. The NRC also requires that thereafter no more than one part in 10^5 of the inventory of radionuclides present at 1000 years after closure may be released annually from the engineered barrier system of a geologic repository. The Department of Energy (DOE) describes general guidelines for the recommendation of sites for nuclear waste repositories[3].

Determinations of Zircaloy durability and whether credit can be allowed for Zircaloy cladding acting as a barrier against radionuclide release must include considerations of the specific Zircaloy, its metallurgical condition, its corrosion resistance and its history in service and storage. Corrosion initiation and behavior will be affected by the type of reactor and exposure of the cladding, the composition of the crud which was present on the fuel rods and how the fuel rods were cleaned. Some aspects of corrosion behavior of Zircaloy and requirements for nuclear waste storage have been discussed previously[4]. It has been concluded that with intact cladding no radionuclide release occurred, and that radionuclide release increased with increased exposed area of the spent fuel[5]. The question regarding whether Zircaloy cladding can be given any credit for acting as a barrier to radionuclide release, however, remains to be answered. An increased understanding of the corrosion behavior of Zircaloy would contribute to this assessment.

A. Purpose

This is a review of selected aspects of the corrosion and technology of zirconium (Zr) and Zircaloy. Information is provided that can be used for gaining a better understanding of the durability of Zircaloy spent fuel cladding.

B. Scope

Zirconium and Zircaloy corrosion resistance and reactions in various environments will be discussed along with selected forms of corrosion. Information on environments other than those expected in the repository is provided to give a better understanding of the corrosion of Zircaloy. Zircaloy is more than ninety eight percent Zr so the corrosion behavior of Zr and Zircaloy are similar. Small differences in corrosion behavior will be discussed. Some background information will be given on the metallurgical aspects of zirconium which relate to corrosion resistance and mechanical durability of the Zircaloy.

Zirconium attains its corrosion resistance through the presence of a surface oxide film, and some information on the oxidation of zirconium will be given. There are many references relating to Zircaloy corrosion in the nuclear power industry, and only a few are cited in this brief review. This paper discusses Zircaloy cladding corrosion only, and oxidation of spent fuel and solubilities of U and UO_2 are not addressed.

II. BACKGROUND

A. Zirconium

Zr has properties which make it an attractive material for the nuclear industry. Its crystalline structure and properties are affected by increasing temperature and alloying.

1. History

Zirconium was discovered in 1789 by Martin Heinrich Klaproth when he was studying semiprecious stones from Ceylon[6]. Klaproth, in 1794, found another new element which he named titanium, but titanium had been discovered in 1791 by Gregory and called Menachin. Zirconium is generally less corrosion resistant than titanium.

Zirconium accounts for 0.028 percent of the earth's crust and is the 19th most abundant element. It is found as $ZrSiO_4$ in beach sand in regions throughout the world and as ZrO_2 and

$ZrSiO_4$ deposits in Florida, California, Oregon, Idaho, Brazil, Australia and India[6,7]. Berzelius produced impure zirconium in 1824, and van Arkel and de Boer produced high purity zirconium in 1925 using an iodide decomposition process. The Kroll process for producing zirconium involves magnesium or sodium reduction of $ZrCl_4$ and was developed in 1946 by the U. S. Bureau of Mines in Albany, Oregon.

2. Properties

Zirconium is pyrophoric, and small pieces with a large surface to volume ratio will ignite easily. Large pieces are oxidation resistant at high temperatures[8].

Some properties of Zr are given in the following table. It is suitable for use in high temperature, high mechanical strength and ductility applications.

Table 1. Properties of Zirconium

Melting point	1930°C (3506°F)
Specific gravity	6.53 g/cc
Tensile strength	110 MPa (16 ksi) at 427°C (800°F) 552 MPa (80 ksi) at room temp.[9]
Modulus of elasticity	9.9×10^4 MPa (14.4×10^3 ksi)
Shear modulus	3.6×10^4 MPa (5.25×10^3ksi)[7].

Zirconium has a low neutron scattering cross section. This, combined with its high temperature mechanical properties, adequate thermal conductivity, and the stability of these properties after irradiation, makes it a good material for nuclear reactor applications.

Nuclear grades of zirconium are free of hafnium. Hafnium has many properties similar to zirconium and usually is found associated with zirconium, and zirconium sponge could contain a few percent of hafnium. The hafnium is undesirable for most nuclear applications because hafnium has a high neutron cross section[8].

3. Crystal Structure of Zirconium and Zirconium Alloys

Zirconium has a close-packed-hexagonal (cph) crystal structure (alpha Zr) at room temperature and undergoes an allotropic transformation to a body-centered-cubic structure (beta Zr) at 870°C (1600°F). Some elements, including Al, Sb, Sn, Be, Pb, Hf, N, O, and Cd, are alpha stabilizers and raise the transformation temperature of alpha to beta. Other elements, such as Fe, Cr, Ni, Mo, Cu, Nb, Ta, V, Th, U, W, Ti, Mn, Co and Ag, are beta stabilizers and have the opposite effect and lower the alpha to beta transformation temperature[8].

Zirconium and its dilute alloys can exhibit strong anisotropy. In the wrought form, these materials have a preferred crystallographic orientation. Orientation textures develop during processing of metals to wrought form and the resulting texture will cause mechanical properties to vary with rolling and transverse directions.

Most of the alloying elements form intermetallic compounds with Zr, and the distribution, size and properties of these phases are important to corrosion resistance in steam or hot water[10]. The main precipitate which is present in Zircaloy-4 is $Zr(Fe,Cr)_2$, while $Zr(Fe,Cr)_2$ and $Zr_2(Fe,Ni)$ are present in Zircaloy-2. Zircaloy-2 and Zircaloy-4 usually are forged in the beta region, then solution treated at 1065°C (1950F) to increase the amount of alloying elements going into solid solution, and this is followed by a water quench. The uniform distribution of fine intermetallic compounds produced by heat treating and quenching, is preserved by hot working in the alpha region below 790°C (1472°F)[8].

B. Zircaloy

1. General Information

Zircaloy-2 and Zircaloy-4 were developed for the nuclear industry, and are used as fuel cladding in power boilers. Both alloys are more than ninety eight percent Zr.

Alloys used for fuel cladding in the nuclear industry are primarily Zircaloy-2 for boiling water reactors (BWR) and Zircaloy-4 for pressurized water reactors (PWR)[11], with Zr-2.5Nb being used in smaller amounts. Compositions of these three zirconium alloys are given in Table 2.

Table 2. Composition of Selected Zirconium Alloys

Alloy	Sn	Fe	Cr	Ni	Nb	Zr
Zircaloy-2	1.5	0.12	0.10	0.05		Bal.
Zircaloy-4	1.5	0.20	0.10	0.005		Bal.
Zr-2.5Nb					2.5	Bal.

2. Corrosion Resistance

Corrosion resistance of these dilute zirconium alloys is slightly diminished but very similar to that of zirconium. One instance in which zirconium alloys can have superior corrosion resistance to the base zirconium metal is in high temperature water or steam. Alloying with small amounts of Sn, Fe, Cr and Ni improves resistance to high temperature water corrosion. The Zr-2.5 Nb is less corrosion resistant than the Zircaloys except in steam at temperatures above 400°C (750°F), and it is used for pressure tubing in some reactors.

C. Welding

The high reactivity of zirconium and Zircaloy necessitates that welding be carried out in a vacuum or as a second choice, in an atmosphere of argon or helium. Studies involving effects of impurities in H_2SO_4 on corrosion resistance of zirconium showed that corrosive effects due to impurities were greater in welded areas[12]. Contamination with hydrogen, oxygen or nitrogen should be avoided by argon purging during welding to prevent embrittlement of the welded area[13].

III. REPOSITORY ENVIRONMENT

The repository environments for locations involving basalt, salt and tuff were reviewed previously[14] and conditions were given in some detail. Some of the information from this reference relating to the tuff repository is presented here. The tuff repository is located in the state of Nevada and is in the Topopah Spring Member of the Paintbrush Tuff at Yucca Mountain. The tuff is in unsaturated devitrified zones with twelve percent porosity and contains five volume percent water[14,15]. Oxygen is expected to be present. Water flow has been stated to be 6 to 8 mm per year, but this could change.

Radiation present will be gamma and will be approximately 10^4 rads per hour. This repository probably will not pressurize after closing, and the water will boil off leaving a residue of salts which may or may not redissolve.

Water taken from the Jackass Flats J-13 Well in the tuff repository area contains a number of ions in small concentrations including Li+, Na+, K+, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{-2}, Be, Al^{+3}, SiO_2. F^-, Cl^-, CO_3^{-2}, HCO_3^-, SO_4^{-2}, NO_3^-, PO_4^{-3}. The pH of the water has been reported to be 7.1 but could go more basic depending on the ion concentration. The water pH could shift to the acidic range due to radiolysis of $N_2/O_2/H_2O$ mixtures. Analytical work still is needed to show whether pore water in the tuff has the same composition as the J-13 water.

Calculations of repository temperatures over extended times involve a given repository design and assumptions used, such as the absence of packing material, and are subject to change. Calculated temperature versus time profiles for a tuff repository are given in reference 14 and show a fuel centerline temperature of 330°C which decreases to 100°C after 300 years. Some other calculations showed that centerline temperatures were in excess of 350°C[15]. The calculated temperature at the canister was approximately 245°C and decreased to 80°C after 200 years.

IV. TYPES OF CORROSION

Corrosion processes within the tubing due to reactions of the cladding with the nuclear fuel and its environment must be considered as well as corrosion behavior of the outer surface of the cladding which is exposed to environments of reactor service, temporary storage and permanent storage. Most cladding failures reported until now appear to have initiated at the inner tubing wall. Causes of these failures include clad collapsing, pellet cladding interactions, hydriding, fretting and some failures due to unknown causes. The problem of collapsing was corrected by pressurizing the clad fuel. Causes of failure on the outside of the cladding include water side corrosion and crud-induced localized corrosion. A discussion of the forms of corrosion and the corrosion behavior of zirconium in various media are given in references 7 and 8. Discussions of Zircaloy cladding corrosion under repository type conditions and effects on radionuclide containment are given in reference 14. Selected information on corrosion behavior is given in the following sections.

A. General Corrosion

General corrosion, also known as uniform corrosion, may be described as an electrochemical attack covering the entire surface of the exposed metal. Metals and alloys subject to uniform corrosion become thinner or completely corrode as a result of this uniform attack over the surface. Zirconium and Zircaloy are resistant to uniform corrosion due to the protective oxide layer which forms on the surface. Uniform corrosion and subsequent thinning of either material would become a problem only if the protective surface oxide film underwent a transition to the thicker, nonprotective oxide described in the section on oxidation.

Some uniform corrosion data on zirconium are tabulated in reference 14 and the part relating to the tuff environment was taken from reference 17. These data[17] were calculated using the formula,

$$\Delta W = 1.12 \times 10^8 \exp[-12529/T(K)]t$$

where ΔW is weight change in mg/dm^2/day, T is the absolute temperature and t is time. Some of the results are shown in Table 3.

Table 3. Calculated Metal Thickness Loss in Zircaloy After 300 Years

Temperature °C	Environment	Thickness Loss (mm)
250	Aqueous	0.02
250	Air or Steam	0.008
300	Aqueous	0.2
300	Air or Steam	0.1
350	Aqueous, Air or Steam	1.0
400	Aqueous	4.4
400	Air or Steam	6.3

The lower temperature data indicate no significant amount of corrosion due to general corrosion, but the higher temperature data indicate amounts of corrosion which exceed the thickness of the cladding wall in less than 300 years. Zircaloy corrosion is sensitive to increases in temperature. These data indicate that additional high temperature oxidation data and knowledge of the repository storage temperature and environment would be needed to make a prediction of the effects of uniform corrosion.

B. Stress Corrosion Cracking

Stress corrosion cracking (SCC) is a complex form of localized corrosion that occurs in the presence of a corroding environment and a tensile stress. SCC can occur without warning and can be catastrophic. SCC is discussed in reference 18. Factors important in determining mechanisms of SCC include chemical composition, electrochemical reactions, mechanical properties and condition of the material. Anodic dissolution at the crack tip and a concentrated stress at the crack tip can lead to failure. Adsorption of ionic species in the strained area of the crack tip can also lead to failure. Some SCC failures appear to result from a series of brittle fractures. There are other mechanisms, related to these, which can lead to SCC failure. The U-bend test, consisting of a rectangular specimen bent around a predetermined radius and maintained under constant strain during corrosion exposure, or other similar tests can be applied to determine whether a metal undergoes SCC, but since SCC can develop over time without showing indications of this problem, the absence of SCC failure does not mean that the material is immune[13]. Metals which are susceptible to SCC can appear sound for extended times can fail suddenly due to SCC. Additional information on a materials susceptibility to SCC can be obtained from slow strain rate testing.

Zirconium and its alloys are resistant to SCC in seawater, most aqueous environments and some sulfate and nitrate solutions. SCC of Zircaloy can occur in concentrated methanol, solutions containing heavy metal chlorides, ferric chloride solutions, copper chloride solutions, organic solutions with chloride, gaseous iodine or fused salts. Liquid metal embrittlement has been reported for zirconium in contact with molten cesium and with liquid sodium or cadmium[15,19,20].

Data show that if the electrode potential of Zircaloy-2 is raised to a value which is slightly more positive than its corrosion potential in neutral dilute sodium chloride solutions at 25°C, SCC will occur[21]. SCC from the fuel side of the cladding can result from effects of fission products such as iodides[20,22].

The estimated in-reactor failure rate for LWR fuel cladding is 0.01 percent[23]. Earlier in-reactor failure rates in BWRs were as high as one percent. Less than 0.002 percent of Zircaloy fuel rod failures, under reactor conditions, are caused by waterside corrosion[15,17]. During in-reactor service, there is some creepdown of the cladding and also expansion of the fuel occurs causing localized stress regions in the cladding.

The hoop stress, s, defined as $s = pr/t$, where p is pressure in MPa, r is the radius of the tube in meters and t is the wall thickness of the tube in meters, can be an important factor in failures initiating from the inside of the cladding. The importance of the hoop stress increases when the ratio of the tube diameter to the tube wall thickness is greater by a factor of ten. Approximate measurements for Zircaloy-2 and Zircaloy-4 are an outside diameter of 12 mm with a wall thickness of 0.9 mm and an outside diameter of 11 mm and a wall thickness of 0.9, respectively.

Calculations of the minimum hoop stress necessary for SCC due to iodine gave values of 200-220 MPa at 400°C[20] and 216 MPa at 300°C[24,25]. Hoop stresses in rods stored below 60°C have been estimated to be in the range of 1.7 MPa to 3.7 MPa with some having a hoop stress of 5.4 MPa[26,14]. In late 1978, General Electric began He pressurizing BWR fuel rods to 0.3MPa, and Westinghouse began He pressurizing PWR fuel rods to 3 or 3.4 MPa[14]. The estimate then for the hoop stress in a BWR rod was 3.1 MPa at 100°C and 9.2 MPa for a PWR fuel rod[27,14].

Calculations of the hoop stress during the containment period at 300°C result in approximately 22.7 for BWR rods and 82.5 for PWR rods[14,17]. These hoop stresses are much lower than the 200 - 220 MPa described as necessary to produce SCC, but the total considerations regarding whether SCC from inside the cladding will occur must also include inner tube wall surface defects, local stresses, texture of the inner surface, localized chemical inhomogeneities either in or on the surface, whether hydriding has occurred and whether the fuel rod was pressurized. Inner surface texture can affect susceptibility to SCC[28], and this effect can be reduced by modifying the texture[29].

C. Effects of Hydrogen

Failures due to hydrogen pick-up by a material are due to the combination of the embrittling effects caused by hydride formation or hydrogen adsorption and the presence of stress. Other factors such as temperature and chemical environment also play a role in this type of failure. Hydrogen embrittlement failures have an induction period as does SCC and crack propagation is similar in hydrogen embrittlement and SCC. Crack initiation mechanisms for SCC and hydrogen embrittlement are different, and cathodic protection methods which can be applied to prevent or delay SCC can be sources of hydrogen and are not appropriate for use against hydrogen embrittlement.

Zircaloy-2 is somewhat more subject to hydrogen pick-up than is Zircaloy-4. Examples of cladding failures attributed to hydrogen adsorption from hydrogen produced during corrosion have been reported[27]. An earlier source of hydrogen was water left in the fuel inside of the cladding, but this was eliminated by drying the fuel.

The solubility of hydrogen in Zircaloys is approximately 60 ppm at 300°C and is 1 ppm at 20°C[15,32,33,34]. Exceeding this solubility will result in the formation of brittle hydrides. The hydrogen content of spent fuel claddings has been reported to be in a range of 80 to 150 ppm and also less than 50 ppm[32]. Sources of hydrogen available to the cladding include hydrogen generation by corrosion processes, hydrogen present in the reactor cooling water and other possible sources. A general or uniform corrosion rate in excess of 3 mils per year would result in embrittlement except in oxidizing environments[13].

D. Pitting

Pitting is a severe form of localized corrosion. In some cases, the full extent of the damage to the structure is not obvious by visual inspection of the surface. Pitting occurs at sites of breakage in the protective surface film, defects in the material and at other discontinuities. The initiation of the pit occurs when the disparity at the pit site permits the exposure of the metal to the chemical ions. There is an electrode potential difference between the pit site and the remainder of the protected metal surface. Once the exposure has occurred, a pit develops as is shown in Figure 1.

The small area of the pit (acting as the anode) compared to the larger area of the remaining surface (acting as the cathode) results in a high corrosion current density at the base of the pit. As pitting occurs, metal ions can react with the environment to form precipitates which in some cases, may cause a film to cover the top of the pit. As pitting progresses, corrosion products, such as metal ions and hydrogen, within the pit, cannot escape. These corrosion processes within the pit lower the pH into a more acid region and pitting is accelerated.

Cathode:

$2H + 2e^- > H_2$

$O_2 + 2H_2O + 4e^- > 4OH^-$

$Me^{+2} + 2H_2O > Me(OH)_2 + 2H^+$

Anode:

$\text{Metal} > Me^{+2} + 2e^-$

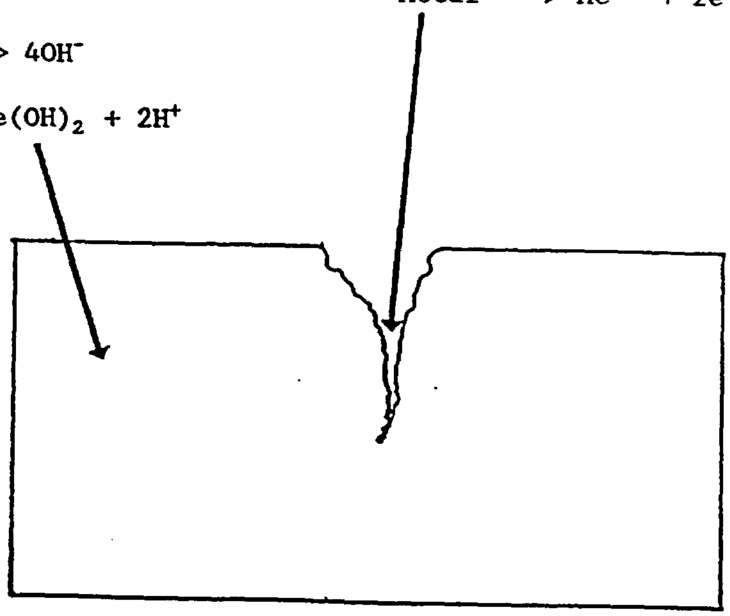

Figure 1. Schematic drawing showing anodic and cathodic areas and some reactions of pitting corrosion.

Materials can be tested for susceptibility to pitting, and a method for this test is described in ASTM F-746[35]. Techniques for pit propagation measurements also have been described[36].

A method of pitting evaluation is described in ASTM G46, Standard Recommended Practice for Examination and Evaluation of Pitting Corrosion[37] and involves locating the pits, then determining the density and depth. The pitting factor is used to show the damage of some pits and can be described as

$$\text{Pitting Factor} = \frac{\text{Deepest Metal Penetration}}{\text{Average Metal Penetration.}}$$

This shows that, in the case of a pitting factor of one, uniform or general corrosion is occurring.

Zirconium surface films readily reform if broken, but zirconium is not completely immune to pitting. Pitting does occur in hydrochloric acid solutions which contain ferric or cupric ions and possibly in other environments. Fluorine, chlorine, bromine and iodine in aqueous or gaseous forms could cause pitting to occur.

E. Crevice Corrosion

Crevice corrosion is a form of localized corrosion which occurs at occluded areas such as gaskets, threads, overlaps and places which are deprived of the surrounding environment. Damaging ionic species can become concentrated in creviced areas causing conditions similar to those developed in pitting. Zirconium is resistant to crevice corrosion since a protective surface film forms; nevertheless, crevice corrosion could occur.

F. Nodular Corrosion and Crud Induced Localized Corrosion

Nodular corrosion and crud induced localized corrosion were found in the late 1970's. These forms of fuel cladding corrosion have been described in detail in reports from the General Electric Company[38,39,40]. Nodular corrosion was first observed in 1979 and it was determined to be related to crud-induced localized corrosion (CILC) which was observed by the same authors in 1978. Although CILC was found first, the explanation of the mechanism indicates that it is preceded by nodular corrosion.

CILC was found to occur in systems which had copper present[38]. The most frequent type of crud found on cladding in BWR service is mostly Fe_2O_3, which is fluffy, loosely adherent, has a low density and has good heat transfer in boiling conditions. If copper is present in the system, even in small amounts, the crud or scale deposits are mostly a combination of Fe_2O_3 and CuO. Such deposits are tightly adherent, have a high density and low thermal conductivity under boiling conditions. Fifty percent of the cation content in these deposits is copper as opposed to ninety percent iron in the more usual crud. These copper bearing cruds flake off. They also have been found between layers of white ZrO_2 on the cladding surface. The protective form of ZrO_2 is black and covers the surface as a thin layer. Reactions of the oxide with copper result in severe local corrosion or pits in the regions 20 to 40 inches and occasionally at 80 to 100 inches from the lower end of the fuel rod. CILC failures are associated with soluble copper in the water which could come from corrosion or wear of tubing or other parts containing copper. CILC failures occur more frequently in $(U,Gd)O_2$ rods but failure can occur in UO_2 rods. The power exposure threshold must be sufficient to produce fuel failure. These failures occur in only a small fraction of the rods.

These damaging crud deposits are most commonly found on top of the protective oxide and are associated with white oxide nodules. The protective film formed on Zircaloy in Boiling Water Reactor (BWR) service is a black oxide. Figure 2 is a schematic drawing of Zircaloy cladding with possible surface oxides or crud coatings.

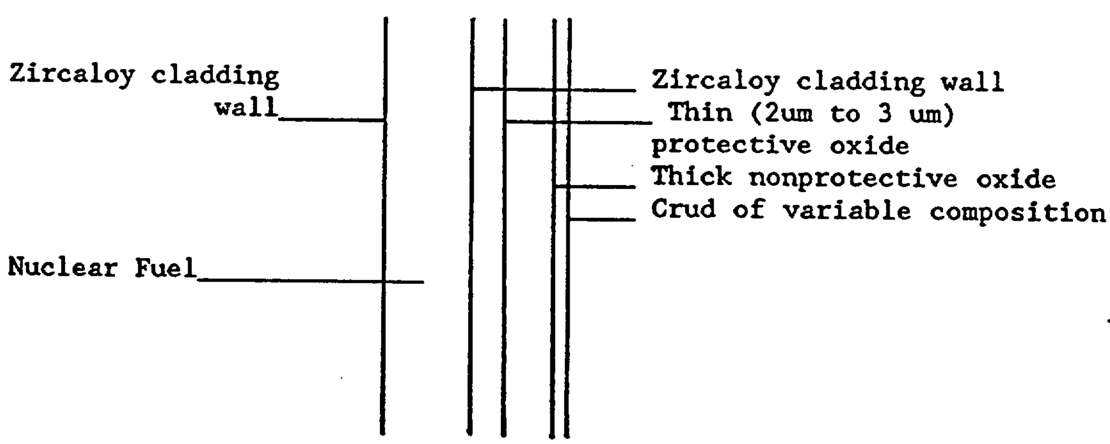

Figure 2. Zircaloy Cladding Section Showing Oxides and Crude Layers on Outer Surface.

Some localized lens-shaped white oxides also develop, and these nodules grow faster than the adherent uniform black oxide film. The nodules are not as adherent or protective and are sites for scaling or other reactions. Nodular corrosion has been studied and variables which affect it have been discussed[40]. The nodules do not form at these precipitate sites or at grain boundaries as might be expected. Both alloys become more resistant to nodule formation after heat treating in the alpha-beta or beta phase regions above 830°C. This increased resistance is attributed to a redistribution of solute elements in the Zircaloy. A mechanism is given based on the effects of the solute depletion on the composition and structure of the black uniform surface oxide.

Detrimental effects of the presence of copper on nodular corrosion have been described[38]. Effects of other elements on nodular and uniform corrosion in steam at 400°C and 500°C have been studied, and results showed that iron and nickel improved both uniform and nodular corrosion resistance of Zircaloy but both increased the amount of hydrogen pick-up. Tin decreased the nodular corrosion resistance, and niobium improved nodular corrosion resistance and improved resistance to hydrogen pick-up[41].

V. OXIDATION OF ZIRCONIUM

Zirconium forms a visible oxide film at 200°C (400°F) which is protective but at a temperature of 425°C (800°F), a thicker, loose white scale develops which is not protective. Oxidation rates for zirconium in various media at different temperatures are tabulated[7,8]. Zirconium and its alloys usually show a decreasing corrosion rate in high temperature water which may be followed by a rapid linear rate of attack. Film growth in the early stages of zirconium oxidation (pretransition) have been described as following cube root kinetics[11,31,42]. This is shown schematically in Figure 3. At a critical thickness, dependent on environmental factors, such as temperatures of 280°C and above, the kinetics change, and a transition to linear growth, with time, occurs. The post transition, thicker film is not protective, and a protective film rapidly reforms to begin a new cycle of film growth. It has been shown that in water at 360°C, these repeated cycles of cube root and linear kinetics occur[43]. In studies of Zircaloy-2 corrosion in high temperature water, it was postulated that oxygen diffuses through the corrosion film by easy paths such as grain boundaries or other discontinuities[44]. Experiments conducted at 355°C to study transport of oxygen and hydrogen (as deuterium) in growing corrosion films showed oxygen diffusion at grain boundaries and other short circuit diffusion pathways[44]. High concentrations of hydrogen also were observed in these studies. Other high temperature studies, with an applied tensile stress, showed a 1.2 to 2 fold increase in the corrosion rate of Zircaloy-2 in steam at 400°C to 475°C over that at 300°C[45].

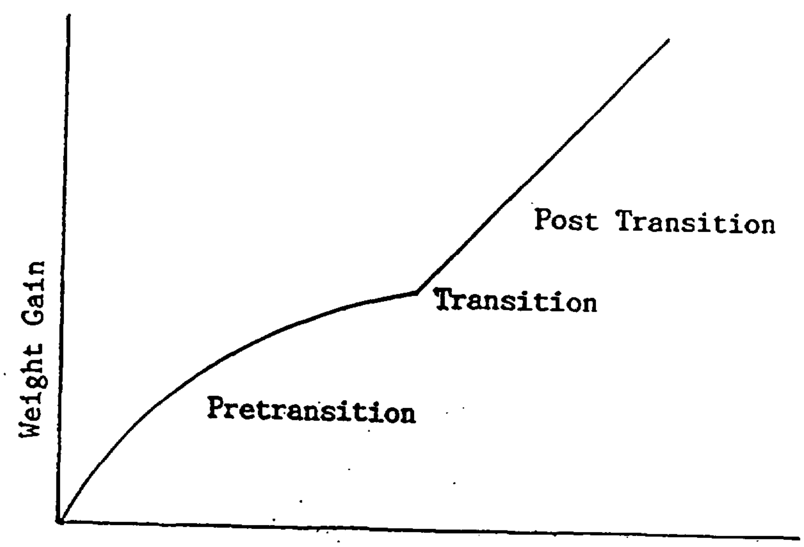

Figure 3. Oxidation of Zirconium

The oxidation rate in the pretransition region is enhanced by reactor radiation and is related to the fast neutron flux[46]. Pretransition oxidation curves for zirconium in water or steam, fused salt or air at 350°C are essentially the same[11]. The structure of the initial oxide film in terms of grain boundaries and other defects appears to be important in the further oxidation or growth of the oxide film.

Calculations based on weight gain at a temperature of 180°C for 10,000 years show depths of oxidized Zircaloy ranging from 4 um to 53 um, and it was concluded that at this temperature and below, failure of the Zircaloy due to oxidation should not occur[31]. Results of other corrosion tests based on oxidation and weight gain are given in reference 14. Some of these data indicate that the cladding would fail. If the water temperature is below about 250°C when the water reaches the Zircaloy cladding, the oxidation mechanism could change and the rate could become considerably lower as is indicated in the post transition region of Figure 3.

Information on the condition of spent fuel and spent fuel cladding is available from reports developed by the Materials Characterization Center (MCC). The Approved Testing Material (ATM) - 106[4,7] is a high burn-up, high fission gas release material from a PWR and is one of five ATMs which are representative of different fuel types and reactor conditions. Metallographic characterization indicated that the oxide layer or reaction product on the interior surface of the cladding was uniform and ranged in thickness from 4 um (0.004 mm) to 9 um (0.009 mm). The exterior cladding surface oxide was thicker in the middle of the rod than at the bottom of the rod. The top of the rod was not analyzed. The exterior oxide in the middle of the rod has a thickness ranging from 11 um (0.011 mm) to 15 um (0.015 mm) and was multilayered with the outside layer being loosely held. Further microstructural analysis indicated that increased hydriding could be correlated with increased cladding oxide thickness. Not all spent fuel has a uniform surface oxide, and ATM-103, representing a moderate burn-up, low fission gas release, material had localized corrosion products with the remaining surface relatively bare.

VI. AQUEOUS CORROSION RESISTANCE OF ZIRCONIUM/ZIRCALOY

Zirconium readily oxidizes to form a protective surface film and is resistant to strong acids, alkalis and to organic acids. Carbon and nitrogen impurity contents of 40 and 300 ppm, respectively, increase the corrosion rate of zirconium. Zircaloy-2 has less than 0.006 percent nitrogen. The addition of tin to Zirconium counteracts detrimental effects of absorbed gas on corrosion resistance[7],[8].

Zirconium is attacked by fluoride ions, wet chlorine, aqua regia, concentrated sulfuric acid, hydrofluoric acid, ferric chloride and cupric chloride. An extensive table showing corrosion rates of zirconium in various media is given in reference 7 which indicated that the information should be used only as a guide and that further tests, in situ, should be conducted to verify the corrosion resistance in a given medium. A table, showing corrosion rates in various media, is included in reference 7. Much of the information on reactions in acids and alkalies is taken from references 7 and 8, but it is verified in numerous other references.

A. Sulfuric Acid

Zirconium is corrosion resistant in sulfuric acid in concentrations up to 60% up to boiling temperatures, and concentrations of 80% at room temperature. This resistance is lower for welded material and heat affected zones even at lower acid concentrations. This resistance is the result of a protective cubic ZrO_2 film with a small amount of a monoclinic zirconium oxide phase present[7]. Corrosion resistance in concentrations of sulfuric acid above 70% is strongly temperature dependent and is affected by the formation of a looser less protective film, $Zr(SO_4)_2.4H_2O$ and also the formation of hydrides. These films, consisting of zirconium sulfate, zirconium hydrides and small zirconium metal particles, can be pyrophoric. Impurities in the sulfuric acid such as Fe^{+2}, Cu^{+2}, Cl^-, NO^{3-} and seawater, have detrimental effects on Zircaloy corrosion resistance to sulfuric acid[12].

B. Nitric Acid

Zirconium is resistant to nitric acid in concentrations up to 65 wt. percent and at a stress limit of 150 MPa up to temperatures of 120°C[48]. Other studies[49,50] showed high corrosion resistance for zirconium in 70 percent nitric acid at room temperature and little effect on the SCC susceptibility by the presence of $FeCl_3$, seawater, NaCl and corrosion products released from stainless steel. Fluoride ions should be avoided and chlorine in the gaseous phase should be avoided as well as high stresses at elevated temperatures in 70 percent HNO_3.

C. Hydrochloric Acid, HCl; Phosphoric Acid, H_3PO_4; Alkalies; Saline Solutions

Zirconium is resistant to all concentrations of hydrochloric acid to temperatures above boiling. Zirconium is resistant to phosphoric acid at concentrations up to 55 percent and at temperatures above boiling. Zirconium is resistant to alkalies. It is resistant to saline solutions to temperatures of boiling except for solutions containing $FeCl_3$ and $CuCl_2$.

D. Water and Steam

Corrosion resistance of Zircaloy-2 and Zircaloy-4 in high temperature water and steam is superior to that of unalloyed zirconium. Corrosion resistance of Zr-2.5Nb is generally less than that of the Zircaloys but in steam, at temperatures in excess of 400°C (750 F), Zr-2.5Nb has superior corrosion resistance. The corrosion resistance of Zr-2.5 Nb can be improved by heat treating.

VII. SUMMARY

Zirconium is a reactive metal which becomes highly corrosion resistant to various media due to the formation of a protective surface oxide film. Low alloy zirconium alloys, such as Zircaloy-2 and Zircaloy-4 which are used for nuclear fuel cladding, essentially maintain this corrosion resistance under specified conditions. Zircaloys-2 and 4 are resistant, within limits, to acids, alkalies and organic acids. Corrosion of Zircaloys in water and steam is increased with temperature and with carbon and nitrogen impurity contents. Zirconium is not corrosion resistant to fluoride ions, wet chlorine, aqua regia, concentrated acids and ferric chloride and cupric chloride.

Additional electrochemical and corrosion data are needed for predicting Zircaloy corrosion behavior in a long term nuclear waste repository. Temperatures may range from 330°C to 100°C for the first 300 years, and general corrosion might not be a problem under these conditions. However, additional information on mechanisms of oxidation and passivity, along with effects of ions present and other environmental factors, would be useful for relating to the occurrence of localized corrosion.

Zircaloy may be subject to stress corrosion cracking initiating from the inside of the cladding or from the outside of the cladding. Hydrogen embrittlement and metal embrittlement may occur, and there is possibility of pitting occurring. Ions such as those of the halides, especially iodine, would be suspect for causing SCC. Ions such as those of copper or iron may react with the surface oxide film and eliminate the film's protection at a local site. The literature contains many references of research carried out to address these localized corrosion problems in reactor service. Research is needed now to address conditions of nuclear waste storage, including environmental and material variations which could occur over time.

The oxidation rate in the pretransition region of oxide film formation on Zircaloy is increased by radiation. Existing data need to be coordinated and more data are needed to determine effects of radiation and temperature on the oxide thickness and transition temperature.

Metallurgical conditions of the cladding including orientation textures, defects, impurities and histories in reactor service and storage should be established and catalogued. These factors, also, will affect the corrosion and durability of the cladding.

Solubility of the spent fuel will be a factor in the amount and type of radionuclides released, and oxidized fuel has increased aqueous solubility. Oxidation of the spent fuel could occur at rates greater than those previously predicted. This increased oxidation could be due to a lower activation energy for oxygen diffusion at grain boundaries in the spent fuel. Spent fuel volume expansion resulting from oxidation could cause stress cracks in the Zircaloy cladding.

VIII. RECOMMENDATIONS

Aspects of Zircaloy corrosion which need further study include the effects of repository conditions on the following topics:

1. Structure of the oxide film, its stability and transition, and how this film and, also passivity, are affected by temperatures, wetting, drying and other conditions of the repository

2. Stress corrosion cracking and other mechanical and corrosion failures in which surface crystallographic texture has an important role

3. Susceptibility of Zircaloy to stress corrosion cracking using various tests including slow strain rate or other appropriate measurements.

4. Susceptibility to pitting or other localized corrosion in environments containing ferric chloride, cupric chloride, fluorine and under conditions of varying pH

5. Welding integrity and localized and general corrosion of welded areas

6. Effects of previous service history, especially relating to hydrogen uptake and hydrogen embrittlement cracking and other localized corrosion

7. Projected stability of initial condition of cladding at time of repository storage using data obtained from characterization of spent fuel approved testing materials (ATMs).

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X. ACKNOWLEDGEMENTS

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APPENDIX D. Corrosion Behavior of Zirconium Alloy Nuclear Fuel Cladding

Corrosion Behavior of Zirconium Alloy Nuclear Fuel Cladding

ABSTRACT

Zircaloy-2 and -4 are used as nuclear fuel cladding. Both alloys are more than ninety-eight percent zirconium and are corrosion resistant to various media. Electrochemical measurements using polarization techniques have been made on these alloys in aqueous media with a pH of 8.5 and varying ionic concentration (1X and 10X) at temperatures of 22°C and 95°C. Results showed that under the test conditions of the study these alloys passivated and had negligible corrosion rates, but there were some variations in passivation due to surface preparation and some crevice corrosion was observed. Data are presented and discussed in terms of passivity, breakdown potential and susceptibility to localized corrosion.

INTRODUCTION

The purpose of this study was to provide data for use in evaluating corrosion behavior of the zirconium alloys, Zircaloy-2 and Zircaloy-4, and for use in determining whether long term credit can be claimed for the cladding in preventing radionuclide release to the environment. The U. S. Nuclear Regulatory Commission (NRC) requires that nuclear waste containment shall be substantially complete for a period of 300 to 1000 years and that thereafter, no more than one part in 10^5 of the inventory of radionuclides present at 1000 years after closure may be released annually from the engineered barrier system[1]. It is not known whether it would be necessary to take credit for the cladding to meet the release requirement.

The cladding tube with a 11 to 12 mm outside diameter and a wall thickness of less than 1 mm surrounds the nuclear fuel, uranium dioxide pellets that have been sintered to 95% theoretical density, for the purpose of reducing coolant activity levels. Zircaloy-2, Zircaloy-4, other zirconium alloy compositions and the 300 series stainless steels have been used as cladding materials, but the bulk of the cladding in the United States is Zircaloy-2 and Zircaloy-4. Metallurgical aspects of zirconium alloys and information on corrosion behavior in various media have been discussed previously[2]. Essentially, Zircaloys-2 and -4 are ninety-eight percent zirconium and are free of hafnium. Zircaloys-2 and -4 are highly corrosion resistant in various media and environmental conditions.

Zirconium materials are highly reactive and obtain corrosion resistance by the formation of a protective film. Ions which penetrate or react with this film, or oxidation temperatures and conditions which change it would have a negative effect on the good corrosion properties of these zirconium alloys. The work reported here provides corrosion data and electrochemical measurements of Zircaloy-2 and -4 in aqueous media at 95°C with a pH of 8.5 and an ionic content representative of that found in the Nye County, Nevada in the J-13 well. These data can be used to characterize the corrosion behavior of Zircaloy under these conditions as it relates to passivity, breakdown of passivity and susceptibility to localized corrosion. Results of this study showed that under the test conditions of the study, the Zircaloy materials usually passivated and exhibited a negligible corrosion rate. There were exceptions, and in some cases, passivation did not readily occur, due to variations in surface treatment, and in selected tests, crevice corrosion was evident after exposure to the tests.

MATERIALS AND METHODS

Materials used in this study were Zircaloy-2 and -4, and the nominal compositions for these alloys are given in Table I.

Table I. Composition of Zircaloy-2 and -4 in Weight Percent

Alloy	Sn	Fe	Cr	Ni	Zr
Zircaloy-2	1.5	0.12	0.10	0.05	Bal.
Zircaloy-4	1.5	0.20	0.10	0.005	Bal.

The Zircaloy-2 and -4 wrought materials are shown in Figure 1 and were obtained from the Teledyne Wah Chang Company, Albany, Oregon. The Zircaloy-2 cladding in the unoxidized and oxidized forms was obtained from the General Electric Co., Pleasantown, California, and the Zircaloy-4 tubing was obtained from Babcock and Wilcox, Lynchburg, Virginia. These cladding tubes are shown in Figure 2.

Test specimens were cut from the raw materials and from the cladding tubes. The size of the cut specimens ranged from 0.5 to 0.6 cm^2 and after masking for corrosion testing, the corrosion test specimen size ranged from 0.4 to 0.5 cm^2. Specimens from the wrought material received from the Teledyne Wah Chang Company, were cut so that the exposed area was a transverse microstructural section. These specimens were mechanically polished through 300 to 600 grit SiC papers and then with 6 um and 1 um diamond paste and were given a final polish with 0.05 um Al_2O_3. Following the polishing, the specimens were washed with water and then ethyl alcohol to remove any polishing material or contaminants.

Specimens from all of the cladding tube materials were cut to expose longitudinal microstructural sections, and both inner and outer tube sections were tested. Two different surface preparation procedures were used for the cladding tube specimens. Some specimen surfaces were polished with 0.05 um Al_2O_3 washed with water and ethyl alcohol and dried. Other specimen surfaces were prepared only by washing in acetone, ethyl alcohol and water. Test specimens were connected to a titanium lead using with a conducting epoxy or by spot welding, mounted in a glass tube and surrounded with a high temperature epoxy. Specimens of 0.5 cm^2 were tested one day after preparation or were stored in a desiccator.

Specimens of all types of materials were prepared for microscopic study. These specimens were mounted and polished as described and then were etched in a mixture of 20 ml Lactic acid, 5 ml HNO_3, 5 ml H_2O_2, 2 ml HF and swabbed for 10 to 30 seconds. Representative photomicrographs of the specimen microstructures were taken using light microscopy.

The testing environment for these specimens was a simulated well water found at Yucca Mountain, Nye County, Nevada. The Brookhaven National Laboratories[3] developed a procedure for preparing artificial J-13 well water, and the chemical content shown in Table 2. The amounts of chemicals used for making four liters of this water with a ten times concentration are given in Table 3.

Table 2. Chemical Content of Simulated J-13 Water

Element/Compound	Amount, mg/L
Lithium	0.05
Sodium	51.00
Potassium	4.9
Barium	0.003
Iron	0.04
Aluminum	0.03
Silica	61.0
Fluoride	2.2
Chloride	7.5
Bicarbonate	120.0
Sulfate	22.0
Nitrate	5.6
Phosphate	0.12

Table 3. Composition of Simulated J-13 Water Used

Chemical Compound	Grams/4 Liters
$NaHCO_3$	6.585
KOH	0.282
$SiO_2 \cdot XH_2O$ (1.87 % H_2O)	2.486
$CaCl_2$	0.464
$CaSO_4$ (0.92 g $CaCO_3$ + 0.88 g H_2SO_4)	1.288
$Ca(NO_3)_2$	0.096
$Mg(NO_3)_2 \cdot 6H_2O$	0.512
MgF_2 (0.093 MgO + 0.193 HF - 48%)	0.144
$LiNO_3$	0.028
$Sr(NO_3)_2$	0.0048
$BaCl_2 \cdot 2H_2O$	0.0036
$Fe(NO_3)_3 \cdot 9H_2O$	0.0144
H_3PO_4 (85%)	0.0056
$Al(NO_3)_3 \cdot 9H_2O$	0.0278

During preparation, the water is heated but not boiled for mixing, and is saturated with some of the chemicals as indicated by the undissolved particles in the container. The pH of this concentrated water is 8.5 at 22°C. The pH of the unconcentrated water[3] was given as 7.1. The pH of the diluted water to a concentration of one prepared from the concentrated water used in this study was 8.3.

Electrochemical testing was carried out in the simulated J-13 water at a temperature of 95 C and a pH of 8.5 for the concentrated solution and a pH of 8.3 for the unconcentrated solution. The pH measurements were made at 22°C. These tests involved measuring the open circuit electrode potential versus time and making anodic and cathodic polarization measurements in preparation for making the cyclic polarization measurements. All electrode potentials were made in reference to a saturated calomel electrode (SCE). Electrical stimulation tests to determine susceptibility to pitting were made using an American Society for Testing and Materials (ASTM) test method[4].

The polarization tests were carried out in the following manner. The specimen for polarization testing was placed in the 95 C solution and left at open circuit potential for fifteen minutes prior to making the measurements. The solution was not deaerated. Some of the polarization measurements were made by applying a potential to the specimen at the rate of 0.01 V/15 sec starting from the corrosion potential and cycling back to the corrosion potential or lower. Other polarization measurements were made at a rate of 0.05 V/sec for applying the potential, and these started and ended at 200 mV negative to the corrosion potential.

RESULTS AND DISCUSSION

Results of this work showed that Zircaloy-2 and -4 are corrosion resistant to J-13 water in both the concentrated and unconcentrated form, but there are some inconsistencies in the corrosion behavior and there are effects due to varying surface preparation. Generally, Zircaloy passivates in the J-13 water at 95 C. There are instances due to the specimen mounting where crevice corrosion occurred. Unless the cladding tubes were mechanically polished, they did not passivate in the same manner as the bulk material indicating the presence of a surface oxide or other layer. Corrosion rates, determined using the polarization resistance method, were in the range of 0.001 to 0.0002 mm/year.

Microstructures

Microstructures for the Zircaloy-2 and -4 specimens are shown in Figures 3 through 14. The magnification is the same for all of the photomicrographs. Light micrographs of the microstructures of Zircaloy-2 and -4 specimens are shown in Figures 3 and 4, respectively. The bulk materials are shown in Figure 1. These micrographs show the materials in the wrought form before being made into tubing. These materials have been chemically etched, but specimens used for corrosion testing were not etched. The microstructures are representative of the transverse section of this bulk material. The grains are distinguishable, and some are equiaxed and others have intermediate to elongated shapes. There are precipitate phases as indicated by the small distinct areas. The precipitates in Zircaloy-2 of Figure 3 are $Zr(Fe,Cr)_2$ and $Zr_2(Fe,Ni)$ and the precipitate that is present in Zircaloy-4 of Figure 4 is $Zr(Fe,Cr)_2$ [5].

Specimens for corrosion testing were mechanically polished and were not etched, and the smooth surface of a Zircaloy-4 specimen is shown in Figure 5. Figure 6 shows the same surface as in Figure 5 after anodic polarization. Some of the precipitate particles are more visible although no significant attack is observed.

The cladding tubes were sectioned to show the microstructure in both the longitudinal and the transverse directions. The respective longitudinal and transverse sections of Zircaloy-2 shown in Figures 7 and 8 do not show much grain elongation due to the drawing direction. Figures 9 and 10 show the location of the precipitates in both sections of the Zircaloy-2 tubing, and these precipitates seem to be randomly distributed with some being at the grain boundaries. The Zircaloy-4 cladding showed a greater effect from the production of the cladding tubes, and this is evident in the elongated grain structure in the longitudinal section of Figure 11 and the fine grain structure of the transverse section of Figure 12. Again, some precipitates are randomly located and others are at the grain boundaries as shown in Figures 13 and 14 that show the precipitates in the longitudinal and transverse directions, respectively.

Passivity

Specimens were immersed in the testing solution (not deaerated) of the J-13 water shown in Table 2 that was held at 95°C and had a pH of 8.5. Upon immersion, the specimens of the wrought Zr-2 and Zr-4 would tend to passivate. This was indicated by the increase in the open circuit electrode potential when monitored versus time. For example, If the initial potential were -0.573 V, it could change to -0.473 V after five to fifteen minutes and to -0.250 V after twelve hours. This change of electrode potential in the positive direction indicates passivation. An example of some potential versus time measurements is given in Table 4.

Table 4. Open Circuit Potential of Zircaloy-2 in J13 Water at 95°C

O. C. Pot., (V vs. SCE)	Time (hour and date)
-0.573	4:00 p.m., 11/28/88
-0.250	9:00 a.m., 11/29/88
-0.438	6:20 p.m., 11/29/88
-0.123	11:30 a.m., 11/30/88
-0.151	11:00 a.m., 12/2/88
-0.321	11:00 a.m., 12/5/88
-0.281	11:00 a.m., 12/6/88
-0.236	11:00 a.m., 12/7/88
-0.201	11:00 a.m., 12/12/88
-0.204	11:00 a.m., 12/13/88
-0.195	11:00 a.m., 12/20/88
-0.172	11:00 a.m., 12/21/88

Specimens for all polarization tests using this material also showed this positive trend for the open circuit potential after the fifteen minute waiting period prior to testing. Specimens of the cladding material, both inside and outside of the tubing, that had the surface polished lightly with 0.05 um Al_2O_3, also showed an a positive trend in the potential after the fifteen minute waiting period. Specimens of the tubing that were washed in acetone and alcohol using the ultrasonic cleaner, but which did not have the surface polished, did not show this positive trend. This information indicated that the surface preparation or surface exposure affects the initial passivation of the Zircaloy.

Polarization

Cyclic polarization measurements, showing the current versus the applied potential, were made on the materials to determine the passive region, the breakdown potential and other features of the corrosion behavior of the Zircaloy materials. The breakdown potential, marked by a sharp rise in current, for the Zircaloy bulk materials ranged from 0.800 V to 1 V. The Zr-2 cladding with the oxide coating did not appear to breakdown until reaching 1.6 to 2.2 V. There was some variation in the breakdown potentials of these materials. The polarization curves for the bulk materials exhibited a wide range of passivity, extending over approximately 1200 millivolts.

Passive regions and breakdown potentials for the cladding tubes were less distinct. Figures 15 and 16 are cyclic polarization curves for Zr-2 and Zr-4, respectively, in J-13 water at 95°C, and were produced using a scan rate for applying the potential of 0.05 V/sec. The hysteresis present can be interpreted as indicating susceptibility to localized corrosion, but this is not necessarily always true since other factors such as the environment, scanning rate of applying the potential during the test and the presence of a surface film prior to the test can cause this effect. The source of the hysteresis needs further study. There were some problems with mounting and shielding the Zircaloy specimens for the tests at the higher temperature. There often was a visual indication of crevice corrosion at the mounting/specimen interface and of limited pitting. In other tests, there was no indication of localized corrosion.

Some tests were conducted in unconcentrated J-13 water, and Figures 17 and 18 are cyclic polarization curves for Zr-4 at temperatures of 22°C and 95°C, respectively. The specimen was kept at a temperature of 22°C for twenty five days. Raising the temperature to 95°C caused a change in the curves indicated by hysteresis and a shift in the corrosion potential as is shown in Figure 18. The curve in Figure 17 that was measured at 22°C shows the return portion to have lower current indicating increased passivity. Representative results of cyclic polarization tests on the inner and outer surfaces of the cladding tubes are given in Figures 19 through 22. The hysteresis in these curves is less than that for the wrought specimens. The current in the passive region is increased and breakdown potential is not sharply defined for the cladding materials.

SUMMARY

cyclic polarization measurements were made on the alloys, Zircaloy-2 and Zircaloy-4 in simulated Nye County, Nevada J-13 well water at 95°C. These measurements were made to obtain data on corrosion of Zircaloy under conditions which could occur in

the nuclear waste repository. Overall, the Zircaloy shows a low or negligible corrosion rate under all of the conditions tested, but there is evidence of localized corrosion in the electrochemical data and at crevice corrosion sites resulting from the specimen mount.

Zircaloy was tested to determine susceptibility to pitting and did not show a pitting potential prior to the breakdown potential. There still are uncertainties regarding the susceptibility to pitting and crevice corrosion as well as measurements of polarization behavior. More data of the type reported here and from other experiments are needed to carefully characterize the corrosion behavior of Zircaloy under repository conditions. Some conclusions indicated from this study are:

1. Exposure of wrought Zircaloy-2 and -4 materials to J-13 water or concentrated (10X) J-13 water results in passivation of the surface as indicated by the corrosion potential shift in the noble direction.

2. Zr-2 and Zr-4 cladding tubes passivate but not as much as the bulk material, and various surface treatments will alter passivation.

3. Some cyclic polarization measurements of Zr-2 and Zr-4 in J-13 water, at 95°C show no evidence that localized corrosion would occur. Other measurements show evidence of localized corrosion, but the protection potential is over 1000 mV more noble than the corrosion potential.

4. The breakdown potential for the wrought materials occurred within the range of +0.800 V to +1 V vs. S.C.E. and higher in some cases, and that for the tubing ranges from +0.300 V to +0.750 V vs. S.C.E. Surface preparation techniques have a strong influence on the breakdown potential.

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SUMMARY

- Exposure of wrought Zircaloy-2 (Zr-2) and Zircaloy-4 (Zr-4) materials to J-13 water or concentrated (10X) J-13 water results in some passivation of the surface as indicated by movement of the corrosion potential in the nobel direction.

- Zr-2 and Zr-4 cladding tubes passivate but not as much as the wrought material, and various surface treatments on the tubing will prevent passivation.

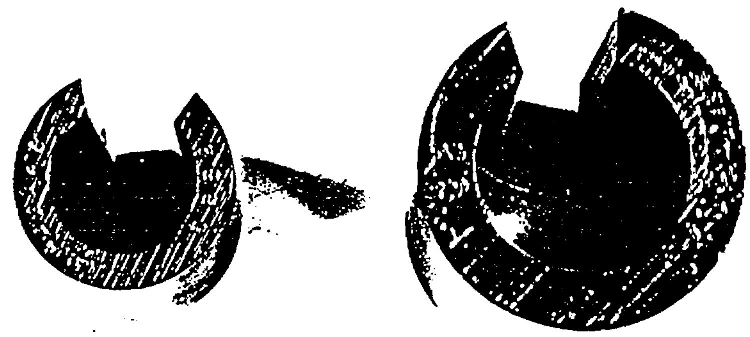
- Some cyclic polarization measurements of Zr-2 and Zr-4 in J-13 water, both concentrated and unconcentrated at 95°C, show no evidence that localized would occur.

- Other cyclic polarization measurements of Zr-2 and Zr-4 in J-13 water at 95°C show evidence of localized corrosion, but even in these cases, the protection potential is over 1000 mV more noble than the corrosion potential.

- The breakdown potential for the wrought materials is at +800 mV vs. a saturated calomel electrode (S.C.E.) and higher in some cases.

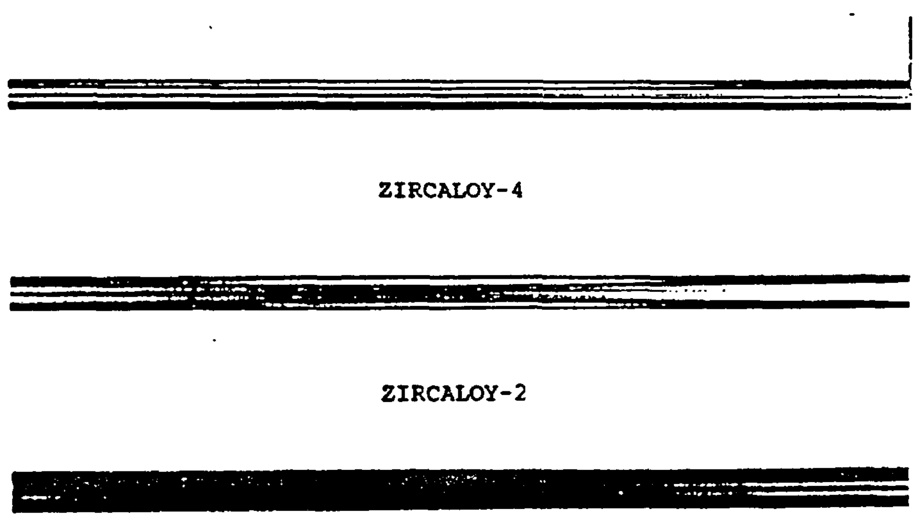
- The breakdown potential for the tubing ranges from 300 mV to 750 mV vs. S.C.E. There is more scatter in the data for the tubing and surface preparation techniques have a strong influence on the results.

- This work was performed to characterize Zircaloy and Zircaloy cladding and to furnish base line data on the corrosion behavior of these materials.



ZIRCALOY-2 ZIRCALOY-4

Figure 1. Zircaloy-2 and -4 from Teledyne Wah Chang Albany, Albany, Oregon.



ZIRCALOY-2 with 0.5 um zirconium oxide (ZrO_2) coating

Figure 2. Zircaloy-4 Tubing from Babcock & Wilcox, Lynchburg, Virginia and Zircaloy-2 Tubing, with and without the ZrO_2 Coating, from the General Electric Co., Pleasanton, California.

Figure 3. Zircaloy-2, etched.

Figure 4. Zircaloy-4, etched.

20 ml Lactic acid, 5 ml HNO_3, 5 ml H_2O_2, 2 ml HF, Swab for 10 to 30 sec.

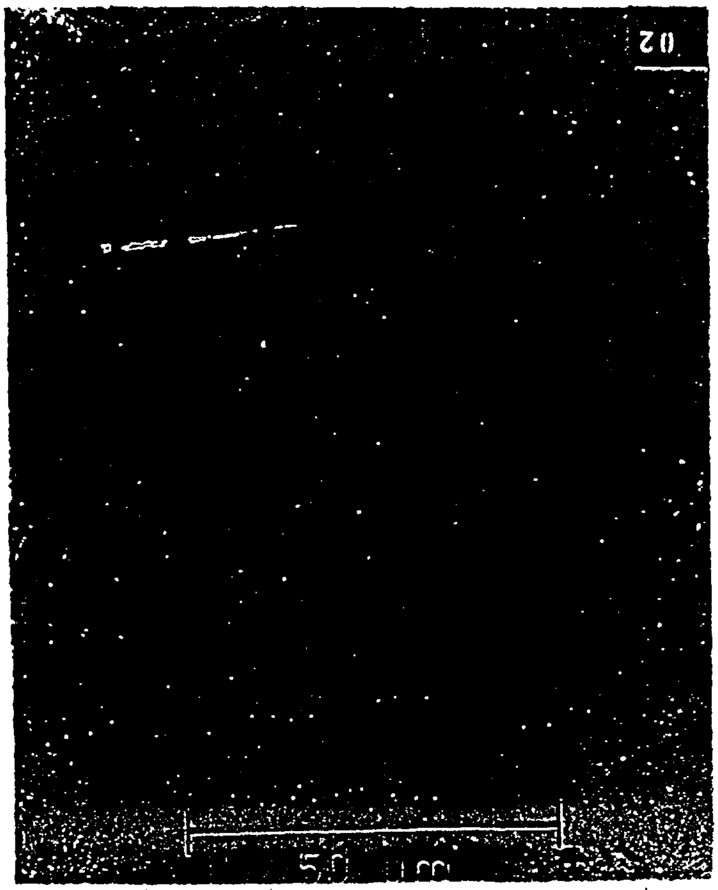


Figure 5. Zircaloy-4, as polished.

Figure 6. Zircaloy-4, after anodic polarization

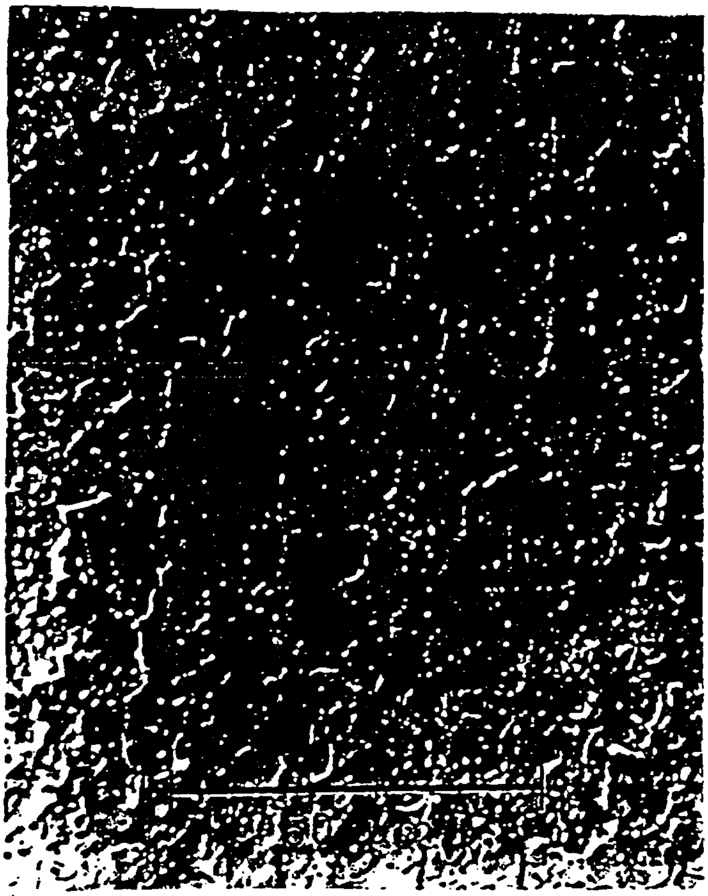


Figure 7. Zircaloy-2 cladding, longitudinal section, etched.

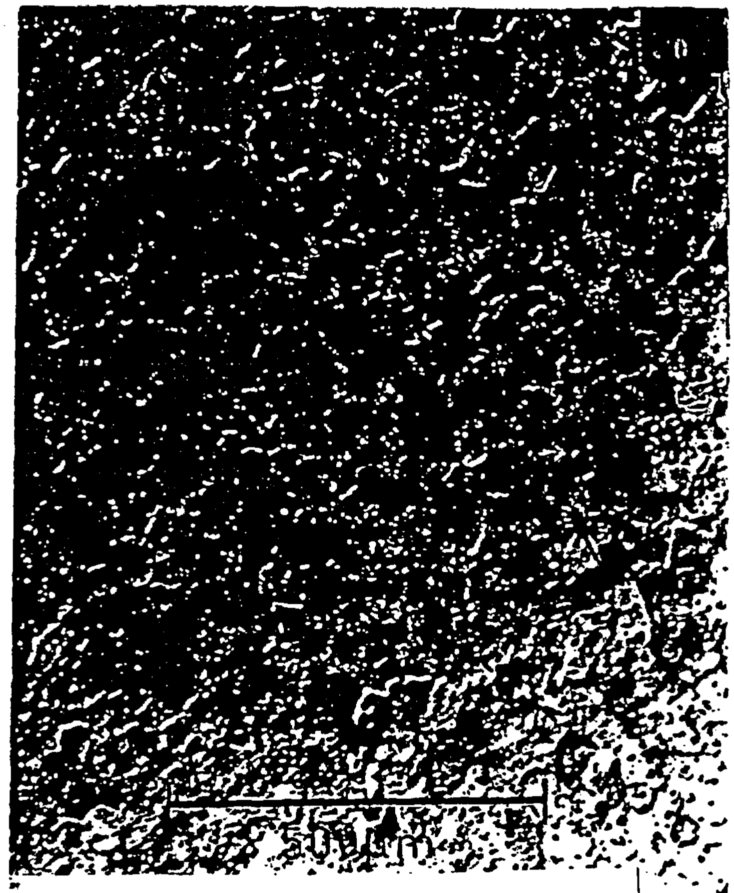


Figure 8. Zircaloy-2 cladding, transverse section, etched.

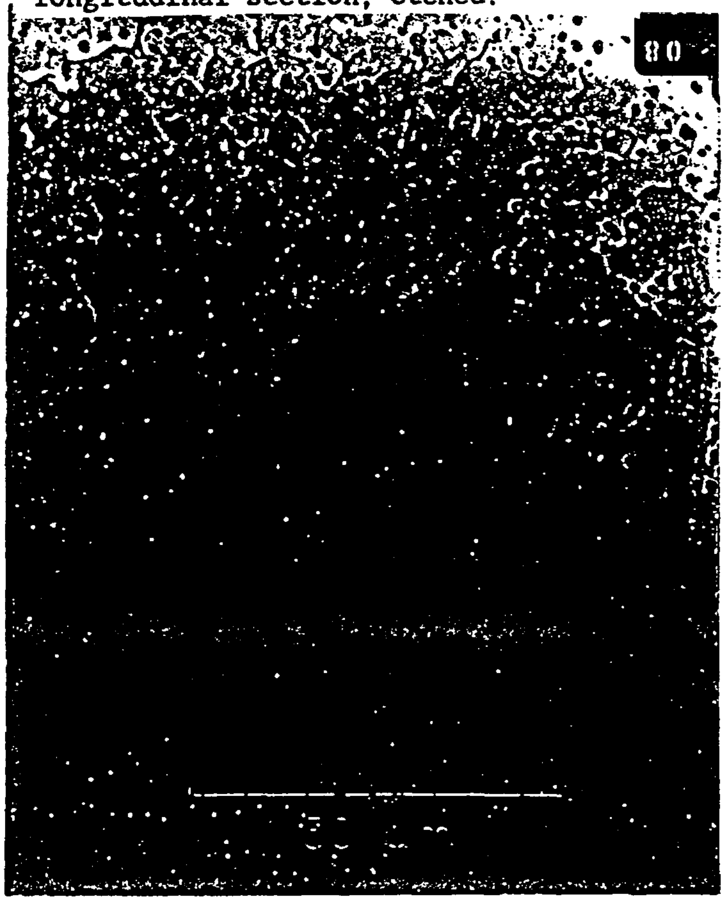


Figure 9. Zircaloy-2, longitudinal section with $Zr(Fe,Cr)_2$ and Zr(Fe,Ni) precipitates.

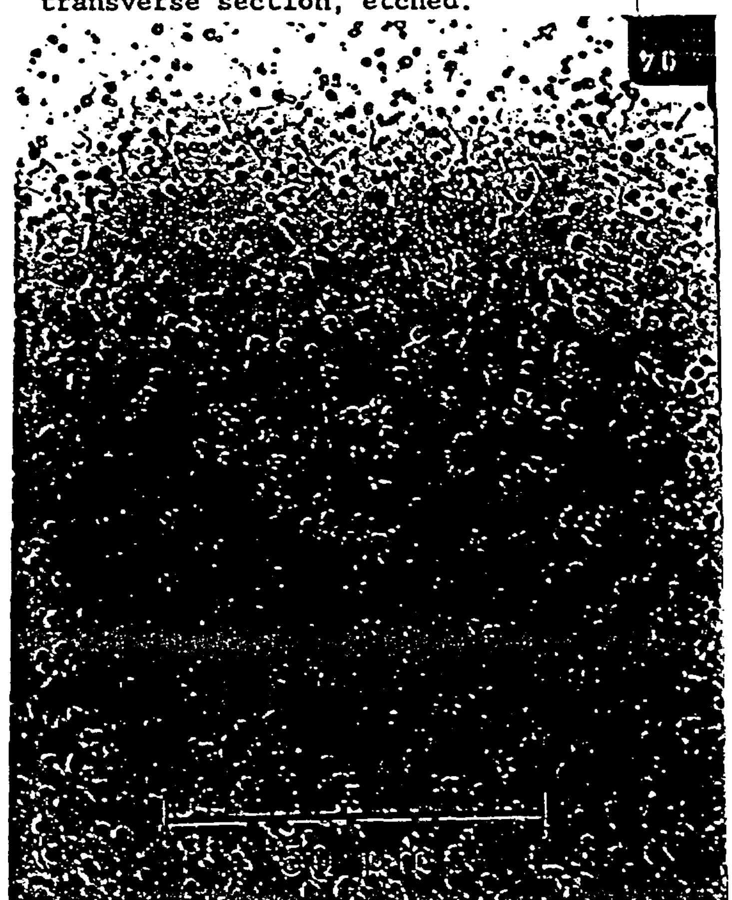


Figure 10. Zircaloy-2, transverse section with $Zr(Fe,Cr)_2$ and Zr(Fe,Ni) precipitates.

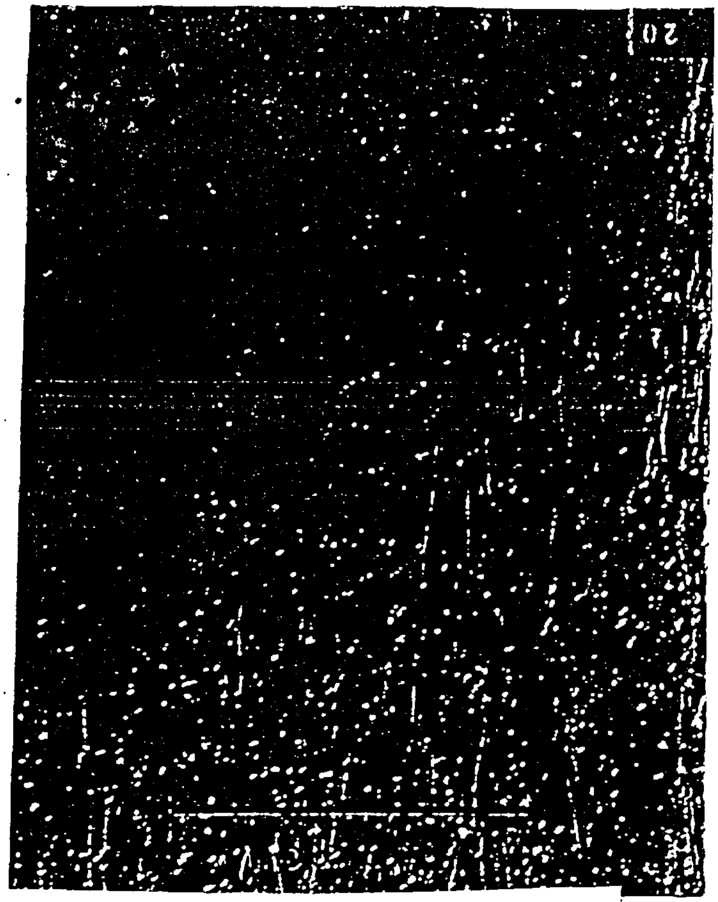


Figure 11. Zircaloy-4, longitudinal section, etched.

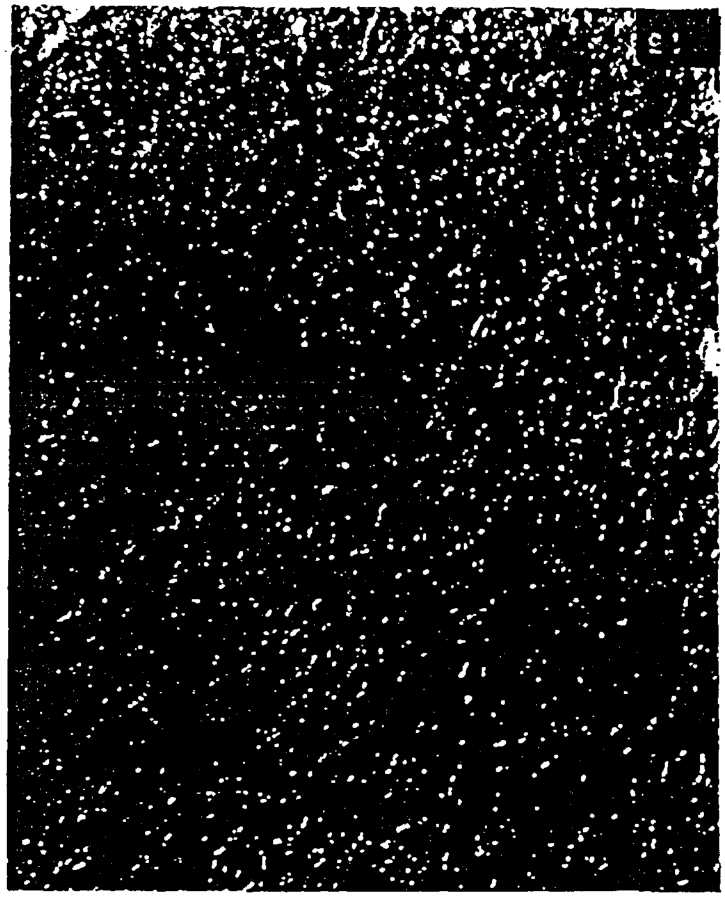


Figure 12. Zircaloy-4, transverse section, etched.

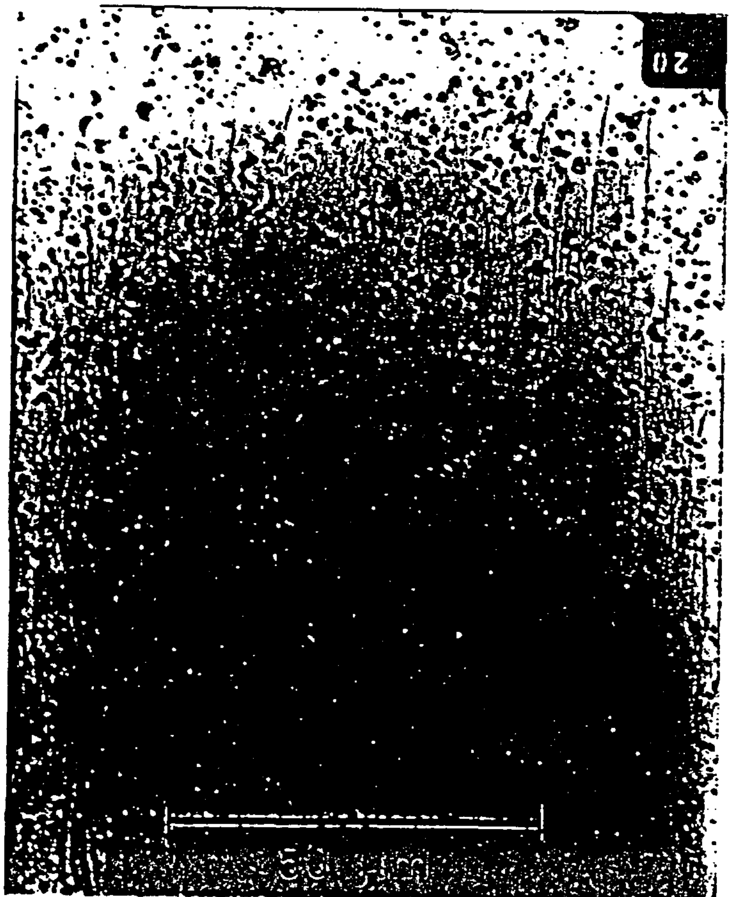


Figure 13. Zircaloy-4, longitudinal section with Zr(Fe,Cr) precipitates.

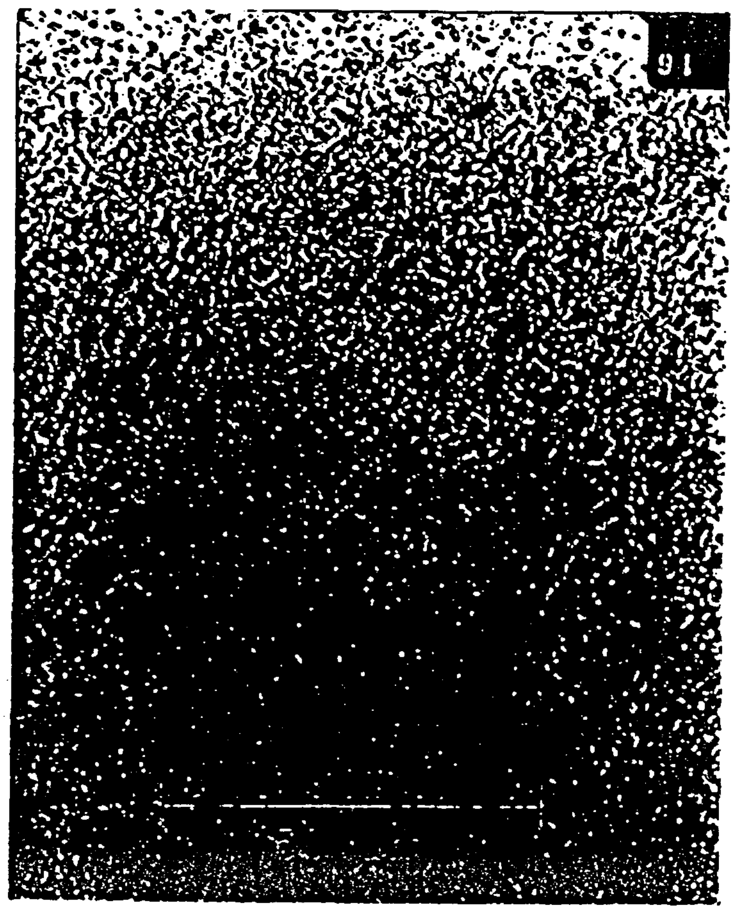


Figure 14. Zircaloy-4, transverse section with $Zr(Fe,Cr)_2$ precipitates.

CYCLIC POLN

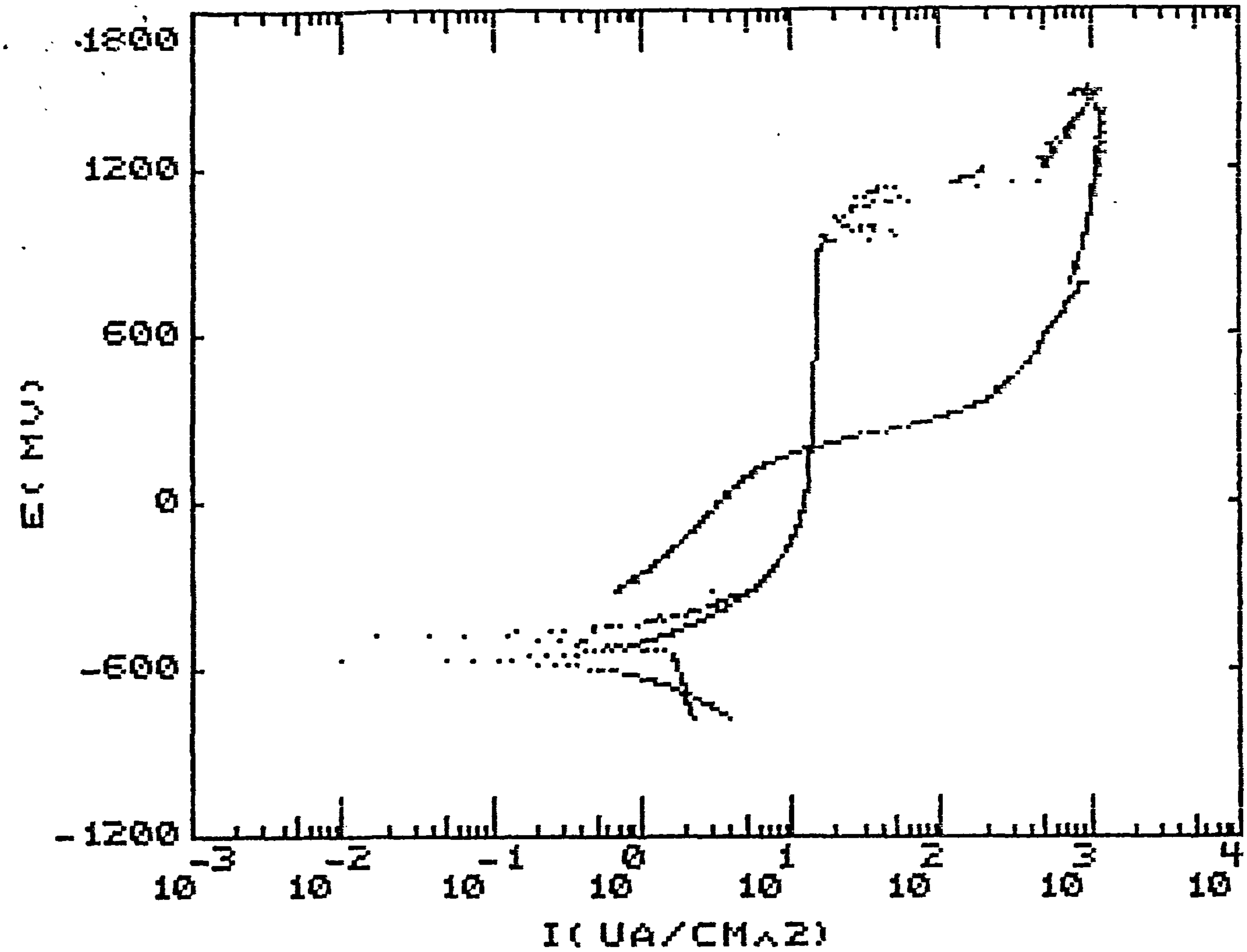


Figure 15. Cyclic polarization curve for Zircaloy-2 in J-13 water, pH = 8.5, 95°C.

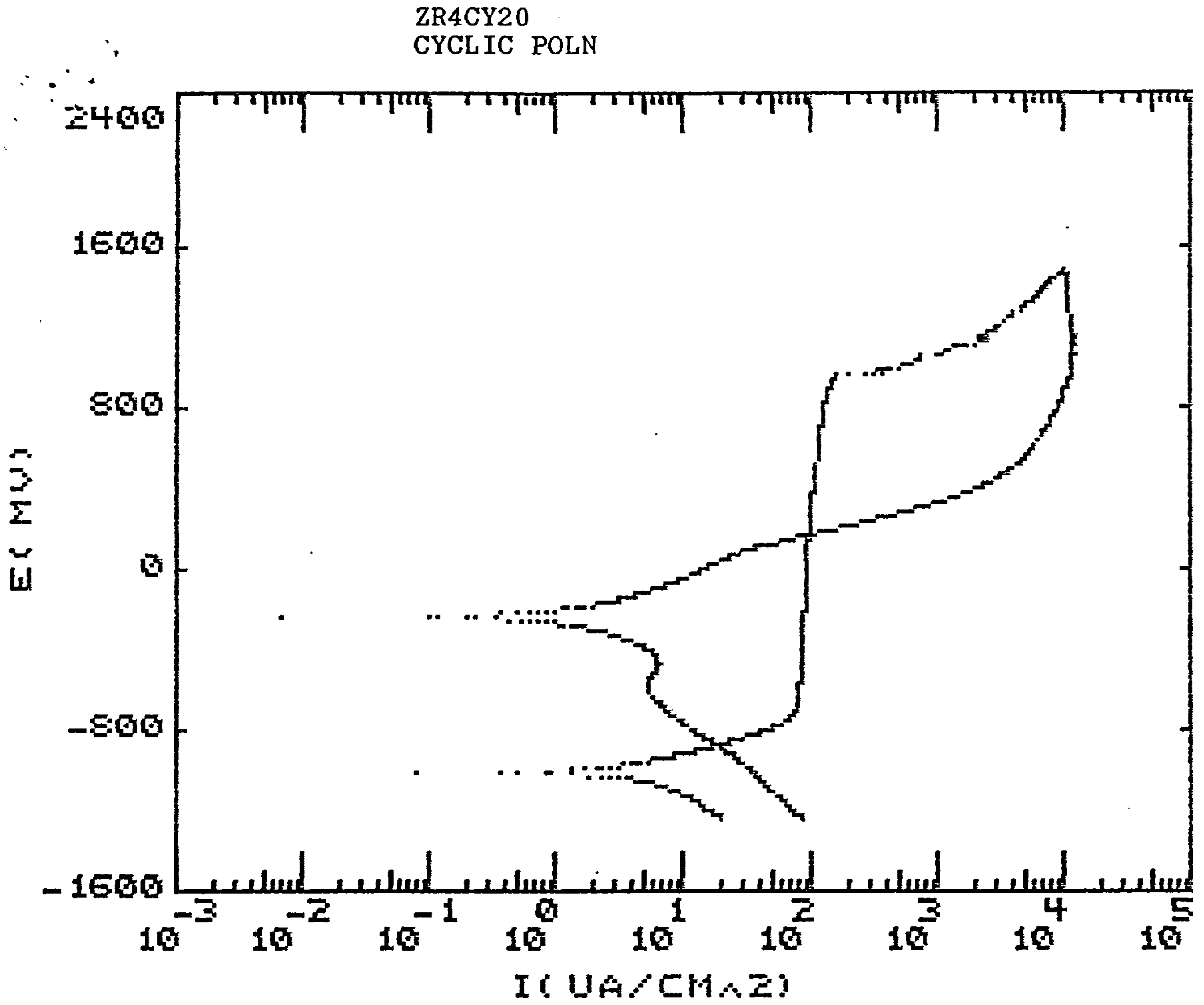


Figure 16. Cyclic polarization curve for Zircaloy-4 in J-13 water, pH=8.5, 95°C.

ZR4CY7
CYCLIC POLN

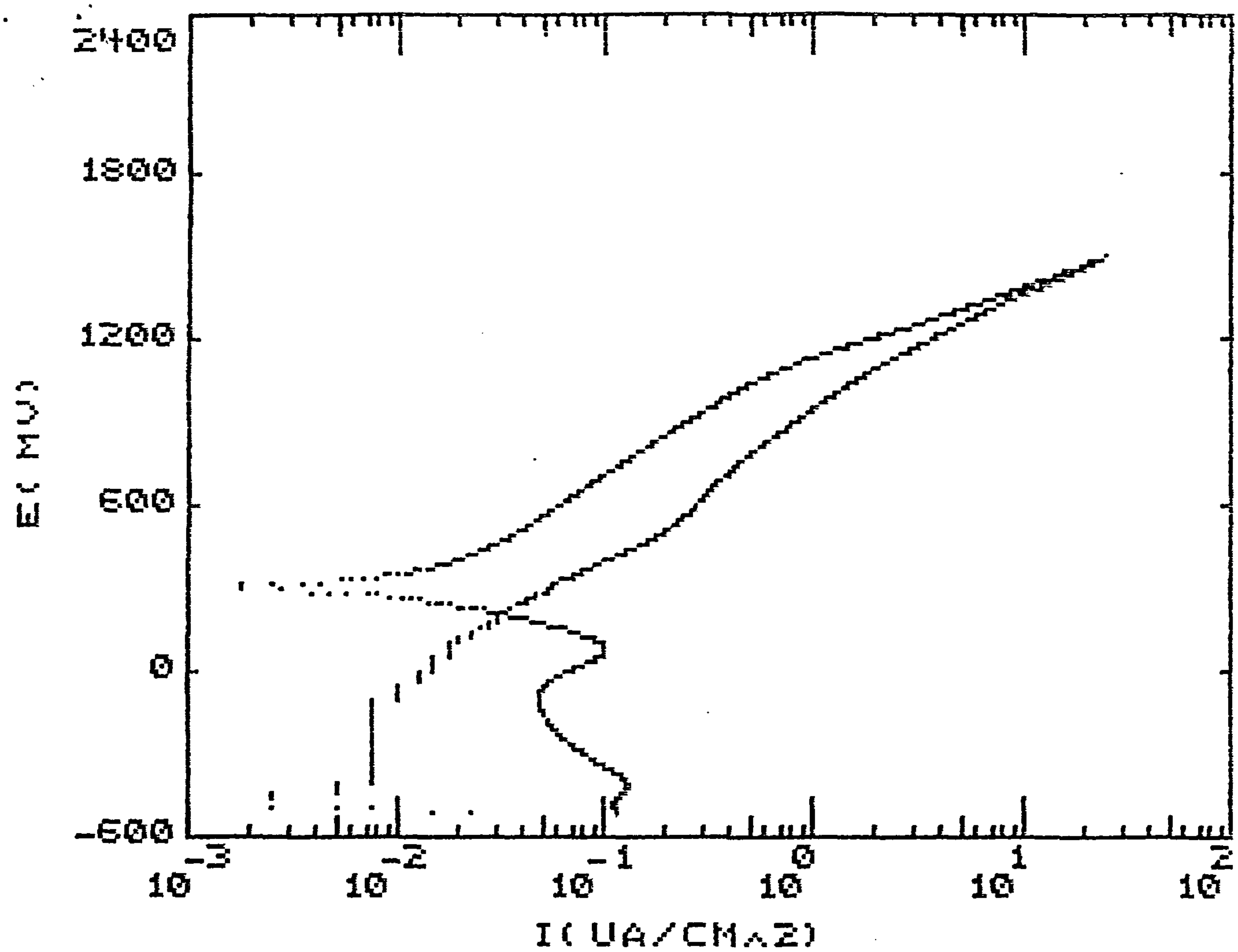


Figure 17. Cyclic polarization curve for Zircaloy-4 in J-13 water, pH=8.3, 22°C

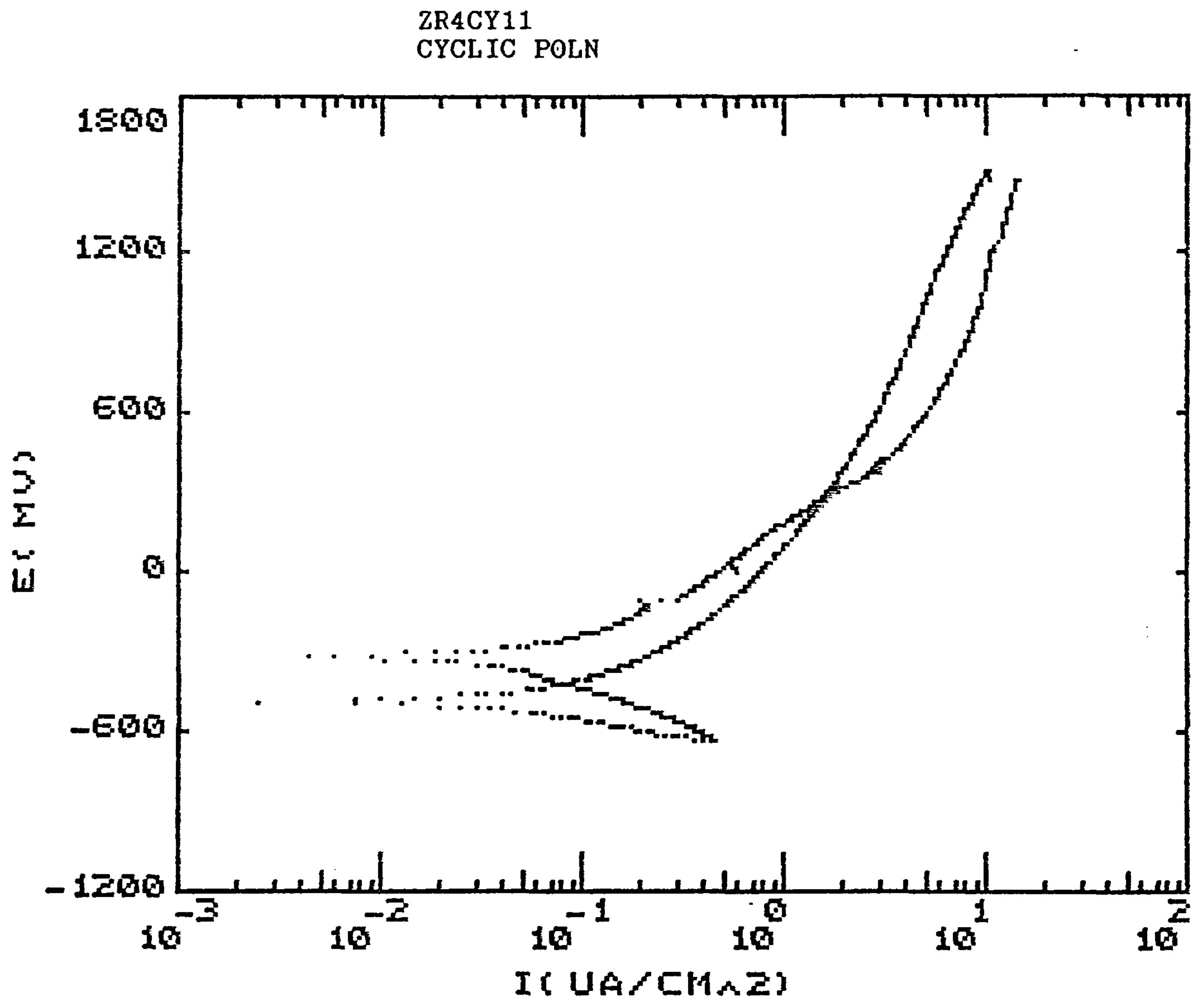


Figure 18. Cyclic polarization curve for Zircaloy-4 in J-13 water, pH=8.3, 95°C.

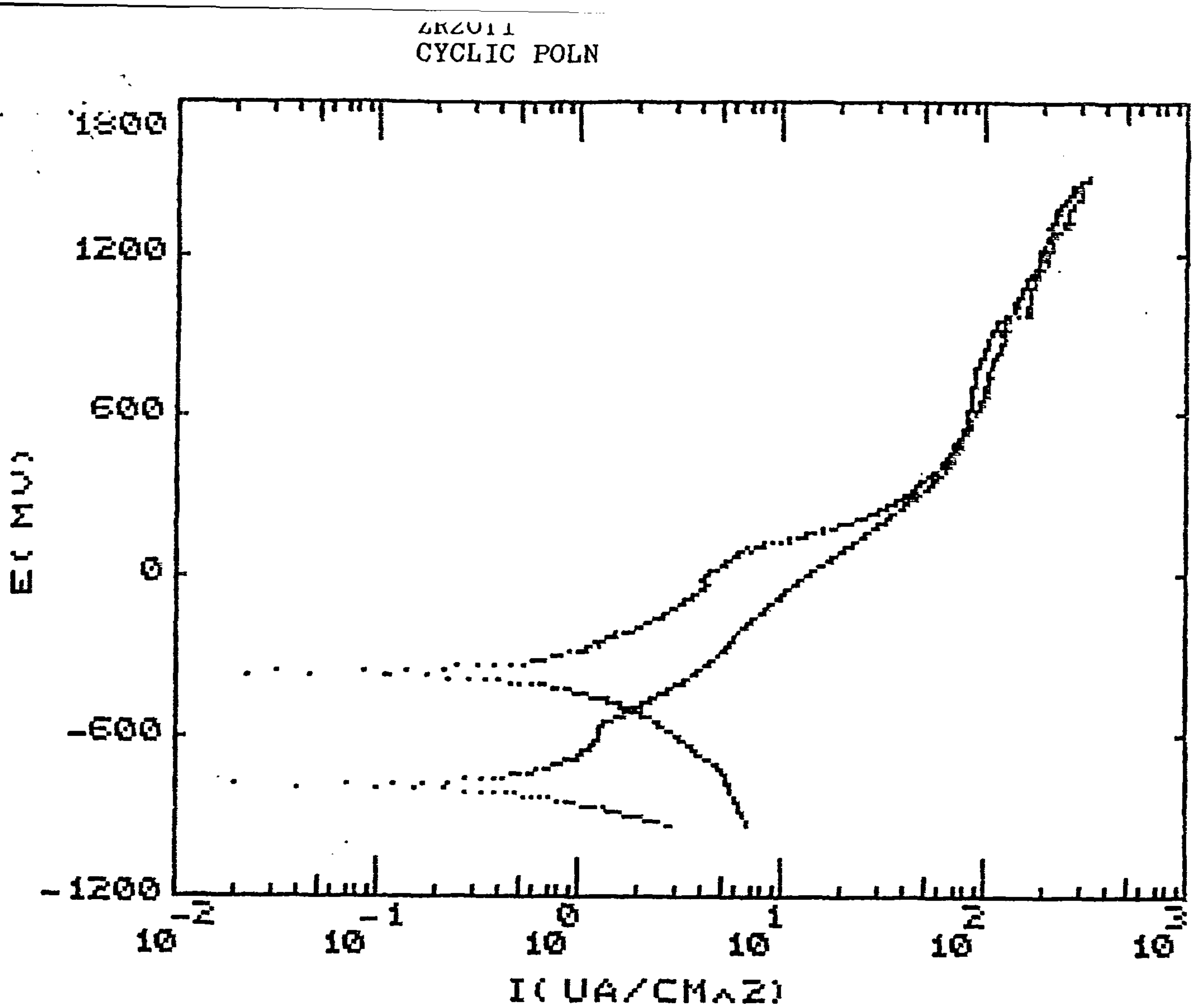


Figure 19. Cyclic polarization curve for inner surface of Zircaloy-2 cladding tube in J-13 water, pH=8.5, 95°C.

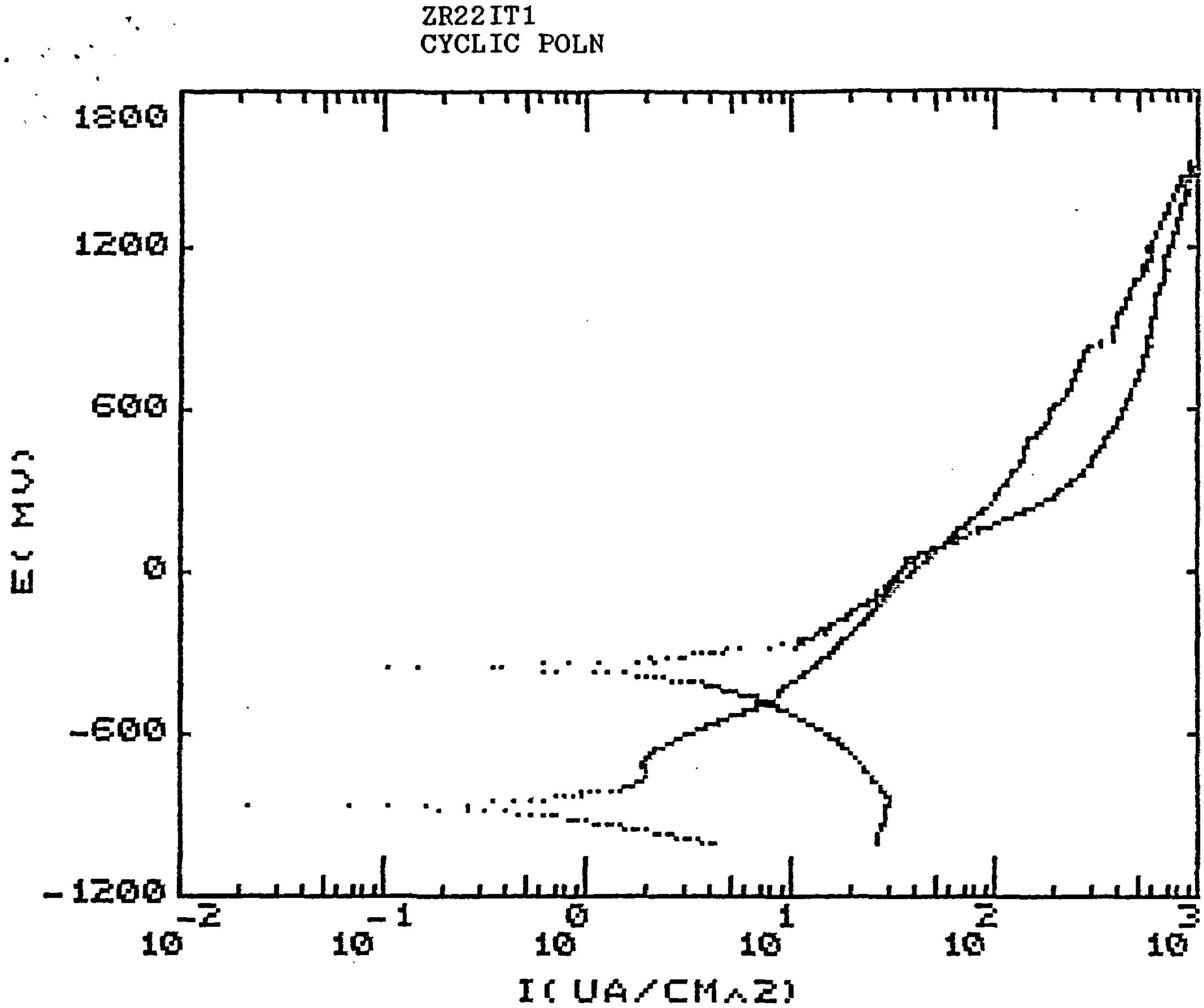


Figure 20. Cyclic polarization curve for outer surface of Zircaloy-2 cladding tube in J-13 water, pH=8.5, 95°C.

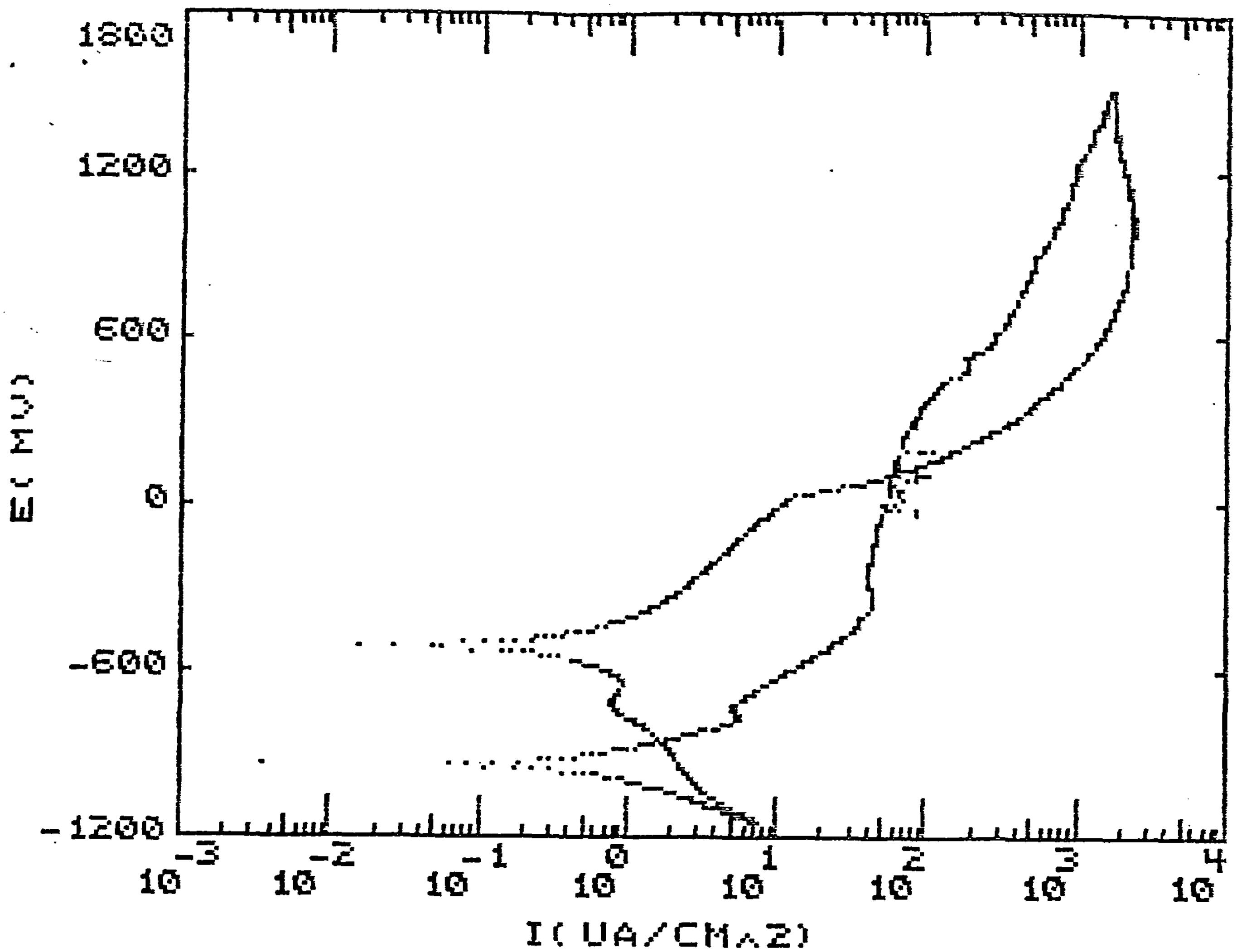


Figure 21. Cyclic polarization curve for outer surface of Zircaloy-4 cladding tube in J-13 water, pH=8.5, 95°C.

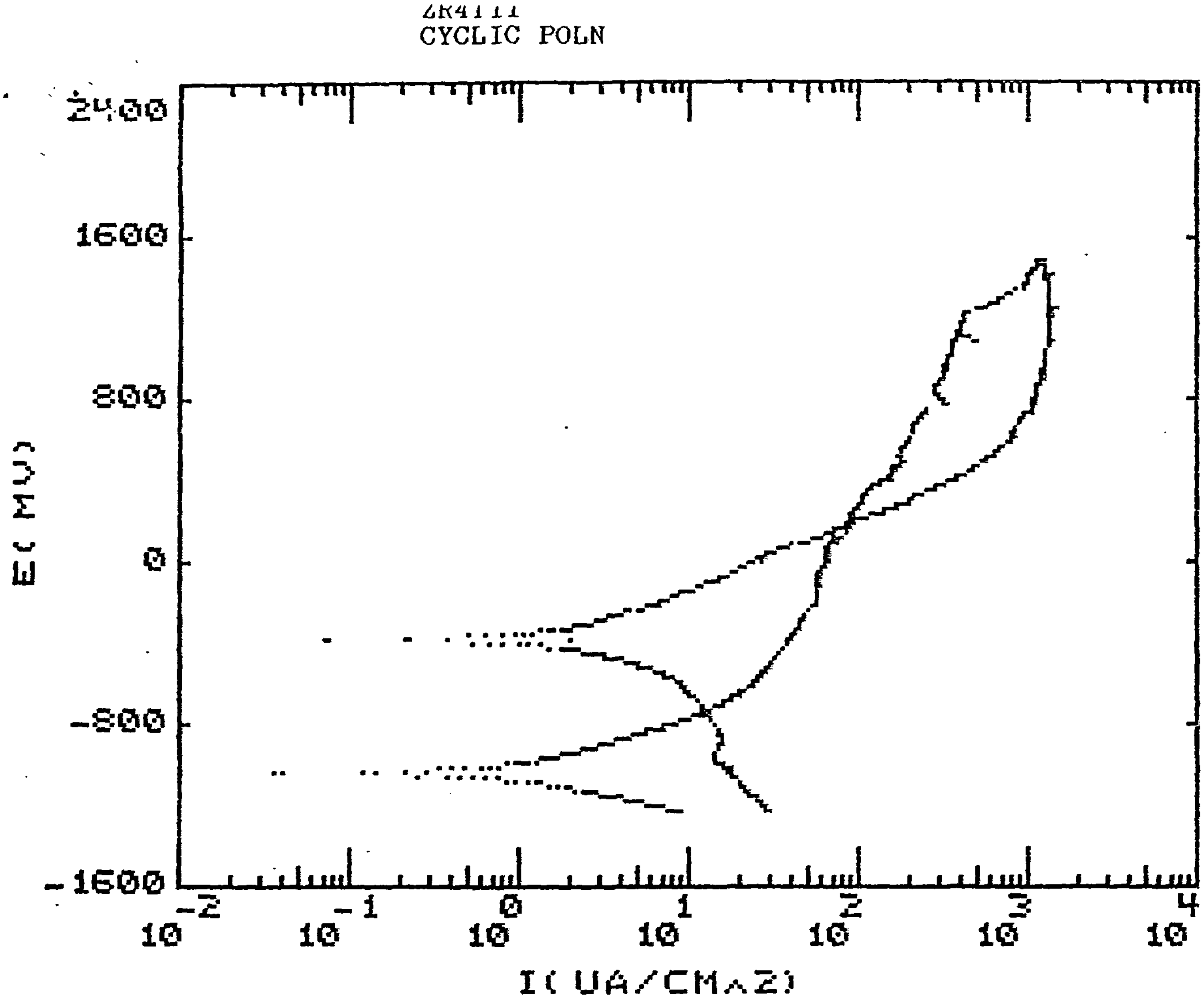


Figure 22. Cyclic polarization curve for inner surface of Zircaloy-4 cladding tube in J-13 water, pH=8.5, 95°C.

Appendix E. ADVANCED REVELATION, Scientific Notation, and Nuclear Waste

ADVANCED REVELATION, Scientific Notation, and Nuclear Waste*

by Carla G. Messina, C. G. Interrante, and Jill Ruspi

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*The work discussed in this article was sponsored the U.S. Nuclear Regulatory Commission, Office of Materials Safety and Safeguards, Contract NRC FIN A-4171.

ABSTRACT

This paper describes developments for handling highly technical records, mainly text, using multiple, variable-length fields that contain a wide variety of commonly used scientific notations such as super- and sub-scripts. It also highlights the development of a database for information on highly radioactive waste. In this database, highly technical information is presented within records of widely varying lengths. These records include symbols and abbreviations and may contain superscripts, subscripts, or special characters such as floating accents and Greek symbols. In this database, the scientific notations can be treated as any other part of the records. This is true for both the data entry procedures required for these records and for the CRT display and the printout of these records.

INTRODUCTION

Under a contract with the U. S. Nuclear Regulatory Commission (NRC), a Data Center for High-Level Waste was established under the direction of Dr. Charles Interrante of the Metallurgy Division, Institute for Materials Science and Engineering, National Institute of Standards and Technology (NIST). A key component of this data center is its database for radioactive high level waste (HLW). The database currently contains records for over 1000 items, as well as about 200 technical reviews of pertinent literature. The reviews are technical evaluations of selected documents contained in the data center and they are conducted by the scientific staff at the NIST. Computer searches are done both on the reviews and on the other items, which are mainly bibliographic records containing information, e.g. citations and abstracts. The technical focus of this database is the engineered barrier system of a permanent repository for HLW. Using Revelation G and then ADVANCED REVELATION, Carla Messina and Steve Harrison created a system for storage and retrieval of this important information. As part of this effort, Ms. Messina implemented the procedures described in this paper.

Earlier database design work in the NIST Standard Reference Data Program provided the basis for several of the innovations that have been implemented in the NIST-HLW System. These include (1) the handling of superscripts and subscripts, such as those found in some chemical notations and (2) development of a report generator that facilitates presentation of a record containing one or more very long fields, which contain up to 8000 characters, and (3) development of code strings that facilitate the porting of files.

SUPERSCRIPTS AND SUBSCRIPTS

To indicate superscripts and subscripts, a series of printable ASCII code strings is used. Using these codes, the base line for printing is shifted to obtain, for example, subscripts, superscripts, superscripts over subscripts, and special characters such as umlaut and angstrom. In addition, these codes are used to turn on and off any special fonts such as boldface and italic.

The codes mentioned above permit any characters to appear in the inferior and superior line position, thus, any character that can be printed can be used as a superscript or a subscript. Two examples are given below:

(1) The designation for H_2O would be H\/2/\O. To the typist, this resembles the command H, down, 2, up, and O.

(2) An isotope of the element plutonium is designated as ^{239}Pu and this is keyed as /\239\/Pu.

At first, this keyboarding convention may seem cumbersome, but it is graphic and easily learned. This can be a very important consideration, especially when entry level typists are employed for keying of data are entry level.

UMLAUTS AND FLOATING ACCENTS

In order to print one character above another, the code string <- is used. This is the symbol for "less than" followed by "a hyphen". Together they are the code for "backup," i.e. back up the (print head or the cursor) by one space. For example, a backup is contained in the name "Čerenkov". This name would be keyed as follows: C<-/\v\/erenkov. Thus, using only three code strings (/\, \/, and <-), it is possible to represent scientific notation, including superscript, superscripts, superscripts over subscripts, and floating accents, like the umlaut.

PORTABLE CODE STRINGS

The code strings used to shift the base line and to backup the print head or the cursor require only the standard ASCII characters. Thus, so that the portability of any records containing these codes is assured, irrespective of the nature of the destination. Therefore, text files of a review created on a word processor are easily ported into the files of the NIST HLW database, or they can be ported into any other system, local or remote, with no requirement to edit or remove any special or "forbidden" characters. What is required, after the porting has been completed, is the transformation from the string of ASCII codes (e.g. /\, etc) to the notations (superscript, etc.) that they represent. This transformation is very easy to accomplish by using a set of macros at the destination (i.e. at the receiving end of the transmission). The macros are specifically designed to transform the ASCII code strings into the local notations used in the code of word processing system in use at the destination.

THE REPORT GENERATOR

As the NIST HLW Database developed, it become evident that apart from the problem presented by scientific notations, a second problem related to presentation existed: tables and windows were not capable of displaying the full record of a technical review, the record for which the database had been designed. For large records, a window is so small that only a fraction of the information can be viewed at one time and for a table there is a finite limit to the number of fields that can be displayed at one time. Therefore, a report generator was developed. The report generator displays and print records taken from fields of any size.' In the NIST HLW Database, it is currently used for fields up to 8000 characters in length. The report generator reads a record and presents the information as a sequence of fields. The sequence and the names of the fields present in the report are specified in a dictionary element as described below. A knowledgeable operator can modify the number of fields and their order. In the report, a label (name) precedes the presentation of the contents of each field. Fields are presented in the hanging indent (paragraph) format. The record is sent either to a CRT or to a printer, and only fields that contain information are included in the record.

To prepare a report generator in Revelation, Carla Messina and William Webber (NIST) developed vocabulary commands that read a DICTIONARY group field called "@FULL," which contains the names of all fields that can be present in this record, i.e. all fields that are present in this file are specified in "@FULL." The order in which these field names are encountered within "@FULL" determines their order in the report. The vocabulary commands read "@FULL" so as to create formatted output that is suitable for sending the report to output devices. A different vocabulary command is required for each output device Cathode Ray Terminal (CRT, laser printer, etc). When the dictionary group field (@FULL) is present the operator can scan an entire file without knowing of any of the specific names for fields, because "@FULL" contains these names. In addition, only a simple command is required to present the full record without the need for any windows, any tables or a specific report generator that applies to a particular file. Thus, a single vocabulary command allows the operator to view all of the field names and the contents of these fields. That command is LIST 'FILE' FULL.RECORD.

Examples of the innovations discussed in this paper are illustrated here with a "dummy" record. These examples demonstrate the features of the system as they would appear on a laser printer, Figure 1, and on a CRT, Figure 2. Figure 1 shows the superscripts, subscripts, subscripts over superscripts, bold, italic, floating accents, and a very long field containing a table. Figure 2 contains the same record but it is displayed as seen on the CRT. The CRT can only display a line at a time and therefore does not permit the use of superscripts and subscripts, but using this system they are presented in a form that is readily understood. Various print formats have been developed for use with this database. These formats give the viewer choices on the form and style of the output record and device. Figure 1 illustrates an output to the laser printer, using the command FULL.RECORD.LASER. The second sample shows the same record as output to the CRT, using the command FULL.RECORD.

References

1. C. Interrante, C. Messina, S. Harrison, et al., "An Analysis of the Requirements for a Computer Assisted Database for Reviews and Evaluations on High Level Waste Data," National Bureau of Standards, NBSIR 86-3363(NRC)(R), June 1986. (Availability restricted.)

2. H. M. Ondik and C. G. Messina., "Computerization and Networking of Materials Data Bases. ASTM STP 1017, J. S. Glazman and J. R. Rumble, Jr., Eds., American Society for Testing and Materials, Philadelphia, 1989, pp. 304-314.

Report Viewer

PAGE 1 12:25:21 22 AUG 1989

CIT.NO FULL.RECORD HLW...

CIT.NO: 9999

REPORT.NO: NOT A REAL REPORT

AUTHORS: Rinaantat, R. P.; Cernkov, A. B.

TITLE: Effect of Groundwater Compostion and Temperature on the Corrosion of Steel

SPONSOR: Department of Energy, Washington, D.C.

DATE: 08-85

CONTRACT.NO: XXXX-XXXX

PAGES: 1-395

ABSTRACT: The effect of Grande Ronde Basalt groundwater composition and temperature on the corrosion rate of American Iron and Steel Institute (AISI) 1020 steel in basalt-bentonite packing was investigated. The studies were based on a Plackett-Burman statistical screening design.

For the present studies, anions (Cl^-, F^-, SO_4^{2-}, and CO_3^{2-}) and temperature were selected as the initial variables affecting

List		Use Direction Keys to View Report (Press <F1> for help)			
	FILTER	Page: 1/2	User		Level

Report Viewer

PAGE 2 12:25:36 22 AUG 1989

CIT.NO FULL.RECORD HLW...

corrosion. A minimum and a maximum value was chosen for each variable. The minimum value was 0 mg/L for the anions and 100°C for the temperature. The maximum values were 780, 76, 576, and 120 mg/L, respectively, for Cl^-, F^-, SO^{2-}, and CO_3^{2-}, and 250°C for the temperature.

Mechanical Properties

Alloy	Ultimate Tensile Strength (MPa)	Ultimate Tensile Strength (ksi)	0.2% Offset Yield Strength (MPa)	0.2% Offset Yield Strength (ksi)	Elongation (%)	Rockwell Hardness (R_B)
304L SS	536	77.8	276	40.1	65.3	85.2
316L AA	562	81.5	254	36.9	59.2	69. 4
Incoloy 825	799	100.6	475	68.9	36.0	95. 0

Reference: T. Znamierowska, Pol. J. Chem., 88 [7-8] 1415-1423

List		Use Direction Keys to View Report (Press <F1> for help)			
	FILTER	Page: 2/2	User		Level

Figure 2: Sample record from the Bibliography File using FULL.RECORD on the CRT. (LIST BIB 9999 FULL.RECORD)

PAGE 1 12:23:38 22 AUG 1989
CIT.NO FULL.RECORD HLW......................

CIT.NO: 9999
REPORT.NO: NOT A REAL REPORT
AUTHORS: Rinåantat, R. P.; Černkov, A. B.
TITLE: Effect of Groundwater Compostion and Temperature on the Corrosion of Steel
SPONSOR: Department of Energy, Washington, D.C.
DATE: 08-85
CONTRACT.NO: XXXX-XXXX
PAGES: 1-395

ABSTRACT: The effect of Grande Ronde Basalt groundwater composition and temperature on the corrosion rate of American Iron and Steel Institute (AISI) 1020 steel in basalt-bentonite packing was investigated. The studies were based on a Plackett-Burman statistical screening design. For the present studies, anions (Cl^-, F^-, SO_4^{2-}, and CO_3^{2-}) and temperature were selected as the initial variables affecting corrosion. A minimum and a maximum value was chosen for each variable. The minimum value was 0 mg/L for the anions and 100°C for the temperature. The maximum values were 780, 76, 576, and 120 mg/L, respectively, for Cl^-, F^-, SO^{2-}, and CO_3^{2-}, and 250°C for the temperature.

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316L AA	562	81.5	254	36.9	59.2	69 4
Incoloy 825	799	100.6	475	68.9	36.0	95. 0

Reference: T. Znamierowska, *Pol. J. Chem.*, 88 [7-8] 1415-1423 (1979).

AVAILABILITY: Internal use only.
9999 RECORD END

1 Records Processed

Figure 1: Sample record from the Bibliography File using FULL.RECORD.LASER on a laser printer. (LIST BIB 9999 FULL.RECORD.LASER (P))