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

October 1, 1991

Dr. Charles Interrante
Materials Engineering Section
Division of High-Level Waste Management
Office of Nuclear Materials Safety and Safeguards
U.S. Nuclear Regulatory Commission
Washington, DC 20555

Dear Dr. Interrante:

Enclosed is the annual report for the project "Evaluation and Compilation of DOE Waste Package Test Data," NUREG/CR-4735, Volume 9 (FIN-A4171). If you have any questions, please call me.

Sincerely,

Anna C. Fraker

Anna C. Fraker
Metallurgist
Corrosion Group
Metallurgy Division

Distribution:
WM Docket Control Center (1-original)

Re enclosure on shelf

9110080404 911001
PDR WMRES EUSNBS
A-4171 PDR

426.1
WM-11
NH14

received with letter dtd 10/1/91

NUREG/CR-4735
Volume 9

EVALUATION AND COMPILATION OF DOE WASTE PACKAGE TEST DATA

ANNUAL REPORT
Covering the Period February 1990 through December 1990

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

with Contributing Reviewers

T. Ahn
U. Bertocci
E. Escalante
A. Fraker
C. Interrante

U.S. Department of Commerce
National Institute of Standards and Technology
Materials Science and Engineering Laboratory
Metallurgy Division
Gaithersburg, MD 20899

February 1990 through December 1990

Prepared for:

U.S. Nuclear Regulatory Commission
Office of Nuclear Materials Safety
and Safeguards
Washington, DC 20555

A-4171

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. (editor), "Evaluation and Compilation of DOE Waste Package Test Data: Biannual Report August 1988-January 1989," National Institute of Standards and Technology, August 1990.

NUREG/CR-4735, Volume 7: Interrante, C. G. (editor), "Evaluation and Compilation of DOE Waste Package Test Data: Biannual Report February 1989 to July 1990," National Institute of Standards and Technology, in press.

NUREG/CR-4735, Volume 8: Interrante, C. G. (editor), "Evaluation and Compilation of DOE Waste Package Test Data: Biannual Report August 1989 to January 1990," National Institute of Standards and Technology, in press.

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 twelve month period, February 1990 - December 1990. This includes reviews of related materials research and plans, information on the Yucca Mountain, Nevada storage 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. Three brief papers on mechanisms of stress corrosion cracking, aqueous corrosion of copper and copper alloys and mechanisms of internal failures of zirconium alloy nuclear fuel cladding are included in the Appendices.

TABLE OF CONTENTS

		Page
Abstract		i
Table of Contents		ii
Executive Summary		iii
Acknowledgements		v
1.0	Introduction	1
1.1	Background	1
1.2	Reviews and Evaluations	1
1.3	Database Activities	2
1.4	Interpretive Reports	2
2.0	DOE Activities	2
2.1	Yucca Mountain -- Location and Environment	2
3.0	NIST Activities	3
Appendix A.	Waste Package Data Review Guidelines	A-1
Appendix B.	NIST Reviews of Documents Concerning the Durability of Proposed Packages for High-Level Radioactive Wastes	B-1
Appendix C.	Interpretative Reports	C-1

EXECUTIVE SUMMARY

This is the ninth annual progress report, from the National 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 storage of radioactive high-level waste (HLW). This report contains NIST reviews, conducted over the period, February 1990 through December 31, 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 of these is a report that discusses some Mechanisms of Aqueous Localized Corrosion of Copper and its Alloys. A second report is on the topic of Mechanisms of Environmentally Induced Fracture and Their Relevance to Storage of HLW in the Tuff Environment and a third report is on the Mechanisms of Internal Corrosion of Zircaloy-2 and -4 Spent.

Seven reviews of technical reports are included in this report. Five of these reports deal with the waste package. Two of these five reviews discuss the six candidate materials (304 stainless steel, 316 stainless steel, Incoloy alloy 825, Copper C10200 (CDA 102), Aluminum bronze C61300 (CDA 613), and Copper-30Ni C71500 (CDA 715) in terms of failure mechanisms and some modeling of mechanical properties and corrosion behavior. One paper deals with low carbon steel and effects of welding, melting and processing on the microstructure and, in turn, on the mechanical properties and corrosion behavior. Another paper is about selection criteria and weighting factors relating to performance of selected topical areas including mechanical properties, corrosion resistance, fabricability, and others. The fifth document provides a set of preliminary set of acceptance specifications and data requirements for waste forms that might be stored in tuff at Yucca Mountain, Nevada. Two other documents are on the subjects of spent fuel cladding and spent fuel. The paper on spent fuel cladding states that cladding exposed to temperatures <1400 C will have less volatile fission products and be less likely to fail, and this paper recommends separation and special treatment for fuel rods with defects. The last paper is on the subject of oxidation processes for the fuel and a statistical approach is applied to develop models of the oxidation process.

There are now 1491 papers in the NIST/NRC database. 117 of the papers have been reviewed. The database uses Advanced Revelation® database management system (DBMS) 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. The database will be transferred to the NRC in Rockville, MD during 1991.

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. Ugo Bertocci, Mr. E. Escalante, and Dr. A. Fraker.

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.

Disclaimer - The use of commercial products in this work does not imply endorsement by the NIST nor does it imply that these products are the perferred ones to use.

1.0 INTRODUCTION

1.1 Background

This is the ninth progress report to the Nuclear Regulatory Commission (NRC) from the National Institute for Standards and Technology (NIST). This is the final report for contract, FIN A4171. Eight biannual progress reports were published previously (1-8). These reports deal with the NIST assessments of some of the Department of Energy (DOE) activities related to the waste package for storage 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 February 1990 through December 1990. Material and activities reported deal only with NNWSI reports or other material pertinent to storage 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 February 1989 through December 1990 are found on pages B-2 through B-36 of Appendix B.

1.3 Database Activities

The NIST/NRC database is composed of 1491 entries and uses a database management system (DBMS). The database includes 117 reviews and evaluations at this reporting period.

A paper entitled, "A Review Process and a Database for Waste Package Documents," by C. G. Interrante, C. G. Messina, and A. C. Fraker (see Appendix D) was presented as a poster at the Symposium on Nuclear Waste, Materials Research Society meeting in Boston, MA. This will be published in the symposium proceedings.

1.4 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 were prepared to provide information and references. These papers are included in Appendix C.

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

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.

3.0 NIST Activities

3.1 Reviews and Summaries

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

Seven are included in this report in Appendix B. A brief description of these reviews follows.

3.1.1 Waste Package

Halsey: 1989

A set of selection criteria has been established and assigns a weighing value to selected topical areas. These areas include mechanical properties, corrosion resistance, fabricability, cost, predictability, combatibility performance and past performance. Corrosion behavior of the material is a dominant factor.

Oversby: 1990

This 53 page document provides a preliminary set of acceptance specifications and data requirements for waste forms that might be disposed of in tuff at Yucca Mountain in Nye County, Nevada. These specifications are limited to the present level of knowledge of this site. Results of ongoing research additional topics need to be included.

Beavers and Thompson: 1990

A review of the literature on the corrosion in a tuff environment of six candidate materials, 304 stainless steel, 316 stainless steel, Incoloy Alloy 825, C10200 (pure copper), C61300 (aluminum bronze) and C71500 (copper-30 nickel), is given. The environmental parameters considered were thermal effects, radiation effects, and microbiological effects. Austenitic steels (types 304 and 316) were found to be potentially susceptible to localized corrosion such as pitting or stress corrosion cracking. The copper base alloys were found to undergo moderate rates of general corrosion and also localized corrosion.

Frost, Muth, and Liby: 1990

Experimental work and information from the literature are used to evaluate the effects of manufacturing variables on the performance of the overpack of various proposed DOE waste packages. Microstructures of low carbon steel castings and weldments are discussed in terms of melting and process

variables. The mechanical properties and corrosion behavior of the materials as related to different microstructures is discussed.

Farmer and McCright: 1989

Austenitic (304 stainless steel, 316 stainless steel and Incoloy 825) and copper-base alloys are candidate materials for waste package containers. This paper discusses results of a literature review of mechanisms and models related to failure by stress corrosion cracking and other localized corrosion. The models consider various aspects of pitting, cracking, fracture and crevice corrosion. Information is provided regarding needed models of specific processes not found in the literature review. The effects of radioanalysis products should be added to this. The paper states that additional laboratory tests are required to quantitatively determine model parameters.

Spent Fuel

Woodley: 1983

Data on light water reactor spent fuel are provided for use in establishing repository acceptance criteria, spent fuel handling procedures and package design requirements. Intact cladding will provide a barrier to radionuclide release. Fuel rods that experienced only moderate temperatures (<1400 C) in service will have less of volatile fission products that potentially could lead to cladding breach. Assemblies known to have defect fuel rods could be retained in pool storage and tagged for special handling.

Stout and Shaw: 1989

"A statistical approach has been developed to represent grain boundary and grain volume oxidation processes for spent fuel from UO_2 to U_3O_7."

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.

UNCERTAINTIES IN DATA

Included here are error bars and uncertainties in the data as stated by the author. This also includes qualitative statements by the author on the reliability 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."

DEFICIENCIES/LIMITATIONS IN DATABASE

Statements by the author on the applicability 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.

CONCLUSIONS

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

COMMENTS OF REVIEWER

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.

RELATED HLW REPORTS

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.

APPLICABILITY OF DATA TO LICENSING -- 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 Listed licensing Issue 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 Reviews of Documents Concerning the Durability of Proposed Packages for High-Level Radioactive Waste

Page

Halsey, W. G.,"Selection Criteria for Container Materials at the Proposed Yucca Mountain High Level Nuclear Waste Repository," UCRL-102285, November 1989 . . . . . B-2

Oversby, V. M."The Nevada Nuclear Waste Storage Investigation Project Interim Acceptance Specifications for Defense Waste Processing Facility and West Valley Demonstration Project Waste Forms and Canisterized," UCID-20165, August 1984 . . . . . B-5

Beavers, J. A. and Thompson, N. G., "Environmental Effects on Corrosion in the Tuff Repository," NUREG/CR-5435, February 1990 . . . . . B-10

Frost, R. H., Muth, T. R., and Liby, A. L., "Effects of Manufacturing Variables on Performance of High-Level Waste Low Carbon Steel Containers," NUREG/CR-5001, April 1990 . . . . . B-14

Woodley, R. E., "The Characteristics of Spent LWR Fuel Relevant to Its Storage in Geologic Repositories," HEDL-TME 83-28, UC-70, October 1983 . . . . . B-23

Stout, R. B. and Shaw, H. F., "Statistical Model for Grain Boundary and Grain Volume Oxidation Kinetics in UO_2 Spent Fuel," UCRL-100859, September, 1989 . . . . . B-27

Farmer, J. C. and McCright, R. D., "Review of Models Relevant to the Prediction of Performance of High-Level Radioactive-Waste Disposal Containers," UCRL-100172, November 1989 . . . . . B-32

WASTE PACKAGE DATA REVIEW

DATA SOURCE

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

Halsey, W. G.
"Selection Criteria for Container Materials at the Proposed Yucca Mountain High Level Nuclear Waste Repository"
UCRL-102285, November 1989.

(b) Organization Producing Data

Lawrence Livermore National Laboratory, Livermore, CA.

DATE REVIEWED: 9/7/90

PURPOSE

This paper describes the selection process for the waste container material.

KEYWORDS

Selection criteria, container materials, Yucca Mountain, geological repository, service environment, material performance, fabricability, cost, nuclear waste storage.

CONTENTS

7 pages of text and 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

A draft set of selection criteria have been developed for selecting a container material to isolate high-level nuclear waste at a proposed repository at Yucca Mountain. There are currently 34 separate parameters considered, and it is expected that the criteria will evolve as additional information is obtained.

COMMENTS OF REVIEWER

This is a brief description of the selection criteria for the waste canister material. The process considers seven parameters of mechanical, chemical, predictability, compatibility performance, and fabricability, cost and past performance.

The reviewer agrees that Chemical Performance (Corrosion) should have the highest weighting factor (30). However, a factor of 5 for Previous Experience is too low. The reviewer believes that Previous Experience should be given more weight because it is on this parameter that future performance will be judged whether through modeling or other means. Granted that our Previous Experience with materials is relatively short term, compared to the 1000 years lifetime necessary for the container. However, short term data are all that we can hope to use in modeling calculations for long term prediction. The factors of Previous Experience and Predictability of Performance should have equal weighting, and both should have a weight factor of 16.

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 design of the waste package container accomodate all potential natural water package-induced conditions?

(b) New Licensing Issues

(c) General Comments on Licensing

AUTHOR'S ABSTRACT

A geological repository has been proposed for the permanent disposal of the nation's high level nuclear waste at Yucca Mountain in the Nevada desert. The containers for this waste must remain intact for the unprecedented service lifetime of 1000 years. A combination of engineering, regulatory, and licensing

requirements complicate the container material selection. In parallel to gathering information regarding the Yucca Mountain service environment and material performance data, a set of selection criteria have been established which compare candidate materials to the performance requirements, and allow a quantitative comparison of candidates. These criteria assign relative weighting to varied topic areas such as mechanical properties, corrosion resistance, fabricability, and cost. Considering the long service life of the waste containers, it is not surprising that the corrosion behavior of the material is a dominant factor.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

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

Oversby, V. M.
"The Nevada Nuclear Waste Storage Investigation Project Interim Acceptance Specifications for Defense Waste Processing Facility and West Valley Demonstration Project Waste Forms and Canisterized" UCID-20165, August 1984.

(b) Organization Producing Data

Lawrence Livermore National Laboratory, Livermore, CA.

DATE REVIEWED: 9/6/90

PURPOSE

The purpose of this document is to provide a set of acceptance specifications and data requirements for waste forms that might be disposed of in a repository in tuff at Yucca Mountain in Nye County, Nevada. These specifications are preliminary in nature and are limited by the present level of knowledge about the Yucca Mountain site. As more information becomes available about the geology and hydrology of the site, particularly following construction of the Exploratory Shaft, it will be necessary to revise these acceptance specifications. The draft specifications provided in this document can serve as guidance for waste form producers in the design and operation requirements for their production facilities, and will be used as input for the preliminary waste package and repository design stage.

KEYWORDS

Literature review, Yucca Mountain, tuff, stainless steel, 304L stainless steel, glass (West Valley reference glass), glass (defense waste reference glass), commercial high-level waste (CHLW), defense high-level waste (DHLW), density, elongation, heat capacity, tensile strength, thermal conductivity, thermal expansion, yield strength.

CONTENTS

This 53-page report consists of the following content:

CONTENTS	NUMBER OF PAGES
1. Background, Program Status and Purpose	3
2. Scope and Classification	2
3. Applicable Documents	3
4. Waste Form Specification	20
5. Quality Assurance Program	4
6. Preparation for Shipping	2
7. Notes	5
8. Data Submitted Requirements	1
Appendix A. Basis and Rationale for Product Specifications and Data Requirements	12
References (16)	2

TEST CONDITIONS

Materials: borosilicate glass from Defense and West Valley
Specimen preparation: appropriate legal designations of waste package

Environment: tuff (Yucca Mountain)

UNCERTAINTIES IN DATA

- "The accuracy of the estimate shall be within + or - 10 relative percent for the per canister inventory determined during production of the waste forms."
- "Accuracy of the measurements must be sufficient to ensure that the fissile nuclide content is below the stated limit at the 99 percent level of confidence."
- "The density of the finished waste form with an accuracy of 10 percent must be supplied to NNWSI."
- "The nitric acid solution must be analyzed for all elements present in amounts greater than 0.01 percent of the initial glass sample weight."
- Plus minus 5 percent: for thermal conductivity, diffusivity, heat capacity, heat generation rates and the coefficient of thermal expansion.
- "Accuracy of the measurements" (canister) "will be plus or minus 20 centigrade degrees."
- "Fe, C, Mn, P, S, Si, Cr, Ni and N, and have an accuracy of plus or minus 2 relative percent for elements present in greater than one percent abundance and plus or minus 10 relative percent for elements present in less than one percent abundance."
- "The required accuracy" for thermal properties data "is plus or minus 5 percent."

- "The limit of ~5 relative percent was selected as a reasonable limit of variation in chemical composition of finished product to allow prediction of product performance based on prior laboratory testing of waste forms."

DEFICIENCIES/LIMITATIONS IN DATABASE

The numerical limits given in the specifications are in some cases controlled by existing regulatory requirements; those limits will change only if the relevant regulations change. In other cases, the numerical limits are based on our current state of knowledge concerning the environment in which the waste form will be placed and the conceptual designs for the repository and the waste package. Those limits will be subject to alteration as our state of knowledge improves and becomes more detailed, and as the designs for the repository and waste package are further developed.

CONCLUSIONS OF AUTHOR

None given.

COMMENTS OF REVIEWERS

This document presents the waste acceptance specifications as the first stage of the NNWSI effort to establish specifications for the acceptance of waste forms for disposal at a nuclear waste repository in Yucca Mountain tuff. The following is the reviewers' complementary view for authors' future extended revision of this work.

1. The specifications quoted here should address premises on which such quoted specifications are valid or legitimate to be used. Most ASTM standards are based on short-term laboratory test results which are inappropriate for the long-term performance of waste packages. Also, the results of currently on-going research programs need to be addressed. For instance, the solubility limits of borosilicate glasses have not been proven to meet 10 CFR 60 though this report suggests they have been.

2. This report consists of many subsections covering a wide range of chemical and physical properties of waste forms. However, the reviewers would also like the following topics included:

- radiation effects
- glass fractures or other microstructural variations
- radioactivity specifications other than neutrons
- corrosion of canisters
- the ratio of glass surface area to solution volume
- Monitored Retrievable Storage consideration

3. Other minor comments:

- Is there any reason why non-canisterized glasses were considered separately?
- Should heat tailoring be considered for thermal specifications by appropriate design of waste packages?

RELATED HLW REPORTS

1. 10 CFR 20, 1979, Standards for Protection Against Radiation, U.S. Nuclear Regulatory Commission.

2. 10 CFR 50, Appendix B, 1978, Quality Assurance Criteria for Nuclear Power Plant and Fuel Reprocessing Plants, U.S. Nuclear Regulatory Commission.

3. 10 CFR 60, 1983, Disposal of High Level Radioactive Wastes in Geologic Repositories, U.S. Nuclear Regulatory Commission.

4. 10 CFR 71, 1979, Packaging of Radioactive Material for Transport and Transportation of Radioactive Material under Certain Conditions, U.S. Nuclear Regulatory Commission.

5. 30 CFR 57, 1982, Safety and Health Standards-Metal and Nonmetallic Underground Mines, U.S. Department of Labor.

6. 40 CFR 191, 1982, Environment Standards for Management and Disposal of Spent Nuclear Fuel, High-Level Transuranic Radioactive Wastes, Proposed Rule, U.S. Environmental Protection Agency.

7. 49 CFR 173, 1982, Shippers-General Requirements for Shipments and Packagings, U.S. Department of Transportation.

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

(a) Relationship to Waste Package Performance Issues Already Identified

2.3.1 What are the physical, chemical, and mechanical properties of the waste form, how do those properties of the waste form change with time, and how will such changes alter the ability of the waste form to contribute to the overall performance of the repository system or impact the performance of other barrier materials and properties of the site?

(b) New Licensing Issues

(c) General Comments on Licensing

ABSTRACT

None given.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

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

Beavers, J. A. and Thompson, N. G.
"Environmental Effects on Corrosion in the Tuff Repository
NUREG/CR-5435, February 1990.

(b) Organization Producing Data

Cortest Columbus, Inc., Columbus, OH.

DATE REVIEWED: 7/11/90; Revised 11/23/90.

PURPOSE

Review of extant literature on the corrosion of candidate materials in a tuff environment.

KEYWORDS

Literature review, general corrosion, pitting, corrosion, electrochemical, irradiation-corrosion test, slow-strain-rate test (SSR), tensile testing, air, J-13 water, tuff, gamma radiation field, copper base, stainless steel, 304 stainless steel, 316L stainless steel, 317L stainless steel, 321 stainless steel, 347 stainless steel, Incoloy Alloy 825, copper C10200 (CDA102), aluminum bronze C61300 (CDA613), copper-30Ni C71500 (CDA715), J-13 steam, corrosion (crevice), corrosion (intergranular), corrosion (irradiation), corrosion (local), corrosion (microbial), corrosion (pitting), corrosion (stress cracking) SCC, cracking (environmentally assisted), cracking (stress corrosion), SCC, passivity, sensitization.

CONTENTS

116 pages, 5 pages of appendices, 44 figures, 44 tables, and 92 references.

AMOUNT OF DATA

No new data given.

TEST CONDITIONS

Literature review, not applicable.

UNCERTAINTIES IN DATA

Literature review, not applicable.

DEFICIENCIES/LIMITATIONS IN DATABASE

Literature review, not applicable.

CONCLUSIONS OF AUTHOR

"This report summarizes the results of a survey of the literature performed under Task 1 of the program. The purpose of Task 1 is to compile repository site-specific data that are necessary to develop and update the work plan, to provide continuity between the individual tasks of the project and to coordinate the project with other NRC projects."

"The focus of the survey is the influence of environmental variables on the corrosion behavior of candidate materials for the Tuff repository. Two classes of alloys have been evaluated by DOE for use as a container material in the Tuff repository; Fe-Cr-Ni alloys and copper-base alloys. The primary candidate Fe-Cr-Ni alloys are Type 304L stainless steel, Type 316L stainless steel and Incoloy Alloy 825. The primary candidate copper-base alloys are CDA 102 (pure copper), CDA 613 (aluminum bronze), and CDA 715 (copper-30 nickel). The environmental parameters considered in this report are thermal effects, radiation effects and microbiological effects."

"The Fe-Cr-Ni alloys were found to be highly resistant to general corrosion under anticipated repository conditions, but the austenitic stainless steels (Types 304 and 316 stainless steels) were found to be potentially susceptible to localized forms of corrosion. For this class of alloys, propagation rates for localized corrosion (pitting and crevice corrosion) are probably too high to provide adequate container life if it initiates."

"The most serious problems for the austenitic stainless steels is stress corrosion cracking (SCC). Transgranular stress corrosion cracking (TSCC) was observed for Type 304L stainless steel under optimum metallurgical conditions in the presence of a radiation field. Incoloy Alloy 825 would be expected to be more resistant to SCC as a result of its higher nickel content and to localized corrosion as a result of its higher molybdenum content."

"The copper base alloys were found to undergo moderate rates of general corrosion under anticipated repository conditions. While linear extrapolation of the reported corrosion rates estimated unacceptable metal loss for 300 - 1000 years, corrosion rates decreased with time and thus, it is not clear whether these alloys have adequate resistance to general corrosion for use as a container material."

"As is the case for the Fe-Cr-Ni alloys, the copper base alloys may experience localized corrosion failures in the tuff repository. The copper-base alloys underwent pitting and crevice corrosion in studies in J-13 well water in the presence of a radiation field. Evidence of localized corrosion was also found in potentiodynamic polarization studies. Thus, for the copper-base alloys, a critical issue is whether rates of pit propagation are acceptable for the long-term performance of the waste containers."

"While no SCC of the copper-base alloys was reported in any of the studies performed to date under simulated repository conditions, a number of potential cracking agents may be present in the repository, such as ammonia and nitrites. Thus, SCC of copper-base alloys cannot be ruled out."

"Microbiological induced corrosion (MIC) of both Fe-Cr-Ni alloys and copper-base alloys is a potential problem after the thermal period when radiation levels are low and temperatures fall below boiling. MIC is a serious problem in many industries in surface water, well water, and underground environments. Thus, MIC may play a role in the long-term release rate of the repository."

COMMENTS OF REVIEWER

This is a review of the work so far performed by DOE contractors on various aspects of corrosion behavior of the materials proposed as containers for HLW. The content of the review relating to the candidate materials, 304 stainless steel, 316 stainless steel, Incoloy Alloy 825, C10200 (pure copper), C61300 (aluminum bronze), and C71500 (copper-30 nickel), is given in the section of this review entitled "Conclusions of the Author". The authors of the report also discuss problems and questions that need to be answered in this conclusions section. There is no discussion of why these classes of candidate alloys were selected, but that was not the subject of the review.

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) General Comments on 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 techniques, such as electrochemical and slow strain rate mechanical test techniques, to examine a wide range of possible failure modes. 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.

This report summarizes the results of a literature survey performed under Task 1 of the program. The survey focuses on the influence of environmental variables on the corrosion behavior of candidate container materials for the tuff repository. Environmental variables considered include: radiation, thermal and microbial effects.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

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

Frost, R. H., Muth, T. R., and Liby, A. L.
"Effects of Manufacturing Variables on Performance of High-Level Waste Low Carbon Steel Containers"
NUREG/CR-5001, April 1990.

(b) Organization Producing Data

Manufacturing Sciences Corporation

DATE REVIEWED: 7/23/90; Revised 11/23/90.

PURPOSE

"The research described here is directed toward evaluation of the effects of manufacturing variables on the performance of the overpack component of various proposed DOE waste package designs."

"The work presented here includes experimentation as well as interpretation of literature particularly significant to the manufacture of low carbon steel overpacks by casting and welding. The focus is on the microstructure of low carbon steel castings and weldments, and on how casting and welding process variables influence that microstructure and the resulting long term performance of high level waste overpacks in the repository environment."

"The experimental objective of the casting portion of the research program was to investigate the influence of melting and casting process variables on the microstructure of ASTM A-216 grade WCA carbon steel castings.

4.4 Quality Assurance

"The basic purpose of such qualification testing is determination of a required minimum skill level."

4.5 Experimental Research

1. Characterize microstructures that will result from material and process combinations that DOE will likely use.

2. Explore process limits applicable to practical fabrication of cast steel overpacks.

3. Investigate changes in microstructure that may arise from repository thermal conditions.

CONTENTS

This 116-page report consists of an abstract, a table of contents, a list of 37 figures, a list of 11 tables, an introduction and the following content.

CONTENT	NUMBER OF PAGES
Survey of Literature and Industrial Practice	50
Experimental Research	49
Results and Conclusions	3
References (193)	12

TEST CONDITIONS

Materials:

- "The reference material of construction for the metal overpack is a cast low carbon steel conforming to ASTM A-216 Grade WCA with alloy chemistry modified to AISI Type 1018"
- EN201, AISI 1008, FeMn, FeSi, FeS_2, Al, FeTi, (Heat Number Alloy A, Alloy B, Alloy C, NRC-5, NRC-12, NRC-14, NRC-15, 1, 2, 3, 4)

Specimen preparation:

- "The waste package typically consists of the waste form sealed in a metal canister, a metal overpack and packing material to fill the annular space between the overpack and the surrounding host rock. The various conceptual designs describe the metal overpack as a cast carbon steel vessel with end caps attached by welding."
- "It is a cylinder 338 cm long, 64 cm inside diameter, and 816 cm wall thickness, and with end caps 16.7 cm thick. It is expected that the cylindrical body will be centrifugally cast, while the heads will be statically cast. The bottom end cap will be joined to the body as a shop assembly operation using the submerged arc welding process. The top end cap will be remotely welded on as a hot cell operation at the repository. Narrow gap gas metal arc welding will probably be used for the final closure to avoid problems of flux handling and removal in the hot cell environment."
- "Low heat input welds such as gas metal arc welds are expected to cool at a rate of 5000 to 10000 C per minute."
- "Submerged arc welds and gas metal arc welds were investigated using consumables and procedures."
- "The steel melting practice consisted of melting bar stock and electrolytic iron to produce an overoxidized condition at melt down."

Environment:

- Basalt Waste Isolation Project, Nevada Nuclear Waste Storage Investigations Project, Office of Nuclear Waste Isolation
- "Corrosion ions can be classified as aggressive ions such as Cl-, SO_4^{-2}, and F-, or as passivating ions such as HCO_3^- and $CO3^{-2}$. The concentration of these ions varied for the various sites and indicated that the pH could vary from 5.0 to 9.8."

UNCERTAINTIES IN DATA

- "The solidification time may be as long as 30 hours."
- "The solidification time will yield a coarse solidification structure with secondary dendrite arm spacing of around 1000 micrometers."
- "For large chunky steel castings it can be expected that 40 to 50 percent of the total tonnage cast will be gates, runners and risers."
- "The shake out times for large pit molded castings can be as long as several weeks."
- "The Watertown method uses a heavy cast iron chill mold which is coated with a refractory mold wash and spun at 1300 to 2000 rpm."
- "The metal is forced out against the mold with a force of up to 200 g's which provides an increase in the feeding force of two orders of magnitude over static castings."
- "Mild steels with carbon contents in the range of 0.1 to 0.2%C will consist of ferrite plus pearlite."
- "Aluminum at low levels of around 0.05 wt.% is sometimes added for deoxidation."
- "All aluminum kill of 0.5 to 0.07 wt.% is charged to the stream after about one third of the heat has been tapped."
- "Electric arc furnaces are designed to produce heats ranging from one ton to as much as 300 tons."
- "A maximum of 0.05 to 0.07 wt.% aluminum should be used for deoxidation."
- "It is estimated that use of the centrifugal casting process to produce the overpack container castings will minimize or bypass many of the above defects."
- "The extent of microsegregation may be estimated by the Scheil Equation or 'Non-Equilibrium Lever Rule,' which is based on a solute balance at the solid/liquid interface, and on the assumptions of: equilibrium at the interface, complete diffusion in the liquid, and no diffusion in the solid."
- "The arc length is held approximately constant, and the welding current is controlled by the electrode velocity."
- "The welding current was found to be approximately independent of the voltage and a linear function of the electrode velocity."
- "Typical welding flux viscosities at 1400 C are of the range of 2-7 poise."

- "The oxygen of wrought steel to be below 100 ppm oxygen, the very lowest weld metal oxygen levels for flux related welding processes arc in the range of 200-300 ppm."
- "Chemical composition of the target alloy element and tramp element contents: S (0.01/0.02%) and P (0.02/0.03%)."
- "Mn added in solution (0.04 ~ 0.4, 0.7 ~ 0.6 and 0.9 ~ 0.8)."
- "It was estimated that the thermal experience would include temperatures in the range of 200 to 300 C for periods of up to 50 years."
- "The cooling rate of a six inch diameter casting cooled from a normalizing temperature of 900 C is approximately 10 C per minute."
- "Two 5/64 inch diameter thermocouple holes were drilled in each weld plate approximately six inches apart as depicted in the figure."
- The heat affected zone in this investigation is approximately 0.125 inch wide."
- "The thermocouple reliability as determined from the ASTM manual on the use of thermocouples was ~ 3.75 C between 538 C and 1482 C. This gives a total cumulative error of ~ 5.50 C with just the system configuration."
- "The combination of the errors previously described, and those produced by the amplification circuitry, gave a possible ~ 5.50 C error in the temperature measurement."
- "Arc efficiency: 0.9 to 0.99 for submerged arc welds and 0.7 to 0.8 for gas metal arc welds."

DEFICIENCIES/LIMITATIONS IN DATABASE

- "Heat transport behavior can be modeled based on the assumption that the heat choke is in the mold and there is little resistance to heat transport in the solidified metal or at the mold/metal interface."
- Chvorinov's rule "is based on the assumptions of uni-directional heat transport, a semi-infinite mold, and the assumption that the heat choke is in the sand rather than in the metal or at the mold-metal interface."
- "It is assumed that perfect thermal contact exists between the mold and the metal, and that the temperature at the mold-metal interface is constant."
- "Review of applicable quality assurance methods has therefore been generalized and are upon assumptions about probable process and material generalized and based upon assumptIons about probable process and material choices."

4.1 Manufacturing Considerations

"Manufacturing considerations were" "limited to those approaches that use casting as the starting point for making the overpack."

4.2 Metallurgical Considerations

"Prediction of corrosion behavior based upon manufacturing history is beyond the scope of this study."

4.3 Defects from Manufacturing

None.

4.4 Quality Assurance

"The manufacture of high level waste overpacks will be done under codes and standards that govern and guide the materials, processes, products, services, and systems used in making the ffnal product. Such codes and standards do not presently exist for direct application to high level waste containers."

4.5 Experimental Research

"Correlation of long term corrosion behavior of mild steel castings and weldments with relatively subtle variations in microstructure remains beyond present understanding".

CONCLUSIONS OF THE AUTHOR

4.1 Manufacturing Considerations

"Preliminary consideration of wrought processing techniques such as forging, piercing, and ring rolling lead to the conclusion that such techniques would probably not be cost competitive with casting."

"Centrifugal casting clearly appears to be the most economical and technically favorable method of making thick-walled steel cylinders of the dimensions applicable to overpacks. It is likely that the ends of the cast steel cylinder would be machined in preparation for attaching end caps by welding. The bottom end would be welded on in the shop where the cylindrical body was made using a high deposition rate welding process such as submerged arc welding."

4.2 Metallurgical Considerations

"Behavior of cast and welded steel overpacks in the repository environment may be determined in part by the choice of material chemistry and manufacturing process conditions. Thermal histories developed during casting, welding, and heat treatment will be reflected as a microstructural signature in the fabricated overpack. Effects of alloy chemistry, solidification processing, and solid state phase transformations on final microstructure of the cast and welded overpack has been examined in detail in chapter 2 of this report."

"The most likely failure mode for steel overpacks is generally felt to be corrosion failure, particularly accelerated forms of corrosion such as pitting of stress corrosion cracking. Failure from such localized or accelerated forms of corrosion is not predictable with certainty for any combination of material conditions, repository environment, and exposure time."

"Radioactive decay of waste may under some repository conditions give rise to temperatures in the overpack that are sufficiently high to cause microstructural changes. Areas of high residual stress and non-equilibrium microstructures such as the final closure weld would be most susceptible to such changes."

4.3 Defects from Manufacturing

"Casting and welding processes used to manufacture overpacks may be the source of defects that can adversely affect the life of the overpack during repository storage. Defects such as porosity, cracks, undercutting, and lack of fusion may shorten life by providing a shorter and more active corrosion path through the defect area. Defects of a chemical nature such as micro and macro segregation also may lead to premature failure due to localized corrosion related to local variations in alloy chemistry."

4.4 Quality Assurance

"The manufacture of high level waste overpacks will be done under codes and standards that govern and guide the materials, processes, products, services, and systems used in making the final product. Such codes and standards do not presently exist for direct application to high level waste containers. The ASME Boiler and Pressure Code has been cited as that existing document that is most nearly applicable. It is likely that some extension of this code, supplemented by internal government standards, will eventually be adopted for application to high level waste containers."

"Various exisiting codes require the qualification and certification of welding procedures and operators who perform the wleding. Likewise, weldments are subject to inspection by qualified personnnel using specified procedures. Exisiting codes do not attempt to regulate quality of castings by qualification of manufacturing personnel or by control of manufacturing methods. Cast products are typically covered by product specifications that seek to define soundness, chemical and metallurgical chacteristics, mechanical properties, and dimensional characteristcs. It is likely tha this situation, procedural contro for welding and product specification for casting, will carry over into codes that govern overpack manufacture".

"Physical inspection of the product is the generally accepted method of determing the compliance of a manufactured item with

codes, standards, or specifications. Body and lid components for cast steel overpacks will be inspected at the place of manufacture using standard. well established methods of nondestructive evaluation such as radiography, ultrasonics, liquid penetrant, and visual inspection. The final closure weld made after waste loading will present a challenge to adequate inspection because the operations must be done remotely. Methods such as ultrasonic inspection, visual inspection through remote video or fiber optics, and continuous process monitoring using acoustic emission are applicable."

4.5 Experimental Research

Representative microstructures were generated using three alloy composition ranges of the ASTM A-216, Grade WCA specification for carbon steel castings suitable for welding. Chemical composition of the three alloy ranges were chosen to vary the hardenability, oxygen content, and the cleanliness in terms of nonmetallic inclusions. Solidification rates were controlled under laboratory conditions to simulate microstructures attainable both for centrifugal and static casting. Weldments were made using the submerged arc and gas metal arc processes, the two processes felt to be the most likely candidates for end cap welding.

"Examination of various cast and welded specimens showed a wide variation of possible microstructures due to variations in alloy chemistry and thermal history. The manganese to oxygen ratio and sulfur content dramatically affect the austenite transformation morphology by influencing the level of nonmentallic inclusions that serve as nucleation sites for formation of acicular ferrite. Ferrite morphology is of primary interest in determining mechanical properties of mild steel weldments. The effect of ferrite morphology on fracture toughness has been well documented. It is likely that the microstructural variations documented by this project will be important in determining the long term behavior of these steels under repository conditions."

COMMENTS OF REVIEWER

1. Literature Review

This report is (1) a compilation of the existing data on manufacturing processes of low carbon steel which earlier was a candidate material for high-level waste packaging. The report emphasizes the process variables in casting and welding, and the subsequent materials performance in mechanical and corrosion properties in terms of micro or macro structural variation. Certainly, this is a valuable work for the manufacturing practice of the design of containers. Also, the authors present some experimental results performed in some research topics.

As addressed in this report, the authors should have a strong objective and direction in assessing the effects of process variables on the long-term performance of this material. What would be the consequences of microstructural alteration on strength, toughness, creep resistance of these materials viewed as a long-term performance in relation to 10 CFR 60. Figure 5 (effect of corrosion rates versus forged and cast steels) is the result from such an effort. With the known data, the allowed tolerance of process variables can be suggested. The selection of the best process should be postponed until this evaluation of long-term performance is completed.

Other minor comments are:

- In the rate-determining step of any reaction kinetics, the interface reaction kinetics also involve diffusion kinetics. Therefore, the long-term performance of general corrosion requires the knowledge of the diffusion-limited kinetics. However, caution should be given to the intermittent oxide spallation which initiates a new kinetics with the exposed pristine surfaces.
- Equation (1) is used mostly to describe the short-term kinetics of the corrosion process. When $t > x/K_2$, the equation is no longer valid, which means the equation may not be applicable to the long-term corrosion. The authors need to address this situation by a carefull calculation of the order of magnitude of the time span.
- Pitting or other localized corrosion generally is accelerated in terms of local cell formation. However, with certain alloying elements, it is possible for repassivation to take place with the dissolved ions of such alloying elements. There is much information from generic corrosion literature in better defined systems. The addressed HCO_3^- $/CO_3^{-2}$ effect on passivation is a very valuable review for this purpose.
- In the solification, it is suggested for the authors provide methods to evaluate defects generated more quantitatively and determine the tolerance limit for these defects.
- In heat transfer, a more critical assessment may be necessary to select the appropriate heat transfer equations based on the consideration of the resulting microstructures of the materials.

2. Experiment

- The compositional variation from heat to heat appears to be significant, and this may not be acceptable.
- There were no data on the mechanical or corrosion performance for various microstructures. This should be a future task.
- In the study of thermal conductivity, the consequent microstructures should be considered for the ojectives to select the proper thermal conduction.

- It is necessary to identify all metasable phases for future studies to determine any long-term alteration of these phases.

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

(a) Relationship to Waste Package Performance Issues Already Identified

2.5 How does the waste package design address releases of radioactive materials to unrestricted areas within the limits specified in 10 CFR 20?

(b) New Licensing Issues

(c) General Comments

AUTHOR'S ABSTRACT

Analytical and experimental research was performed to determine the effect of manufacturing variables on the performance of cast steel overpacks. The work examines the influence of casting and welding processing variables on the long-term performance of low carbon steel overpacks in the repository environments.

Centrifugal casting was indicated to be the most economical and technically favorable manufacturing approach for cast steel overpacks. A bottom would be welded into a hollow crylinder to make the container and final closure welding to secure the lid in place would be done at the respository. Effects of alloy chemistry solidification processing, and solid state phase transformations on final microstructure of the cast and welded overpack has been examined in detail in this report.

Codes and standards governing the manufacture of overpacks do not presently exist. An extension of the ASME boiler and pressure vessel code supplemented by government standards could be adopted for the purpose. Standard, well-established methods of non-destructive evaluation are adequate for the purpose of identifying likely manufacturing defects.

Experimental work focused on material and process combinations to be used in manufacture of overpacks. Practical process limits were explored and changes in microstructure due to repository thermal conditions were investigated.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

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

Woodley, R. E.
"The Characteristics of Spent LWR Fuel Relevant to Its Storage in Geologic Repositories"
HEDL-TME 83-28, UC-70, October 1983.

(b) Organization Producing Data

Hanford Engineering Development Laboratory, Richland, WA

DATE REVIEWED: 10/4/90

PURPOSE

"The present report provides data, where available, on the pertinent characteristics of spent LWR fuel." "The information will be used to establish repository acceptance criteria, spent fuel handling procedures, and package design requirements."

CONTENTS

This 57-page report consists of an abstract, an acknowledgment, a summary, an introduction, 16 figures, 7 tables, a conclusion and the following content:

CONTENTS	NUMBER OF PAGES
Spent Fuel Characteristics, A. General	17
Spent Fuel Characteristics, B. Physical	7
Spent Fuel Characteristics, C. Chemical	14
References (42)	4
Appendix. Zircaloy Corrosion	3

TEST CONDITIONS

Materials: - LWR spent fuel (UO_2 pellets)
- Zircaloy tube

Specimen preparation:

- 7 x 7, 8 x 8, 14 x 14, 15 x 15, 16 x 16, 17 x 17, fuel assemblies - 49 and 63 fuel rods within a given assembly
- chamfered pellets
- LWR fuel burnup: 50,000 MWd/MTU for PWR 40,000 MWd/MTU for BWR

- Table 1: Summary of general electric BWR fuel designs
- Table 2: Mechanical design parameters of PWR fuel assemblies
- Table 3: Mechanical design parameters of BWR fuel assemblies
- Table 4: Typical linear power values for various LWRs
- Table 5: Variation in the average linear power with the number of fuel Rods/Fuel assembly

Environment:

- helium encapsulation of the pressure from 1 to 3 atom : BWR
- 30 atm internal helium pressure : PWR

UNCERTAINTIES IN DATA

- The internal helium pressure in PWR fuel assemblies is about 30 atm.
- "It is estimated that about 3% of the total fuel assemblies in storage contain fuel rods clad in stainless steel."
- The lower bound of LWR fuel failure levels is 0.01% to 0.02%.
- "During the soak period, it is assumed that fission gases will be released from any defective BWR rods because of the increase in fuel rod temperature from decay heat."
- "There are ~33,000 LWR fuel assemblies in pool storage as of the end of 1982."
- LWR Zircaloy degradation:
  - no attack in shipping port reactor for nearly 21 years
  - nozzle separation for Prairie Island PWR fuel less than six years
- LWR cladding failure: 0.01 ~ 0.02%
  BWR fuel rod failure: ≤0.002%
  LWR fuel rod failure: below 0.01%
- LWR burnup: about 8000 MWd/MTU, about 24,000 MWd/MTU (1978), about 22,900 MWd/MTU (1982)
  PWR burnup: about 5000 and 38,000 MWd/MTU
- Figure 12 (average burnup versus year for LWR fuels) shows uncertainties error bars
- Fission gas release:
  - ~236 cm^3 STP/initial kg U/at. % burnup.
  - about 20% of the fission gas formed resides in intergranular bubbles at ≤1400 C
  - ≤ 1.5% release after an extended burnup
- The temperature anticipated in spent fuel repositories: about 400 C

DEFICIENCIES/LIMITATIONS IN DATABASE

- "The identification of individual failures can be accomplished only when individual fuel rods can be removed from the assembly and shipped separately. This is seldom done."

- "Unfortunately, fuel temperatures are ordinarily only imprecisely known."

CONCLUSIONS OF AUTHOR

Certain characteristics of spent LWR fuel may affect its storage in a geologic repository. The numbers and dimensions of LWR fuel assemblies will affect their handling and storage in a logistical sense, but will exert little influence on their behavior with regard to interactions with the repository environment. In the latter category are properties such as cladding integrity and conditions within the fuel rods established during their reactor residence. The intact cladding of the great majority of the fuel rods will provide a barrier to radionuclide release. Even for the small percentage of fuel rods with failed cladding, most defects are very small and, consequently, the cladding as well as the fuel itself will still provide a significant measure of containment for the fission products and higher actinides of particular concern.

Fuel burnup determines its inventory of higher actinides and fission products. The former tend to be more concentrated on the fuel pellet circumference where their production is greatest, but their solution as oxides in the urania lattice deters their movement. The location of the more volatile fission products, such as cesium, will depend on the fuel temperature during irradiation.

Temperatures in excess of 1400 C promote the release of volatile fission products into the fuel-cladding gap, where they are available for immediate release should a cladding breach occur. The movement of fission products into the gap parallels the release of fission gases into the fuel rod free volume. In the absence of a detailed operating history, if warranted, a nondestructive measurement of the concentration of fission gases in the fuel rod plenum would provide a reasonable measure of fission product redistribution.

Based on the foregoing consideration, the ideal fuel rod (or assembly of rods) for repository storage would be one with intact cladding that had experienced only moderate temperatures ($T < 1400$ C) during its reactor residence. It appears from the available data that the majority of fuel rods meet these criteria. The remaining fuel assemblies known to contain defected fuel rods could be retained in pool storage and tagged either for early reprocessing or for special handling at the repository depending upon the options available in a timely manner.

COMMENTS OF REVIEWER

This report is a general data tabulation on the pertinent characteristics of spent fuel to establish repository acceptance

criteria, spent fuel handling procedures, and package design requirements. The following issues may be added or explored further in future reviews to complement this report.

1. The radionuclides redistribution due to transmutation of non-radioactive impurity elements in cladding.
2. The importance of the data in this report in relation to 10 CFR 60 or Monitored Retrievable Storage (MRS).
3. Burnup after 300 to 1000 years during the permanent waste package emplacement.

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

(a) Relationship to Waste Package Performance

2.3.1 What are the physical, chemical, and mechanical properties of the waste form, how do those properties of the waste form change with time, and how will such changes alter the ability of the waste form to contribute to the overall performance of the repository system or impact the performance of other barrier materials and properties of the site?

(b) New Licensing Issues

(c) General Comments on Licensing

ABSTRACT

This report summarizes data on spent LWR fuel. Fuel rod cladding integrity and conditions within fuel rods established during rector residence as they affect storage in geologic repositories are emphasized.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

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

Stout, R. B. and Shaw, H. F.
"Statistical Model for Grain Boundary and Grain Volume Oxidation Kinetics in UO_2 Spent Fuel."
UCRL-100859, September, 1989.

(b) Organization Producing Data

Lawrence Livermore National Laboratory, Livermore, CA.

DATE REVIEWED: 7/16/90; Revised 8/24/90; 12/21/90.

PURPOSE

"This paper addresses statistical characteristics for the simplest case of grain boundary/grain volume oxidation kinetics of UO_2 to U_3O_7 for a fragment of a spent fuel pellet."

"Concepts from statistical mechanics are used to define a density function for grain boundaries" "in a spent fuel fragment." "Combining the integral forms of mass conservation and this grain boundary density function, a model for the global rate of oxidation for a spent fuel fragment is obtained. For rapid grain boundary oxidation compared to grain volume oxidation, equations of the model are solved and results compared to existing data."

KEYWORDS

Theory, PDF probability distribution functions, weight change, laboratory, Yucca Mountain, air, ambient pressure, ambient temperature, spent fuel, thermal expansion, oxidation.

CONTENTS

This 21-page report consists of a table of contents, an abstract, an introduction, acknowledgement, 1 figure, a summary and the following content

CONTENT	NUMBER OF PAGES
Statistical Description of Grain Boundary/Volume Oxidation Processes	14
References (17)	2

TEST CONDITIONS

Materials: a fragment of a UO_2 spent fuel pellet

Specimen preparation: the boundaries of an arbitrary grain are assumed to consist of a set of planar area segments

Environment: oxidizing

UNCERTAINTIES IN DATA

- "Grain volume oxidation front appears to remain approximately self-similar to the outer geometrical shap of the grain volume." In other words, the oxidation distance into a grain volume is assumed to be constant along the associated periphery of the grain boundary.

- "To develop the expression for oxygen flux at the grain volume oxidation front," "a generic pyramidal volume of a grain" is considered. Strictly speaking, the shape of a grain is not pyramidal.

DEFICIENCIES/LIMITATIONS IN DATABASE

- "The formulation in this report assumes: (a) "grain boundary oxidation is completed," (b) "the time interval for completion of grain boundary oxidation is negligibly small in comparison to the subsequent time interval for grain volume oxidation," and (c) "for rapid grain boundary oxidation compared to grain volume oxidation, equations of the model are solved and results are compared to existing data." Other than these cases, new formulations are necessary.

- "In this short article, only the case of a small sized fragment and large grain sizes will be analyzed in details."

- "This short paper addresses statistical characteristics for the simplest case of grain boundary/grain volume oxidation kinetics." It also presents a limited discussion of future extensions to this simple case to represent the more complex cases of oxidation kinetics in spent fuels."

- Equation (11) is for the evaluation of the oxygen states of UO_2 spent fuel" with V_f at a given time in terms of N_F of V_f and C. And the equation (11) is approximated "when the ratio $(N_B - N_F)/N_F)$ is small and/or at early times when the grain volume oxidation front has propagated only a small fraction of the length of vector c." (N_B: the value of N along all grain boundaries. N_F: the value of N along all grain oxidation fronts propagating into the grains). When the ratio is large and/or at later time, new formulations are ncessary.

CONCLUSIONS OF AUTHOR

"A statistical approach has been developed to represent grain boundary and grain volume oxidation processes for spent fuel from UO_2 to U_3O_7. For small fragments, the statistical approach represents well the physically observed geometrical features of a grain boundary oxidation front propagating rapidly through a fragment followed by dense sets of grain volume oxidation fronts propagating more slowly across individual grains. Using the statistical formulation, equations are developed for this case that can be made equivalent to empirical expressions that have been used to correlate with existing experimental data. In showing this equivalence, phenomenological coefficients in the empirical expressions are given a physical interpretation in terms of the diffusion coefficient, grain size, and boundary values of oxygen concentration. As discussed in the future work section, this physical interpretation will be very useful in developing models that describe oxidation kinetics for the typical large fragments from UO_2 spent fuel pellets that can be expected in failed fuel rods."

COMMENTS OF REVIEWER

- The authors have attempted to quantify the oxidation kinetics of UO_2 pellets in a statistical manner, taking into consideration the grain size distribution and grain boundary effects. Certainly, the topics chosen are believed to be very important in the assessment of spent fuel dissolution.

- The major shortfall of this work is that the authors did not finalize the mathematics, tensors or distribution, in order to arrive at significant conclusions. Specifically, neither the continuity equation nor the probability density function has been evaluated. The authors simply attribute this negligence to the simplicity of the problem only in need of statistical bookkeeping using the conservation equation or related ones. However, it must be noted that

(a) The conclusion obtained from this analysis can be attained from any diffusion textbook considering only a single grain

(b) There is no information throughout this paper about (1) grain size distribution and (2) grain boundary/volume density function, either before or after grain-volume oxidation.

- In the treatment of materials transport through many paths, scientists normally couple two independent transport equations either in parallel or in series. In any of these cases, normally they arrive at an extreme case solutions for practical purposes

except for transient effects. There is a need for the exact description of diffusion along grain boundary and across the grain volume.
Likewise, for these practical purposes, the geometrical attributes of grain boundaries appear to be insignificant.

- The authors have listed the models development in progress. However, the reviewers are concerned about the existence of experimental data supporting this analysis. Most experimental results do not appear to be that sophisticated to differentiate these listed cases.

- The authors note there would be a volume expansion associated with the oxidation process. The diffusion mechanism should be modified taking into account the resulting strain fields or cracks generated.

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

(a) Relationship to Waste Package Performance Issues Already Identified

2.3.2.1 What are the possible dissolution mechanisms of the waste form under the range of potential repository conditions?

(b) New Licensing Issues

(c) General Comments on Licensing

ABSTRACT

The Yucca Mountain Project of the U.S. Department of Energy is investigating the suitability of a site in the unsaturated zone at Yucca Mountain, NV, for a high-level nuclear waste repository. Most of the waste will consist of UO_2 spent fuel in Zircaloy-clad rods from nuclear reactors. If failure of both the waste containers and the cladding occurs within the lifetime of the repository, then the UO_2 will be exposed to oxygen in the air and higher oxides of uranium may form. The oxidation state of the spent fuel may affect its dissolution behavior if later contacted by water. A model for the kinetics of spent fuel oxidation under repository-relevant conditions is thus necessary to predict the behavior of the waste form for assessing the performance of the repository with respect to the containment of radionuclides. In spent fuel experiments, the UO_2 oxidation front initially propagates along grain boundaries followed by propagation into grain volumes. Thus, the oxidation kinetics is controlled by two processes and the oxidation of spent fuel fragments will depend on the density and physical attributes of grain boundaries. With

this in mind, concepts from statistical mechanics are used to define a density function for grain boundaries per unit volume per unit species in a spent fuel fragment. Combining the integral forms of mass conservation and this grain boundary density function, a model for the global rate of oxidation for a spent fuel fragment is obtained. For rapid grain boundary oxidation compared to grain volume oxidation, equations of the model are solved and results compared to existing data.

WASTE PACKAGE DATA REVIEW

DATA SOURCE

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

Farmer, J. C. and McCright, R. D.
"Review of Models Relevant to the Prediction of Performance of High-Level Radioactive-Waste Disposal Containers"
UCRL-100172, November 1989.

(b) Organization Producing Data

Lawrence Livermore National Laboratory, Livermore, CA.

DATE REVIEWED: 7/12/90; Revised 12/15/90

PURPOSE

Purpose of the paper is to collect and summarize mechanisms and models describing various forms of localized attack, "to help develop predictive models", as the authors state, relevant for HLW containers.

KEYWORDS

Literature review, corrosion (crevice), corrosion (intergranular), corrosion (pitting), corrosion (stress cracking) SCC, cracking (stress corrosion) SCC.

CONTENTS

37 pages, 11 figures, 2 tables, and 121 references.

AMOUNT OF DATA

None given.

TEST CONDITIONS

None given.

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

CONCLUSIONS OF AUTHOR

"The models discussed in this review fell into the following categories: (1) pit initiation on passive surfaces of austenitics; (2) propagation of pits on active metal surfaces; (3) propagation of pits on surfaces covered by salt films; (4) crack initiation at pits; (5) propagation of cracks on active metal surfaces; (6) propagation of cracks due to periodic fracture of passive films at crack tips; (7) propagation of cracks due to film-induced cleavage of the base metal; (8) crevice corrosion on active metal surfaces; and (9) crevices that behave like active-passive concentration cells. In some instances, the models are interactive. For example, stress corrosion cracks may initiate at pits having a critical depth."

"Most of the models discussed here are applicable to worst-case scenarios in which a concentrated electrolyte contacts the container surface. In one scenario, condensation dissolves salt scales that form as a result of refluxing of ground water below the repository horizon has a neutral pH, about 10 ppm chloride, 20 ppm sulfate, 120 ppm bicarbonate, dissolved oxygen, and some nitrate. Another worst-case scenario involves the SCC of copper and some of the copper-based alloys due to nitrite or ammonia. Since these species do not occur naturally in the ground water below the repository horizon, they could only be introduced into the environment by gamma radiolysis or biological activity. The gamma dose rate around the high-level radioactive-waste containers will be 10^2 to 10^4 rad/h for the first 50 y, depending on the type, age, and design features of the waste package. Gamma radiolysis of air and water in close proximity to the containers can result in the formation of hydrogen peroxide, nitrate, nitrite, and hydrogen ions."

"For austenitic alloys, the linear equations for pit incubation time developed by Okada, Chao, and others can be fitted to data obtained from factorially-designed experiments. Then, equations such as these could be used to calculate the time required for initiation of a pit on a hot container surface in contact with concentrated electrolyte (a worst-case scenario). After initiation, the Tuthill-Turnbull approach can be used to model pit propagation through the container wall in cases involving an active surface at the base of the pit. The Pickering-Frankenthal and Galvele models give useful qualitative insight into pit-propagation mechanisms, but they are not useful for quantitative predictions of propagation rate. After the pit has grown to a critical depth, penetration at an accelerated rate by a film-fracture crack-propagation mechanism should be taken into account by application of the Ford-Andresen model. Initiation of cracks by strain-induced fracture of the oxide should also be considered."

"Our review of the literature on available models has revealed the following needs. First, a comprehensive model must be developed for estimating the effect of refluxing on the concentration of ions in condensate films. Such effects will become important after the temperature of the container wall drops below the dew point (approximately 96 C in the repository). Furthermore, such modeling will enable intelligent planning of accelerated testing programs. A quantitative model applicable to the initiation of pitting on copper was not found and is needed. A pit-propagation model is also needed for describing the complex mechanisms in copper discussed by Lucey. A film-rupture model should be adequate for predicting SCC in copper-based alloys. Possible crevice geometries must be determined. Finally, additional laboratory tests are required to quantitatively determine model parameters. For example, parameters for the Ford-Anderson model will have to be determined for the copper-based alloys in moist air exposed to gamma irradiation.

COMMENTS OF REVIEWER

As a help in tracing down a good part of the relevant literature on modeling localized forms of corrosion, this paper is certainly useful, but there is no attempt to discuss the validity of the models and mechanisms surveyed. What was foremost in the minds of the authors, it seems, was to find out formulae which could be used in constructing numerical models, to the point that departing from its character of a review paper, a discussion is inserted on how to devise experiments leading to the determination of certain quantities necessary for the quantitative use of some formulae relative to pitting. In this respect, this paper is also useful in giving an idea of the difficulties in applying current ideas on localized corrosion mechanisms to quantitative predictions.

In the summary, the authors make a list of things, mostly models concerning some specific processes, which they did not find in their survey and which they think necessary for the successful development of a comprehensive predictive model applicable for HLW containers. Here, it is surprising that they don't mention the lack of information on how radiolysis products will accumulate in the repository as one of the most important uncertainties for estimating HLW container survival.

A final criticism is that the authors keep using the expression "worst case scenario" without giving much thought in defining it. On the contrary, it seems, to make predictive models credible, a thorough analysis of possible sharp deviations of the local conditions from the present, and their probability of occurrence is extremely important.

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 containers?

(b) New Licensing Issues

(c) General Comments

AUTHOR'S ABSTRACT

Austenitic and copper-based alloys are candidate materials for fabrication of the metal containers to be used in disposing of high-level radioactive waste at the prospective repository at Yucca Mountain, Nevada. The selection of the alloy that is best suited for this application will be based in part on predictions from models of alloy degradation under repository conditions. To help develop predictive models, we have reviewed numerous mechanisms and models in in the literature that are relevant to two worst-case scenarios: container failure by localized corrosion and container failure by stress corrosion cracking. The models considered fall into the following categories: (1) initiation of pits on passive surfaces of austenitics; (2) propagation of pits on active metal surfaces; (3) propagation of pits on surfaces covered by salt films; (4) initiation of cracks at pits; (5) propagation of crack on active metal surfaces (6) propagation of cracks due to periodic fracture of passive films at crack tips; (7) propagation of cracks due to film-induced cleavage of the base metal; (8) crevice corrosion on active metal surfaces; and (9) crevices that behave like active-passive concentration cells.

APPENDIX C. Interpretative Papers

MECHANISMS OF LOCALIZED AQUEOUS CORROSION OF COPPER AND ITS ALLOYS

PURPOSE

The purpose of this report is to examine the known evidence on localized aqueous corrosion, particularly stress corrosion cracking (SCC), in copper-base materials, together with the possible environmental conditions in the High Level Waste (HLW) repository, in order to estimate the likelihood of the occurrence of localized attack, and to identify the most important data and other information necessary to improve our predictive capabilities.

SCOPE

This report is limited to aqueous corrosion, and will not cover dry oxidation as a possible failure mode. As a first installment of a more comprehensive work dealing with all forms of localized corrosion, this report will focus on stress corrosion cracking (SCC) of pure copper and its alloys.

1. INTRODUCTION

Copper-base metals have been proposed as three of six candidate materials for the high-level waste containers at Yucca Mountain. Since there are significant uncertainties as to the environment that they will have to withstand, as well as to their behavior in certain circumstances, the possibility that copper-base containers may fail because of some form of localized attack, mainly pitting and stress corrosion cracking (SCC), cannot be easily discounted.

It seems appropriate, therefore, to undertake a review of what is currently known about localized corrosion of copper and its alloys, with particular emphasis on stress corrosion cracking, in order to put the problems into sharper focus, taking into account the Yucca Mountain repository environment and its uncertainties.

The environmental conditions in the repository, because of the heat generated by radioactive decay, are expected to lead to dry oxidation of the metal containers for very long times. However, aqueous corrosion is a significant possibility, particularly if the conditions deviate somewhat from those anticipated. The present paper will not concern itself with dry oxidation, but will consider aqueous corrosion, whether due to liquid water percolating through the rock or moisture condensing on the metal surface.

2. ELECTROCHEMISTRY OF COPPER AND ITS ALLOYS

2.1 Copper

Copper is a fairly noble metal, and this characteristic confers on it a certain protection against galvanic corrosion, as well as from attack in water, with H_2 evolution as the cathodic reaction. This, however, has been challenged recently, and corrosion of Cu with H_2 evolution in pure water has been reported[3]. The oxidation of copper occurs in two steps

$$Cu = Cu^+ + e- \qquad (1)$$

and

$$Cu^+ = Cu^{++} + e- \qquad (2)$$

and the interplay of these two reactions is the most important factor in shaping the electrochemical behavior of copper. For a general survey of the electrochemistry of copper, see reference 4, and for its corrosion behavior, see reference 5.

Copper is oxidized to Cu_2O or CuO in the presence of oxygen, or, in aqueous solution, by any reaction represented in a galvanic cell by a Cu anode and a cathodic reaction with an equilibrium potential more positive than about 300 mV vs. Normal Hydrogen Electrode (NHE) in acidic solutions, but much lower (about -200 mV) in alkaline solutions. Although the stability of the oxides decreases with increasing temperature, this effect does not confer thermodynamic immunity on Cu in the temperature range expected in the repository.

Copper readily forms complexes soluble in H_2O with halide ions and ammonia. Complexing can make Cu much less noble, with the consequence of making it more easily oxidizable, and also reducing the domain of stability of the oxides, which in most cases form protective films on the metal. An extreme case is that of sulfides, which decrease so much the activity of Cu^+-ions in solution, that it is thermodynamically possible to oxidize copper by decomposing water

$$2Cu + S^{2-} + 2H_2O = Cu_2S + H_2 + 2OH^- \qquad (3)$$

Much of the corrosion resistance of copper depends on the formation of oxide surface films in neutral and alkaline, non-complexing solutions. As part of the study of passivity in metals, the formation of anodic oxides on copper has drawn much interest. The oxidation involves first the growth of Cu_2O followed by subsequent oxidation to divalent Cu, in the form of CuO or $Cu(OH)_2$.

in the absence of an oxide film, the electrode reaction between Cu and its ions in solution proceeds fairly rapidly. Moreover, the existence of two copper ions corresponding to Cu(I) and Cu(II), can cause what has been called an "autocatalytic" acceleration[6] of metal attack by oxygen. This occurs typically in aqueous ammonia, where the Cu^+ ions are stabilized with respect to Cu^{++}. The latter ions (or rather their ammonia complexes), although not consumed in the overall reaction, effectively increase diffusional transport so as to accelerate the corrosion reaction

$$4Cu + O_2 + 2H_2O = 4Cu^+ + 4OH^- \qquad (4)$$

by orders of magnitude.

An important distinction for copper-containing aqueous ammonia solutions is between "tarnishing" and "non-tarnishing", because their effect on SCC of Cu-base materials can be quite different. The terminology stems from the fact that an oxide tarnish film is formed on the metal immersed in tarnishing solutions. That is caused by exceeding the solubility of Cu_2O at the metal-solution interface, where the reaction

$$Cu + Cu^{++} = 2Cu^+ \qquad (5)$$

is taking place. Formation of Cu_2O occurs when its solubility product

$$[Cu^+][OH^-] = K_s \qquad (6)$$

is exceeded. Therefore, the factors influencing this reaction, and determining whether a solution is tarnishing or not, are the concentration of Cu^{++} ions in solution, which influences Cu^+ production at the interface through the rate of (5), NH_3 concentration, which, by complexing Cu^+, mainly through the reaction

$$Cu^+ + 2NH_3 = [Cu(NH_3)_2]^+ \qquad (7)$$

decreases the activity of $[Cu^+]$ whose value appears in (6), and finally the pH, which determines $[OH^-]$, the other term

in (6). So, the composition shifts from non-tarnishing to tarnishing by increasing the Cu^{++} concentration or the pH, and by decreasing the NH3 concentration.

The formation of a tarnish film, however, does not depend only on the solution composition, but to a much smaller extent on the composition of the metal. A solution which forms a film on pure copper may not form it on brass, because part of the corrosion reaction, instead of producing Cu^{+}, produces Zn^{++}

$$2Cu^{++} + Zn = 2Cu^{+} + Zn^{++} \qquad (8)$$

The effect, although experimentally confirmed, is a minor one, so that talking of tarnishing or non-tarnishing solutions is justified. Altering the thickness of the diffusion layer by stirring has, of course, a great effect on the rate of (5), which is essentially transport-limited as long as the tarnish film does not form. However, since stirring also removes Cu^{+} from the interface, the tarnish limit is practically unaffected.

Another concept mentioned in the discussions concerning SCC, with which the reader may not be familiar, is that of a solution in equilibrium with copper metal. The composition of such a solution must be so that both reactions (1) and (2) are in equilibrium. This entails specific values of the ratio of the activities of the two copper ions. In solutions where copper ions do not form complexes, there is, roughly, a 1000:1 ratio between Cu^{++} and Cu^{+}, and since there is no complexing, activities and concentrations are about the same. Corrosion of copper, then, is caused by oxygen in solution oxidizing Cu^{+} to Cu^{++}, which causes (1) to proceed anodically. Since, however, the equilibrium concentration of Cu+ is very small, transport by diffusion is slow, and the corrosion reaction is so small as to be often neglected.

The situation is quite different in complexing solutions, of which aqueous ammonia is typical. Here Cu^{+} and Cu^{++} both are complexed, the first according to (7), the second according to

$$Cu^{++} + 4NH_3 = [Cu(NH_3)_4]^{++} \qquad (9)$$

and

$$Cu^{++} + 5NH_3 = [Cu(NH_3)_5]^{++} \qquad (10)$$

The equilibrium potential can be shifted by some 600 mV with respect to the value in uncomplexed solutions, which

indicates that the activity of $[Cu^{+}]$ and $[Cu^{++}]$ can be of the order of 10-12 M and 10-18 M, respectively. Their concentrations, in the form of complexes, are much higher, in the 10-2 to 10-3 M range; in order to satisfy the equilibrium conditions most of the copper in solution must be in the monovalent form. Given the great tendency of Cu^{+} to react with atmospheric oxygen to give Cu^{++}, the preparation of a solution in equilibrium with copper metal is not easy, and practically all SCC experiments have been performed in solutions containing Cu^{++} in great excess over equilibrium, which, because of reaction (5), tend to be highly corrosive. Tests in equilibrium solutions, however, are of significance, to see if anodic dissolution of copper is necessary to observe cracking, since the conditions inside a crack may be quite different from those prevailing outside, and can, in a number of cases, approach equilibrium conditions.

2.2 Copper Alloys

The main purpose of adding alloying elements to copper is to improve the mechanical properties, but significant effects on the corrosion behavior are also found. In a number of cases, the protective film formed on Cu-Al and Cu-Ni alloys confers additional corrosion resistance under certain conditions, but can also have important detrimental effects, for instance because of selective leaching of the alloying component. However, by far the most troublesome consequence of alloying copper is the much greater susceptibility to SCC of most alloys in many environments, compared to pure copper.

The presence of impurities in solution which impair the stability of the passive film can induce accelerated corrosion, in environments which, otherwise, would not be very aggressive. An example is the corrosion of Cu-Ni alloys in seawater, polluted with small amounts of sulfides, as shown by Syrett and coworkers[7]. Such an example emphasizes how the corrosion resistance provided by a passive film can be affected by small amounts of harmful chemicals in the environment.

3. ENVIRONMENTAL REPOSITORY CONDITIONS

Many of the environmental conditions inside the repository at Yucca Mountain are subject to considerable uncertainties, ranging from the thermal history, which depends on the type and age of the nuclear waste, as well as the specific design of the containers and repository layout, to the quantity and direction of flow of the underground water. Even greater

uncertainties are introduced by the disruption of the natural conditions produced by the actual building of the network of tunnels of the repository, by the heat generated by radioactive decay and by the chemical alterations caused by the radiation field. In this report, we will briefly discuss these uncertainties, pointing out environmental scenarios which could be most important from the point of view of influencing the failure modes of the metal containers.

Concerning the question of the temperature to be expected in the repository, McCright[8] reports two different time/temperature plots, one for spent fuel waste and one for vitrified waste. They differ markedly, so that for the second the time at which water could condense on the container walls is of the order of 150 years, while for the first it extends up to about 900 years. This curve, however, has a very shallow slope, so that small changes in the vertical position of the curve could vary the time at which the container wall cools to the boiling point of water by hundreds of years. Considering that no firm decisions have been taken as to the specific geometry of the containers and repository tunnels, and that the physical constants pertaining to heat flow on the rock are not too precisely known, and are subject to variations from place to place in the repository, it can be concluded that a very important parameter such as the time when liquid water can begin to exist in contact with the container, can vary by one order of magnitude, from 100 to 1000 years.

3.1 AVAILABILITY OF OXYGEN

A first general question concerns the availability of oxygen. Tuff is permeable to gas, so that the containers are surrounded by air. On the other hand, in order to oxidize 63 g of Cu to CuO at a temperature of 400 K all the O_2 in about 80 liters of air must be consumed. How much time is necessary to have this volume of air sweep through? Each canister can easily weigh 1000 Kg. Complete oxidation would require some 1200 m^3 of air.

To estimate if oxygen transport can be rate-limiting, let's assume that a uniform corrosion rate of 0.3 μm/day, closely corresponding to a current density of 10 $\mu A/cm^2$ or 10-10 equivalents/cm^2 s, is the upper limit for an acceptable corrosion rate. such a rate would result in a penetration of 1 cm in 91 years, so that a satisfactory containment time could be achieved with thicknesses of 5 or more cm. It may be argued that such a corrosion rate, because of lack of uniformity in the attack, would result in an unacceptably

large number of container failures, so that the chosen limit is not conservative enough, but it is unlikely that a higher corrosion rate could be considered safe. Therefore, this value can be used to calculate the minimum rate of oxygen transport by diffusion which is necessary for oxygen availability to be rate-limiting.

A rough estimate indicates that the surface area of all copper containers is about one tenth of the surface area of the horizontal cross-section of the repository (an extreme value for the ratio may be one, if the canisters are buried very close to one another). The flux Φ of oxygen into the repository perpendicularly to the cross-section, under steady state conditions, has to be about 10-11 equiv/cm^{2}s.

If diffusional transport of oxygen is rate determining, the equation

$$\Phi = D\frac{\Delta C_{O_2}}{\delta} \qquad (11)$$

should allow the calculation of the length of the diffusion layer δ, assuming that the concentration of oxygen at the copper surface is zero. The unaffected oxygen concentration in the tuff (15% porosity and 350 K) is given by

$$C^{o}_{O_2} = \frac{0.21(x_{O_2}\ \text{in air}) \times 4(\frac{\text{equiv}}{\text{mol}}) \times 273(\text{K}) \times 0.15(x_{air}\ \text{in tuff})}{22415(\text{cm}^3\ \text{at}\ 0\,\text{C}/\text{mol}) \times 350(\text{K})} = 4.4 \times 10^{-6}(\frac{\text{equiv.}}{\text{cm}^3})$$

This number, however, does not take into account that a significant part of the pores is filled with water. The actual available space could be half of that assumed, corresponding to a porosity of 7 to 8%.

Assuming that the diffusion coefficient D of oxygen in air is unaffected by the porous rock, a value of 0.2 cm^2/s[9] can be chosen, so that the diffusion layer δ is equal to

$$\delta = \frac{0.2(\text{cm}^2/\text{s}) \times 4.4 \times 10^{-6}\text{equiv}/\text{cm}^3)}{10^{-10}(\text{equiv}/\text{cm}^2\text{s}) \times 0.1(\text{area ratio})} = 880\ \text{m}$$

The resulting diffusion layer is so large that it seems likely that convective motion, as caused, for instance, by atmospheric pressure fluctuations or by the radioactive decay heating, might prevent oxygen transport

from becoming rate-limiting. The value of the diffusion layer, however, is subject to considerable uncertainties. If the containers are packed tight, and if it turns out that diffusion through the pores is reduced more than in proportion to the porosity of the rock, the diffusion layer could go down to a few tens of meters. Unless nuclear heating, or all the tunnels dug in the mountain, increase convection, O_2 transport could become rate-determining.

The estimation of the availability of oxygen is complicated by the consideration that studies carried out on the alterations that tuff undergoes when heated, have shown that the fractures in the rock will heal, so that the permeability can decrease by three orders of magnitude[10] In this case, oxygen could very well disappear around some containers or groups of containers, making some failure modes very unlikely, but also opening the possibility of other forms of corrosion, such as by formation of copper sulfides.

3.2. AVAILABILITY OF WATER

As long as transport is unimpaired from the space around the containers to the rock away from the repository at a temperature around 30 C, the partial pressure of the water vapor should be between 4 and 5 kPa, corresponding to saturation at the unaffected rock temperatures. Capillary forces in the tuff, actually, could lower this value considerably. If that is the case, it is unlikely that condensation on the container wall, even considering the presence of a porous salt or oxide layer, will occur at temperatures higher than 50 C. Cooling to such a temperature should take more than 1000 years.

If, however, liquid water happens to flow into the heated part of the repository, and/or transport of the generated steam away to the cold areas is hindered, there may be areas, which, for significant times, will have water vapor partial pressures corresponding to a boiling point of 80 to 90 C. In this case, moisture can condense in the pores of the oxide on the container walls, activating a number of corrosion processes, at fairly high temperatures.

It is not clear what role a reduction in permeability of the tuff, caused by heating, would play in increasing

locally the partial pressure of water vapor and the likelihood of condensation of moisture films. On the one hand it might decrease the amount of water percolating through the rock, which is estimated to be a few millimeters per year[11], but on the other it might favor the formation of pockets of high temperature, nearly saturated steam.

In conclusion, if the hydrological conditions inside the decommissioned repository will remain close to the description given today, low water availability combined with long term radioactive decay heating could reduce aqueous corrosion to negligible amounts. However, if the conditions will depart from the present forecast, a number of the metal containers could spend long times partially or totally immersed in hot water and saturated steam, with the water containing a significant quantity of chemicals produced by the interaction of heat and γ radiation with the environment.

3.3. RADIOLYSIS PRODUCTS

The main problem, as far as the influence of radiolytic products on corrosion is concerned, is not the initial period when the γ field is intense, but the temperature is too high for aqueous corrosion to be important, but a later time, when radiolysis is negligible, the temperature is low enough, and only stable radiolysis products which have accumulated during the preceding period can affect the corrosion processes.

Although a fair amount of information is available as to the chemical species which are formed by irradiating air, dry or in the presence of liquid or gaseous water[12] it is almost impossible, with the present knowledge, to estimate which concentrations should be expected after tens or hundreds of years of γ radiation in the repository environment.

The species that can have important effects on the corrosion of the metal containers are

1) hydrogen peroxide, H_2O_2
2) nitric acid, HNO_3
3) nitrous acid, HNO_2
4) ammonia, NH_3

Other reactive compounds are formed, but either they are highly unstable, such as radicals, or they are gases, such as various nitrogen oxides, which will tend to form nitrate and nitrite upon contact with water. That does

not mean that they cannot promote metal oxidation in the gaseous form if they come into contact with the metal, but dry oxidation is not being considered in this report.

From a number of experiments[13], it is known that hydrogen peroxide is the principal radiolysis product which influences the electrochemistry of metals in aqueous solutions. However, when the γ field will be intense and H_2O_2 production significant, liquid water is unlikely to be present at the metal surface. H_2O_2 might diffuse and be dissolved in liquid water in the cooler part of the rock, away from the hot containers, but, considering its tendency to decompose, it seems unlikely that much of it will be present when, after years of cooling, liquid water might contact the metal.

While generation of NH_3 is controversial and not clearly established, there is no doubt that nitric and nitrous acids are generated if water is available. For HNO_3, a formula for its rate of production is given by Burns and coworkers[14]

$$\frac{d(HNO_3)}{dt} = 5.5 \times 10^{-5}\ CDR\ \frac{(mol)}{L.h} \qquad (12)$$

where C is the N2 gas concentration in mol/L, D is the radiation dose rate in Mrd/h, and R is the ratio of the volume of gas space to the volume of liquid. These values can be known in a controlled laboratory experiment, but in the repository they are hard to define, depending as they do on the geometry considered, as well as on many other factors. As an upper limit, the production rate of nitric acid could conceivably be as high as 10-6 mol/L.h. If the acid could accumulate for, say, 10 years in the cool rock adjacent to the containers, the concentration could approach 0.1 M. Even this extreme number is of uncertain significance, since it is hard to derive from it a value for the total mass of nitrate per unit surface area of metal which could, as a worst case, be available to influence corrosion. All that can be said at this moment is that dilute solutions of nitrate, and probably nitrite salts might result as a consequence of the radiolytic processes around the containers.

4. MODES OF FAILURE BY LOCALIZED ATTACK

4.1 STRESS CORROSION CRACKING

4.1.1 Copper

The literature shows that several instances of SCC in pure copper have been reported. The first is a communication by Pugh and coworkers[15], who found evidence of cracking in high concentration (>10 M) aqueous ammonia containing quantities of Cu^{++}-ions of the order of 0.03 M. Tensile specimens immersed in such a solution and stressed with a constant load failed at least in part by intergranular SCC. Although the specimens were attacked during the test at a rate estimated to be about 5 mA/cm^2, no formation of a surface oxide film was observed. This experiment was repeated with greater care on very pure copper with the same results[16]. Also, in parallel experiments, it was found that copper did not crack in ammonia solutions which formed a tarnish film. It is also noteworthy that the failures occurred under constant stress. These results were disputed in a very recent work by Said Saleet[17]. He found no cracking under constant stress in solutions in which cracking had been previously reported, namely 15 M NH_3+2.5 g/L of dissolved Cu, 1 M $NaNO_2$, and dilute ammonia solutions (0.03 M, 0.05 M and 0.07 M).

Suzuki and Hisamatsu[18] also observed cracking of pure copper in the presence of ammonia, but in their case the NH3 concentration had to be kept below 0.07 M, and the cracking was transgranular in character. In such an environment, a thick, adherent oxide film formed.

Cracking of pure copper was also observed in $NaNO_2$ solutions, using the slow strain technique at a rate if 10^{-6}/s, at the open circuit potential[19]. Here the surface was covered by an oxide layer. Extensive tests for Cu in nitrite were carried out more recently, to study the influence of nitrite concentration, electrode potential and temperature on crack propagation[20]. A minimum threshold of 0.5 M nitrite was found. The severity of the transgranular cracking, as indicated by a decrease in the area reduction and an increase in crack propagation rate, increased with electrode potential in the interval -150 to +50 mV vs. SCE. Similar results, in 1 M $NaNO_2$, were reported by Sieradzki and coworkers[21], who, by correlating fractography, acoustic emission and current transients, confirmed that the brittle fracture occurred

discontinuously. It was also found that, if the dynamic straining was stopped, the crack quickly stopped growing.

In another study on the cracking of copper, Aaltonen and coworkers[22] tested copper by the slow strain technique at a rate of $4.5.10^{-7}$/s not only in nitrite, but also in a simulated groundwater containing small amounts of chlorides and sulfates, at 25 C and at 80 C. Their results seem to have extended the conditions under which copper undergoes environmentally assisted cracking: T-SCC was observed at 0.3 M $NaNO_2$ both at 25 and 80 C. Moreover, from 25 to 80 C, the elongation to fracture was found to decrease in any environment from 35% to about 24%, and further to 14% if the concentration of chlorides and sulfates was raised to 7 g/L and 1 g/L respectively.

Cassagne[23] undertook a thorough study of the conditions leading to SCC in copper. He found T-SCC in nitrite solutions, and also in acetate, confirming previous reports[24]. The presence of an oxide film was found to be necessary for cracking, so that in acetate solutions no SCC was found at pH=3, where no oxide forms. Cracking was also dependent on electrode potential and strain rate, indicating that when the strain rate is too fast (thus decreasing the time available for film growth) and the potential is too negative (thus reducing the driving force for oxide formation), brittle fracture does not occur.

This survey of published results shows good agreement among the various workers concerning the conditions under which brittle fracture has been observed in pure copper. Intergranular SCC, on the contrary, is less well established, since the only attempt to repeat the results of Pugh[15] was unsuccessful[17]. The test, however, was not run exactly in the same conditions. The author reports a dissolved Cu concentration of 2.5 g/L, twice as much as that used previously. That brings the composition of the solution very close to the tarnishing range (particularly since concentrated aqueous ammonia, as received from the vendor, although nominally 15 M, is often close to 13 M), where there is general agreement that no cracking occurs.

4.1.2 Brass

Cu-Zn alloys, known as brasses, have not been proposed as material for HLW containers. However, since their various forms of SCC have been extensively investigated, and they have been used as a model material for perhaps the greatest part of mechanistic studies, so that, often,

the results of these studies are extrapolated to other Cu-base alloys and to pure copper, they are of particular importance. We will here summarize their SCC behavior, while the mechanisms proposed for the cracking of brass will be examined, and their relevance for the understanding of SCC in other Cu alloys discussed.

Aqueous ammonia is generally considered the principal environment which causes SCC of brasses in service. This was known as "season cracking", and was favored by a damp atmosphere containing ammonia vapor. It was also observed that SCC was more severe in brasses of higher Zn content, where additional phases are formed. However, it was soon found that also alloys containing other materials, such as Al, As, Ni, P, Sb or Si, were susceptible to SCC in the presence of ammonia.

A systematic examination of SCC of brass in NH_3 was carried out by Mattsson[35], who made use of potential-pH diagrams to explain the relationship between pH an severity of cracking. His results, as well as those of others, have established that SCC can occur under either tarnishing and non-tarnishing conditions, the first favoring I-SCC, the second T-SCC. Conditions under which copper tends to dissolve anodically have also been shown to be unnecessary, so that cracking was observed in solutions which, at the open circuit potential, were in equilibrium with copper metal[2], and even when the brass was cathodically polarized by a few mV, so that copper deposition, at very low rates, was going on[36]. Extensive studies in the last twenty years have shown, however, that SCC of brass is not limited to aqueous ammonia. The list of the species which cause cracking in aqueous solutions has lengthened considerably over the years[37] as shown in Table 4.1.1. Indeed, recent work by Parkins[38] has shown that a-brasses can undergo SCC in oxygen-containing pure water in slow strain rate tests. It seems reasonable to conclude that the circumstances leading to SCC in brass do not depend on the specific properties of the chemical species involved.

4.1.3. Other Cu alloys

Stress corrosion cracking has been observed in aqueous NH_3 both in Cu-Al and Cu-Ni alloys[15], the severity of cracking in general decreasing with increasing alloying metal content. In non-tarnishing solutions cracking was found to be predominantly intergranular for Cu-Ni and for Cu-Al containing up to 3% Al, but transgranular at higher Al content. The time to failure was approximately equal in Zn, Al and Ni alloys. In tarnishing solutions,

Table 4.1.1

Stress Corrosion Cracking of brass other than in NH_3

Chemical Reference Species	Failure Mode	Test Method	
= sulfur dixoide	I	constant stress	25
= carbonates = pyrophosphates	I	constant stress	26
= citrate, pH=10.3; tartrate, pH=13	I	constant stress	27
= sulfates			
= Sodium sulfate, pH=2	I	constant strain rate	28
= copper sulfate	T	tube, no external stress	29
= Sodium sulfate, various pH's	T	constant strain rate	30
= nitrites	T	constant strain rate	31
=	T	constant strain rate	32
=	I & T	constant strain rate	33, 70
= nitrates, chlorates = molybdates, chlorides = tungstates	T	constant strain rate	35
= acetate, formate = hydroxide	I & T	constant strain rate	34

however, where the susceptibility decreases in the order Zn > Al > Ni, cracking was always intergranular. Another study of the cracking behavior of Cu-Al alloys[39] showed that the susceptibility to SCC increased with Al content in the alloy, with Cu concentration in solution and with stress level. The cracking was intergranular, and a tarnish film was present.

Aluminum brass has been observed to fail intergranularly when exposed to steam at 150 to 220 C[40].

A number of Cu-Ni alloys failed, mostly by transgranular cracking, when exposed to an industrial atmosphere, and to a minor extent, to a marine atmosphere[41]. However, this occurred only to alloys containing large quantities of Zn (CDA 762, 766, 770 and 772), but not to those (706, 725) with little or no zinc.

5. MECHANISMS

5.1 MECHANISMS OF STRESS CORROSION CRACKING

The most widely accepted mechanism for SCC is probably that involving the rupture of a protective film caused by plastic deformation, with consequent localization of the anodic attack where the rupture occurred[42], and the underlying metal is exposed to the corrosive environment. Repassivation of the exposed area may occur again, but the applied stress will break the film at some other point along the crack front, repeating the cycle. The cracking, however, is thought to advance continuously, in average. The intergranular path is favored because of the larger number of defects and/or impurities at the grain boundaries. Since a thin portion of the metal is anodically dissolved, no matching crystallographic features are found on the two sides of the crack.

This mechanism is believed to be responsible for intergranular SCC in brass and other Cu-base alloys in solutions and at potentials where an oxide film forms, typically the so-called tarnishing ammonia solutions. However, the view that tarnishing solutions are associated only with intergranular cracking in a-brass is clearly an oversimplification. Transgranular cracking has been observed in tarnishing solutions, for instance:

1) in cold worked Cu-30Zn[43]
2) in thicker sections of annealed Cu-30Zn
3) in Admiralty metal[44]

The reasons for these cases have not been established.

The mechanistic picture is complicated by the fact that both intergranular and transgranular cracking can occur in ammonia and in other environments. Generally, it is agreed that I-SCC and T-SCC are caused by different mechanisms. This seems to be the case because the phenomenology and morphology of the cracking are very different. The transgranular crack propagates by a series of brittle fracture (cleavage) events, which have been correlated with current transients and acoustic emission signals. It is generally believed that, during a crack advance, typically a few μm, the velocity is close to the speed of sound in the material. This rapid advance is followed by a quiescent period, lasting several seconds, during which the conditions at the crack tip leading to another advance are generated. As further

proof that the cleavage is accompanied by little or no anodic dissolution, the two sides of the cracked surface show closely matched crystallographic details at a microscopic scale. Before presenting and discussing the various mechanisms proposed to explain brittle fracture in otherwise ductile materials, it may be useful to point out that there are still a few cases of intergranular cracking reported in the literature, which occurred in the absence of a detectable film, these being pure copper, Cu-Al below 3% Al, and Cu-Ni alloys. These cases have to be considered unexplained by our present models, and, if unequivocally confirmed, would require a thorough study to understand their causes.

Following a recent review of this subject by Pugh[45], four mechanisms for T-SCC can be listed. They are:

A) Hydrogen embrittlement
B) Adsorption
C) Selective dissolution
D) Film-induced cleavage

They will be summarized here, and their validity in explaining cracking in Cu-base alloys discussed.

A) Hydrogen embrittlement

With the exception of copper alloys, materials that are susceptible to transgranular cracking also undergo hydrogen embrittlement, so that it is reasonable to speculate that SCC results from cathodically generated hydrogen adsorption at the crack tip. The possibility that T-SCC in Cu-base alloys is a form of HE is attractive in that it can account for the observed kinetics of cracking. For instance, in the case of Cu-30Zn, the diffusivity of hydrogen at room temperature, required to account for the embrittlement of 10 μm ahead of the crack tip in 100 seconds, is 10-9 cm^2/s; extrapolation from high temperature diffusion data indicates that such a value is reasonable. On the other hand, the hydrogen approach for T-SCC has serious difficulties. As mentioned above, there is no evidence of conventional HE in a-phase Cu alloys. Because of the nobility of Cu, the possibility of hydrogen discharge at the crack tip is seriously in doubt. In the brass/ammonia case, cracking occurs at externally measured potentials (-200 to -300 mV vs. NHE) considerably more positive than the potential for H_2 evolution (-600 to -750 mV). Modeling of the electrochemical processes at the crack tip, in order to

calculate the minimum potential to be expected, have shown that H+ reduction is a very remote possibility[46]. More recent calculations, modeling the case of Au-Cu alloys[47] (which undergo T-SCC morphologically identical to a-brass), have completely excluded hydrogen discharge. It should also be remembered that pure copper also can crack transgranularly, and in this case no hydrogen discharge is possible. For these reasons it is now believed by many researchers in the field that hydrogen is not involved in causing brittle cracking in all Cu-base materials.

B) Adsorption

This mechanism is similar to the HE decohesion model, in that embrittlement results from a reduction in bond strength which is caused by the adsorption of a critical species at strained bonds at the crack tip[48]. It differs from the hydrogen decohesion model in that embrittlement is considered to occur only at the surface, instead of within the lattice. In SCC, the embrittling species are presumedly ions or molecules in the aqueous phase. As in decohesion, there is no independent evidence of the hypothesized bond strength reduction.

Lynch has suggested a radically different form of this model[49]. According to him, the cleavage-like surfaces do not result from brittle fracture, but rather from a plastic process involving adsorption-enhanced generation of dislocations at the crack tip. His view is based on the claim that the fracture surfaces exhibit extremely small dimples that are characteristic of ductile fracture. His fractographic observations and the model based on them have generated much discussion, but they remain highly controversial.

C) Selective dissolution

Selective dissolution, or dealloying, has been proposed as the cause of the cracking, but the causal relationships between dealloying and cracking are not clearly defined, and hard to reconcile with the experimental evidence. For instance, Pickering and Swann[50] have suggested that selective dissolution leads to a weakening of the metal ahead of the crack, and Forty[51] has advanced the hypothesis that embrittlement in brass is due to vacancy injection caused by the selective dissolution of Zn. The idea that selective dissolution plays a role in SCC is incorporated in the most recent mechanism proposed, that of film-induced cracking, as one

of the ways in which a surface film of altered properties is generated.

D) Film-induced brittle fracture

The experimental evidence supporting the idea that transgranular cracking occurs by brittle fracture has been thoroughly examined and discussed recently by Sieradzki and Newman[52], not only for Cu-base materials, but for other alloy systems as well. These authors have proposed a mechanism, in which the brittle fracture is initiated in a surface film having appropriate characteristics, which then proceeds for distances up to several μm into the ductile metal. Such a surface film can be an oxide, or it can result from selective leaching of one of the components of an alloy. A number of other film types can be conceived as well. These authors have supported their views with extensive work, experimental as well as theoretical, and by computer simulations.

While this mechanism has sufficient generality to cover a wide range of materials and environments, the specificity of embrittlement systems can be attributed to the necessity of a suitable relationship between film and substrate. Thus, in the case of oxides, it appears that a specific epitaxial relationship would be required, in analogy with requirements in computer simulations.

The film-induced cleavage model represents a promising new approach to understanding the mechanism of T-SCC. It is attractive because it has generality and is amenable to experimental verification. There are still a wide range of controversial points, and for these reasons it is not yet accepted by many experts in the field. We will mention here a couple of instances, where the evidence can be considered contradictory or at least dubious. The first is the all-important, and unique, case of pure copper. Since dealloying cannot be invoked, the brittle fracture is believed to initiate in an oxide film. At first glance, this appears to agree with the fact that brittle fracture occurs only when a film is present. However, the results of Cassagne[23], who did a detailed study of the film, correlating electrochemical and ellipsometry measurements, indicate that the adherent oxide film which first forms on copper, rapidly breaks down, becoming loose and poorly protecting. It is hard to think that such an oxide layer has epitaxial relationships with the metal, so that fractures initiating in it can proceed into the metal.

A second case is that of a-brass in chloride solutions. Here there is a range of solution compositions where no surface film forms, dezincification proceeds rapidly and copper ions are complexed by chloride. Such solutions have many close analogies with non-tarnishing NH_3 solutions, but SCC is not observed. It has been argued that Cu surface mobility is different than in ammonia, resulting in a porous layer with a structure which does not favor brittle crack initiation. This may very well be the case, but support for these assertions is weak. The experimental evidence, no cracking, seems to be used backward to deduce the existence of a film not suitable for cracking.

It should be obvious from this review that there are still many important questions to be answered, before our understanding of the causes of SCC in Cu-base alloys will allow to predict with great confidence what will happen to a specific material in a particular environment. Nevertheless, by examining the circumstances and comparing them with past experience, it is possible to outline the areas of concern, and to suggest where further testing is most needed.

6. RELEVANCE FOR REPOSITORY CONDITIONS

There is some uncertainty in the definition of stress corrosion cracking, which can be important in assessing if a material is susceptible to it. A first, traditional definition may be the following: if we subject a material M to a tensile stress in a certain corrosive environment, and the specimen breaks, while it would not break without the applied stress in the same environment, or in a reference environment (usually air) under the same stress, we say that M is susceptible to SCC in that environment. Of course, the applied stress must be significantly below the ultimate strength of M, so that failure is not due to a slight reduction in cross section because of corrosion.

In the last twenty years a new testing technique has been developed, which consists in applying a constant, and usually low, rate of tensile strain to the specimen. The test is obviously much more severe than the previous one, because in this case, given sufficient time, all materials will fail. Therefore, criteria for establishing whether or not a material is susceptible to SCC have to be chosen. A widely accepted criterion is based on the time to failure: if the environment shortens it, susceptibility to SCC is assumed. However, some uncertainty is introduced if corrosion during the test

thins the specimen, therefore affecting the time to failure, but microscopic and fractographic examination does not reveal any difference with a sample tested in the reference environment.

The problems arise when the material appears to be susceptible according to the slow strain rate test, but not under constant stress. In this case, it is a matter of judgement which test is more relevant to the application considered for the material. Other criteria, such as whether cracks are detected, or whether the mode of failure has changed, for instance from ductile to brittle, would be very important for reaching a conclusion. These problems have to be kept in mind when, after an examination of the empirical evidence, it has to be decided if certain mechanisms of SCC can represent a threat to the integrity of the HLW metal containers under repository conditions.

The first case to consider is that of the chances of pure copper to undergo SCC. Even with some uncertainties as to the mechanism operating, all known evidence indicates that brittle fracture occurs only under dynamic conditions, and it is hard to imagine how something like continuous strain can be applied to the HLW containers. The worrisome part is that environmental conditions that lead to T-SCC can occur at the site. A sufficient amount of nitrites could be generated by radiolysis, and, in view of the results of Aaltonen[22], they may not even be necessary.

The other failure mode observed in Cu, I-SCC in concentrated ammonia, seems to be rather remote. Reports on generation of NH_3 by radiolysis are conflicting. Perhaps NH_3 synthesis requires a significant concentration of H_2 in the air, which is unlikely. Thermal gradients and temperature cycling have caused at times large enrichments in ammonia, so as to cause cracking in condenser tubes. The likelihood of all these circumstances to happen, however, seems low.

Cu-Al alloys have cracked under constant stress, so that its occurrence cannot be excluded on mechanical reasons. It is in general true that Cu-Al alloys are less susceptible than brass to SCC, and that thorough stress relief of the containers would further lower the chances of cracking. Nevertheless, the only way to quantify the probability of SCC will depend on a better understanding of the repository environment, particularly concerning what accumulation of radiolysis products can reasonably

be expected, and how much water, either as a liquid or saturated steam, may collect around the containers.

Very similar arguments can be made for Cu-Ni, where the susceptibility is in general less than for Al alloys. The only transgranular cracking reported was in industrial atmospheres, and one cannot imagine circumstances creating gaseous pollutants within the repository.

A point which may deserve more attention is that little experimental work has been done on the effect of temperature on the cracking behavior of Cu-base alloys. One reference in the literature[22] suggests that there could be loss of ductility by testing at 80 C. Some experimental work, therefore, seems to be necessary in order to dispel possible doubts as to the behavior of the candidate materials at repository temperatures.

7. CONCLUSIONS AND RECOMMENDATIONS

It is apparent that the validity of any estimate of the likelihood of SCC depends heavily on a correct assessment of the repository conditions. Therefore, the principal conclusion to be made is that our knowledge of the local environment and of the alterations which will be caused by emplacing the HLW containers is too scanty to go beyond rather general statements.

It can be concluded, however provisionally, that

A) The probability of brittle fracture of pure copper is very low
B) The probability of SCC of Cu-Al, is low, but not insignificant
C) The probability of SCC of Cu-Ni is lower than Cu-Al, and in part depends on rather unlikely occurrences.

The principal recommendations concern our knowledge of the environment, but some specific testing for SCC susceptibility under relevant conditions is also advisable:

A) Air and water vapor transport inside the rock should be studied, and the effects of heating examined in detail.
B) The probability of localized liquid water flow should be assessed.
C) The thermal history of the rock close to the containers should be predicted with accuracy

greater than that available now, and the factors which could lead to significant variations examined.

D) The effects of radiolysis in a tuff environment should be studied, with particular concern to the possibility of accumulating radiolysis products.

E) The circumstances under which NH_3 can be formed should be understood.

F) To verify that there is no possibility of brittle fracture of pure Cu under constant stress, a series of experiments should be carried out in all environments where T-SCC has been reported.

G) Testing at temperatures in the 200 C to 100 C range is advisable, since little is known, at the present time, about the influence of temperature on the SCC of copper-base materials, particularly in the presence of high partial pressures of H_2O.

H) The temperature at which moisture condenses in a porous oxide or mixed oxide/salt layer should be determined as a function of the H_2O partial pressure.

REFERENCES

1. Site Characterization Plan. U. S. Department of Energy. December 1988.
2. U. Bertocci, F. I. Thomas, E. N. Pugh, Corrosion, 40, 439 (1984)
3. G. Hultquist, Corrosion Sci., 26, 173 (1986)
4. U. Bertocci and D. R. Turner, in "Encyclopedia of the Electrochemistry of the Elements", A. J. Bard, ed. Vol.2, Chapter 6, M.Dekker, New York (1974) U. Bertocci, D. D. Wagman, in "Standard Potentials in Aqueous Solutions", A. J. Bard, R. Parsons, J. Jordan, eds. p. 287. M. Dekker, New York (1985)
5. H. Leidheiser, "The Corrosion of Copper, Tin, and their Alloys", J. Wiley, New York (1971)
6. E. N. Pugh, W. G. Montague, A. R. C. Westwood, Trans. ASM, 58, 665 (1965)
7. B. C. Syrett, Corrosion Sci., 21, 187 (1981); L. E. Eiselstein, B. C. Syrett, S. S. Wing, R. D. Caliguri, ibid. 23, 223 (1983)
8. R. D. McCright, UCID-20509, Lawrence Livermore Laboratory (1985)
9. Handbook of Chemistry and Physics, 54 th Edition. p. F 56. CRC Press (1974)
10. W. Lin, W. Daily, UCLR-53602, Lawrence Livermore Laboratory (1984) W. Daily, W. Lin , T. Buschek, UCRL-94363, Lawrence Livermore Laboratory (1986)

11. P. Montazer, W. E. Wilson, USGS-WRI-84-4345, US Geological Survey (1984)
P. Montazer, E. P. Weeks, F. Thamir, S. N. Yard, P. B. Hofrichter, Proceedings of the NWWA Conference on Characterization and Monitoring of the Vadose (Unsaturated) Zone, Nov. 1985, Denver CO, p. 439. Nat. Water Well Assn, Worthington, OH. (1986)
12. D. T. Reed, R. A. Van Konyenburg, UCRL-97936 (1987)
13. R. S. Glass, G. E. Overturf, R. A. Van Konyenburg, R. D. McCright, UCRL-92311 (1985)
R. S. Glass, R. A. Van Konyenburg, G. E. Overturf, UCRL-92941 (1985)
14. W. G. Burns, A. E. Hughes, J.A.C. Marples, R.S. Nelson, J. Nucl. Mat., 107, 245 (1982)
15. E. N. Pugh, W. G. Montague, A. R. C. Westwood, Corrosion Sci., 6, 345 (1966)
16. E. N. Pugh, J. V. Craig, W. G. Montague, Trans. ASM Quarterly, 61, 468 (1968)
17. M. Said Saleet, Ph. D. Thesis, Iowa State University, Ames Laboratory (1986)
18. Y. Suzuki, Y. Hisamatsu, Corrosion Sci., 21, 353 (1981)
19. S. P. Pednekar, A. K. Agrawal, H. E. Chaung, R. W. Staehle, J. Electrochem. Soc., 126, 701 (1979)
20. J. Yu, R. N. Parkins, Corrosion Sci., 27, 159 (1987)
21. K. Sieradzki, R. L. Sabatini, R. C. Newman, Metall. Trans. A, 15A, 1941 (1984)
22. P. Aaltonen, H. Hanninen, H. Illi, M. Kamppainen, PVP, 99, 329 (1985)
23. T. B. Cassagne, Ph. D. Thesis, The Johns Hopkins University, Baltimore, MD (1988)
24. E. Escalante, J. Kruger, J. Electrochem. Soc., 118, 1062 (1971)
25. R. G. Johnston, Sheet Metal Ind., 14, 1197 (1940)
26. A. V. Bobylev, Intercrystalline Corrosion and Corrosion of Metals under Stress, I. A. Levin, ed. p. 298. Consultants Bureau, New York (1962)
27. H. E. Johnson , J. Leja, Corrosion, 22, 178 (1966)
28. H. W. Pickering, P. J. Byrne, Corrosion, 29, 325 (1973)
29. T. R. Pinchback, S. P. Clough, L. A. Heldt, Corrosion, 32, 469 (1976)
30. A. Kawashima, A. K. Agrawal, R. W. Staehle, J. Electrochem. Soc., 124, 1822 (1977)
31. A. Kawashima, A. K. Agrawal, R. W. Staehle, in "Stress Corrosion Cracking- The Slow Strain Rate Technique", G.M. Ugiansky, J.H. Payer, eds. ASTM STP 665, p. 266 (1979)

32. M. G. Alvarez, C. Manfredi, M. Giordano, J. R. Galvele, Corr. Sci., 24, 769 (1984)
33. J. Yu , N. J. H. Holroyd, R. N. Parkins, in "Environment-Sensitive Fracture: Evaluation and Comparison of Test Methods", P.288. ASTM STP 821 (1984)
34. R. N. Parkins, N. J. H. Holroyd, Corrosion, 38, 245 (1982)
35. E. Mattsson, Electrochim. Acta, 3, 279 (1961)
36. R. C. Newman. Private communication.
37. U. Bertocci, E. N. Pugh, Proc. of the 9th International Congress on Metallic Corrosion, p. 144. NRC of Canada, Ottawa (1984)
38. R. N. Parkins. Private communication.
39. A. W. Blackwood, N. S. Stoloff, Trans. ASM, 62, 677 (1969)
40. S. Sato, K. Nagata, Boshoku Gijutsu, 23, 125 (1974)
41. J. M. Popplewell, T. V. Gearing, Corrosion, 31, 279 (1975)
42. F. A. Champion, in "Symposium on Internal Stresses in Metal and Alloys", p. 468. Inst. of Metals, London (1948); H. L. Logan, J. Res. NBS, 48, 99 (1952)
43. H. S. Tong, Ph. D. Thesis, University of Illinois, Urbana-Champaign, IL (1977)
44. B. C. Syrett, R. N. Parkins, Corrosion Sci., 10, 197 (1970); M.
45. Kermani, J. C. Scully, ibid., 18, 883 (1978); J. A. Beavers, E. N. Pugh, Met. Trans. A, 11A, 809 (1980)
46. E. N. Pugh, Corrosion, 41, 517 (1985)
47. U. Bertocci, E. N. Pugh, in "Corrosion Chemistry within Pits, Crevices and Cracks", A. Turnbull, ed. p.187 .H. M. S. O. London (1984)
48. U. Bertocci, J. Electrochem. Soc., 136, 1357 (1989)
49. E. G. Coleman, D. Weinstein, W. Rostoker, Acta Met., 9, 491 (1961)
50. S. P. Lynch, in "Atomistics of Fracture", p. 955. Plenum Press New York, NY (1983)
51. H. W. Pickering, P. R. Swann, Corrosion, 19, 373 ((1963)
52. A. J. Forty, , in "Physical Metallurgy of Stress Corrosion Cracking", p. 99. Interscience, New York, NY (1959)
53. K. Sieradzki, R. C. Newman, Phil. Mag. A, 51, 95 (1985)

MECHANISMS OF ENVIRONMENTALLY INDUCED FRACTURE AND THEIR RELEVANCE TO STORAGE OF HLW IN THE TUFF ENVIRONMENT

PURPOSE

The purpose of this document is to evaluate our current understanding of the processes by which environments can induce crack initiation and propagation and to evaluate the limitations in using this understanding to model and predict high level waste (HLW) container failure rates in the TUFF environment.

SCOPE

This document will focus on environmentally induced cracking mechanisms which are currently considered viable by the research community. This is not intended to be a compendium of observations of cracking in a specific alloy system, but it is intended to be a review of mechanisms which may cause cracking in container alloys. It is hoped that by presenting this information in a brief concise format that it will aid the NRC staff in understanding and critically evaluating DOE's experiments and modeling efforts on environmentally assisted fracture.

1. INTRODUCTION

1.1 Definition

Environmentally induced fracture (EIF) is a generic term which encompasses a variety of cracking processes such as stress corrosion cracking (SCC), hydrogen embrittlement (HE) liquid metal embrittlement (LME), solid metal embrittlement (SME) and corrosion fatigue (CF). For HLW containers, SCC is the primary concern but HE may be a concern for some container alloys. The others will be a concern only if the TUFF environment deviates significantly from that expected due to human error during container fabrication, handling or emplacement or something else alters the environment.

1.2 Important Features

Stress corrosion cracks can initiate and propagate with little outside evidence of corrosion and no warning as catastrophic failure approaches. The cracks frequently initiate at surface flaws which are either pre-existing or

formed during service by corrosion, wear or other processes. These cracks may grow with little macroscopic evidence of mechanical deformation in metals and alloys which are normally quite ductile. Crack propagation can be either intergranular or transgranular and sometimes both types are observed on the same fracture surface. Crack openings and the deformation associated with crack propagation may be so small that the cracks are virtually invisible except to special non-destructive examinations. Usually, the stress intensity, plastic deformation and the crack opening increase as the crack grows and as final fracture is approached the plastic deformation becomes appreciable. However, for the repository the stress responsible for crack propagation may not be due to the application of a constant load and the stress intensity at the tip of a propagating crack may decrease as the cracks grows slowing propagation and, perhaps, arresting crack growth.

1.3 Causative Factors

Stress corrosion cracking is subcritical crack growth due to the combined and synergistic action of mechanical stress and corrosion reactions. For this form of crack propagation, both stress and corrosion are required. However, SCC is not ductile overload fracture at points of corrosion generated stress concentration. That is, SCC is not corrosion assisted ductile fracture nor is it stress assisted corrosion. SCC is crack propagation which occurs as a result of the interaction of chemical and mechanical factors at the crack tip. The exact nature of these interactions is the subject of research and numerous hypotheses have been proposed to explain the interactions that cause crack propagation and there may be more than one environmental interaction that can result in crack propagation. These "mechanisms" for crack propagation will be discussed in greater detail in a later section.

1.3.1 Tensile Stress

The tensile stress required to cause SCC is usually below the macroscopic yield stress and may be quite low. This stress is usually externally applied but, frequently, residual stresses cause SCC. In fact, the stresses which cause SCC may result from corrosion products if, as is usually the case, the volume of corrosion products is greater than the volume of the metal consumed. Continued growth of corrosion products inside a crack can act to "wedge open" the crack keeping the stresses at the crack tip high when, for many loading conditions, crack propagation would relieve the stress[1,25].

For the repository, the container should not experience external loading. However, geologic events could cause shearing of the rock which could then press against the container wall. Another possibility is that the bore hole could become filled with particulate or other deposits which become tightly packed so that when corrosion occurs, the volume increase that accompanies the corrosion reactions results in loading of the container wall. Careful design of the container, bore hole and bore hole liner could reduce the probability of these types of events and geologists may be able to estimate the probability of these types of events and demonstrate the they are insignificantly small. Similarly, careful design of the interior of the container, careful placement of the container contents and good design of container stiffeners or partitions (if they are used), so that dimensional changes due to corrosion or thermal oscillations do not case stresses, will eliminate the possibility of loading of the container wall from the inside. Then, the only potential sources of stress in the container wall are the natural loading due to the weight of the container and its contents and residual stresses. Careful design of the container, the fabrication processes and the bore hole will minimize these stresses but, they cannot be eliminated. Residual stresses could arise from fabrication processes such as welding or from handling of the container during fabrication or emplacement. Frequently, designers try to avoid SCC failure by avoiding tensile stress. Techniques such as stress relief annealing, shot peening (to generate compressive stresses at the surface) or loading critical components in compression instead of tension are frequently used. However, cases exist in the literature where SCC was observed in components that were designed to be free of tensile stress and it was not until after failures occurred that a source of stress was identified. As a result, the avoidance of tensile stresses is a desirable means of avoiding SCC but, it should not be relied upon.

1.3.2 Environmental Species

Usually, SCC is associated with bulk aqueous solutions but, SCC may occur in other environments. SCC can occur in organic solvents and has been observed in gaseous environments though a thin layer of condensed moisture may be responsible for these observations. SCC of stainless steel alloys 304, 316 and 347 in the vapor space above a heated (200 C) dilute chloride solution was reported in the late 1950's by Kirk et al.[2] and by Staehle et al.[3]. Cracking was observed in samples which were above the solution level of an autoclave with stresses as low as 2,000 psi and chloride (NaCl) concentrations as low as 50 ppm in the solution. These same alloys required chlorides

concentrations as high as 20,000 ppm and stresses as high as 30,000 psi for SCC to occur during total immersion in the solution. More recently, SCC has been observed for samples placed above the solution level in autoclaves partially filled with J13 water[4]. Since Staehle et al.[3] found that cracking could be prevented by shielding the samples from wetting by droplets of condensate, it appears that these failures are due to the drying and concentration of solutions on the surface of the samples. However, the low stresses and bulk chloride ion (or other halide ion) concentrations required to cause failure under these conditions and the possibility that similar wetting conditions may occur in the repository make this subject a candidate for further study.

1.3.3 Alloying Elements

Typically, SCC is considered to be alloy/environment dependent. That is, cracking of a specific alloy will occur only if certain environmental species are present in significant quantities, but another alloy may be unaffected by the same species. For example, in practice SCC of copper alloys is virtually always due to the presence of ammonia (though other environmental species can cause cracking of these alloys) while stainless steels and many other alloys exhibit SCC in environments that contain halide ions. Environmental factors such as temperature and pressure as well as chemical composition will influence crack propagation. Also, the exact chemical composition and metallurgical condition of the alloy can have a strong influence on the rate of SCC crack initiation and propagation. As a result, it is very difficult to identify a specific value for the concentration of a specific alloying element which will yield the alloy immune to cracking. Similarly, it is difficult to identify the maximum acceptable level of an aggressive environmental species which will not cause cracking as the value of this parameter will vary with the chemical composition of the alloy, the metallurgical condition of the alloy, the surface preparation technique, residual stresses in the sample, dissolved gasses in the test solution and surface films on the sample. As a result, complete characterization of the TUFF environment and characterization of the range of variations in this environment is a mandatory part of any experimental or theoretically modeling program. Also, the sample preparation techniques must reflect the surface conditions of the HLW container and the metallurgical and chemical composition of the container wall to be representative of the behavior expected in the repository.

Copson[6] and more recently Speidel[7] studied the influence of Ni content on the SCC susceptibility of Fe-Ni-Cr alloys

(stainless steels) in sodium chloride solutions and they found that as the concentration of Ni increased above about 20%, the resistance to SCC improves rapidly, figure 1. Speidel[7] also examined the influence of Mo on SCC and found that the stress required to initiate SCC increased with Mo content, figure 2. Table I is a comparison of the composition of the alloys in the reference alloy system for use as HLW container materials. By examining this table, it can be seen that the Ni and Mo content of the alloys in the reference alloy system (304L, 316L and 825) have considerably different Ni and Mo contents. Of course, the more expensive alloys contain more of these elements but, based on figure 1, they will have significantly greater resistance to SCC. It should be noted here that the alloy selection decision should be based on experiments conducted in the repository environment and not on these data which are from experiments in concentrated chloride solutions.

In general, SCC is observed in alloy-environment combinations which result in the formation of a film on the metal surface. These films may be thin passivating layers, tarnish films or dealloyed layers. In many cases, these films reduce the rate of general or uniform corrosion making the alloy desirable because of its resistance to other forms of corrosion in the environment. As a result, SCC is of greatest concern in the corrosion resistant alloys exposed to aggressive aqueous environments. The exact role of the film in the SCC process is the subject of research and will be discussed in the section on mechanisms.

2. SCC EXPERIMENTAL TECHNIQUES

2.1 Why Discuss Experimental Techniques

The SCC resistance of a material can be characterized or quantified by a variety of experimental techniques. The mechanisms that have been proposed to explain SCC are based on the physical observations that are made during these experiments and from the evaluation of service failures. As a result, before one can discuss SCC processes or mechanisms, one must clearly define the experimental techniques and the terminology upon which our understanding of SCC is based. Also, if engineering decisions are to be made on the basis of test results, then the decision makers must have some understanding of the actual physical meaning of the measurements they are using for the basis of their decisions and the advantages and limitations of each experimental technique.

2.2 Tests on Smooth Samples

The simplest type of test for SCC resistance is to apply a load to smooth samples, place them in the environment and then check them periodically to see if failure has occurred. There are two different ways that the load can be applied to these samples and each technique results in different behavior. First, the stress can be applied to the sample by the application of a fixed load to the sample. Since the load is constant for this type of test, the stress distribution around the tip of the propagating crack increases as the crack gets longer and the mechanical contribution to crack propagation increases as the crack grows until the crack fails by mechanical fracture of the remaining ligament of the sample. On the other hand, the stress could be applied to the sample through the application of a constant displacement. This is usually achieved by placing the sample in a rigid fixture and then deforming the sample a fixed amount with a bolt or some other device. For this type of loading, the compliance of the sample increases as the crack becomes longer and, usually, the mechanical contribution to crack propagation decreases as the crack grows and the crack may stop growing before failure occurs.

There are a large number of different loading schemes that are used for these types of tests but there are two that are frequently used by DoE for their tests that should be discussed here. First, the load can be applied by bending a flat sheet of the alloy into a "U" shape and holding in this shape with a bolt while exposing it to the environment. These "U-bend" samples are loaded by a fixed displacement but, the displacement is very large with respect to the compliance changes that occur during crack propagation and SCC cracks rapidly propagate to failure once they initiate in these samples. The second type of test is the slow strain rate test (SSRT). This test is frequently referred to as the constant extension rate test (CERT), slow extension rate test (SERT) or the straining electrode test. For these experiments, a sample is loaded in tension by a machine which very slowly increases the load in the sample by increasing the displacement applied to the sample at a constant rate (typically 1×10^{-6} in·■s^{-1}). This has been found to be a severe test and some materials that do not fail in service demonstrate a susceptibility in this test. The severity of this test is usually attributed to the fact that during this test the constant straining results in the rupture of the normally protective surface films stimulating corrosion and crack initiation. However, one cannot conclude that the slow strain rate test is a definitive test of SCC susceptibility because the environment used in the

test may not accurately reflect the environmental conditions that occur in service. For example, Westerman et al.[4] conducted SSR tests under conditions of complete immersion in J-13 water and found no indication of cracking but, during their autoclave tests, samples failed by cracking in the environment where alternate immersion may have occurred. That is, alternate wetting and drying, condensed moisture, pitting or crevice corrosion conditions may not be accurately modeled during the test and these may lead to crack initiation and failure in service. Several investigators have tried variations on this test method in order to improve the ability of this method to evaluate SCC susceptibility under different corrosion conditions.

For smooth samples, corrosion reactions begin immediately on immersion but crack initiation may not occur until after some incubation time. The processes which cause crack initiation are not thoroughly understood and this is a difficult phenomena to study because crack initiation is a relatively small event requiring special equipment to observe it and may not actually be a discrete event but instead a continuous growth process. Once a crack has initiated, it then propagates by some time dependent mechanism. The different phenomena that have been postulated for this growth mechanism will be discussed in section 3. It is not clear at this time whether or not the mechanism of crack initiation is the same as that of crack propagation. As a result, the time to failure is the sum of the time required for crack initiation and the time required for crack propagation or

$$t_f = t_{in} + t_{cp} \qquad (1)$$

The results of these tests may be plotted as number of failures for a given time or as time to failure as a function of the applied stress as shown in figure 3. In this figure, it can be seen that the time to failure appears to asymptotically approach infinity at a stress which is commonly referred to as the threshold stress s^{th}). However, there are several problems with this type of approach. First, since the time to failure is the sum of the time spent in crack initiation and crack propagation, the measured times to failure are for the specific sample size and shape. Second, since crack initiation is dependent on the surface finish and the presence of flaws in this finish, the time to failure in dependent on the surface finish. Third, since you cannot easily identify the point of crack initiation, then you cannot quantify the rate of each stage from these results. And finally, corrosion damage to the surface during environmental exposure will increase the

magnitude of the stress at surface flaws and generate new flaws making evaluation of a cracking threshold stress difficult, time consuming and highly questionable. These are not techniques which readily contribute information to SCC failure prediction models. As a result, the use of these types of tests for lifetime prediction models which will asses the probability of failure by SCC is questionable and probably would require samples that emulated the container size, shape and surface condition as much as possible. However, these types of test (especially the slow strain rate tensile test) are excellent ways of characterizing the relative susceptibility of different alloys to SCC in different environments and are useful for demonstrating that a material is not susceptible to SCC in a given environment keeping in mind that the test environment must accurately reflect the environment and not just the ideal environment but all reasonable variations.

2.3 Crack Propagation Experiments

Since the results of tests on smooth samples vary with sample size shape and surface finish, they do not readily lend themselves to mathematical quantification of SCC behavior and the prediction of time to failure or failure rates. As a result, researchers have looked for a more thorough approach to the measurement of SCC behavior, breaking down the failure process into stages and quantifying the behavior in each stage. Normally, SCC crack propagation is divided into three stages: (1) crack initiation and early propagation, (2) steady state propagation and (3) accelerated propagation rates due to contributions of ductile processes at the crack tip. These stages are not distinctly different and transition between these stage occurs in a continuous manner with the distinction between the stages being arbitrary. Since for most SCC crack propagation conditions the bulk environment does not change during the course of crack propagation, the only significant difference between these stages is the mechanical contribution to crack propagation although the applied load or the nominal stress has not changed. That is, as the crack grows the magnitude of the stress concentration at the crack tip changes. Therefore, before one can study crack propagation rates, one must have a method for quantifying the influence of stress on stress distribution at a crack tip because it is this stress and not the macroscopically applied load or the nominal stress that is responsible for crack propagation. Fortunately, a method for doing this exists and has been used for a considerable number of years by the fracture, fatigue and SCC research communities. Figure 4 is a diagram of the stress distribution that is predicted by the assumptions of continuum mechanics and linear elasticity. This combination

of linear elasticity and continuum mechanics to calculate stress distributions to determine fracture behavior is frequently referred to as linear elastic fracture mechanics (LEFM). The assumption of linear elasticity has some limitations one of which is evident in figure 4. In this figure it can be seen that the assumption of linear elastic behavior leads to a stress normal to the fracture plane that approaches infinity at the crack tip for any nominal applied stress. As a result, the assumptions of LEFM have to be modified to accommodate the occurrence of plastic behavior in a small zone at the crack tip. This can be done rather simply by assuming that the stress at the crack tip cannot exceed the bulk yield stress and a zone of plastically deformed material forms at the crack tip. More thorough corrections for plasticity are the subject of research but for this discussion this simple explanation is sufficient. This important feature of figure 4 is the relationship between the applied stress and the stress distribution at the crack tip.

$$\sigma_{yy} = \frac{K}{\sqrt{2\pi r}} \cos\frac{\theta}{2}\left[1+\sin\frac{\theta}{2}\sin\frac{3\theta}{2}\right] \qquad (2)$$

This relationship can be broken into two parts. The first part contains terms which describe the location of the volume element of interest. The second contain the terms that describe the external loading parameters and their magnitude. That is, the stress distribution around any crack is essentially the same only the magnitude changes. Of course, the "plastic zone" changes with the applied stress. If we combine all of the external loading factors into a single term, we get

$$K = Y\sigma\sqrt{\pi a}$$

$$Y = \text{Crack geometry and shape factor} \qquad (3)$$

which is the "stress intensity factor" for the crack. This stress intensity factor or K for the crack describes the magnitude of the stress distribution at the crack tip. For the same nominal applied stress, the magnitude of the stress distribution at the crack tip can vary considerably for different values of the other parameters in equation (3). As a result, the quantification of the mechanical driving force which causes crack propagation is more accurately reflected by the stress intensity factor than by the nominal applied stress. However, in order to quantify the stress intensity factor, all of the terms given in equation (3)

must be accurately known for the sample. This requires careful design, fabrication and measurement of the sample and the crack length. As a result, these types of tests are more expensive and time consuming and best for environment/material combinations where crack initiation is not difficult.

Frequently, the results of crack propagation experiments are presented by plotting the rate of crack growth (da/dt) against the stress intensity factor as shown in figure 5. In this figure the three stage of crack propagation can be seen. Once a crack has initiated, the crack will propagate in the manner shown in figure 5. For constant load tests, the initial stress distribution at the crack tip, as quantified by the stress intensity factor (K), is low and increases as the crack grows. As a result, the crack velocity will initially increase with crack length or K as shown for stage 1 in figure 5. However, as the crack grows the crack velocity will approach a value which will be relatively constant with respect to crack length over a relatively large range of stress intensities as shown in the region labeled stage 2 in figure 3. Eventually, as this crack propagates, the stress in the remaining ligament of the sample will reach the fracture stress (K_c) and the remaining ligament fails by rapid critical fracture as shown in the region of figure 3 labeled stage 3.

Tests on statically loaded pre-cracked samples are usually conducted with either a constant applied load or with a fixed crack opening displacement and the actual rate or velocity of crack propagation (da/dt) is measured[8]. The magnitude of the stress distribution at the crack tip (the mechanical driving force for crack propagation) is quantified by the stress intensity factor (K) for the specific crack and loading geometry. As a result, the crack propagation rate (da/dt) is plotted versus K as illustrated in figure 5. These tests can be configured such that K either increases with crack length (constant applied load), decreases with increasing crack length (constant crack mouth opening displacement) or approximately constant as the crack length changes (special tapered samples). Each type of test has its advantages and disadvantages. However, in service, most SCC failures occur under constant load conditions such that the stress intensity increases as the crack propagates. As a result, it is usually assumed in SCC discussions that the stress intensity is increasing with increasing crack length.

Typically, three regions of crack propagation rate versus stress intensity level are found during crack propagation experiments. These are identified according to increasing stress intensity factor as stage 1,2 or 3 crack propagation

as shown in figure 2. No crack propagation is observed below some threshold stress intensity level (K_{Iscc}). This threshold stress level is determined not only by the alloy but also by the environment and metallurgical condition of the alloy and, presumably, this level corresponds to the minimum required stress level for synergistic interaction with the environment. At low stress intensity levels (stage 1), the crack propagation rate increases rapidly with the stress intensity factor. At intermediate stress intensity levels (stage 2), the crack propagation rate approaches some constant velocity which is virtually independent of the mechanical driving force. This plateau velocity is characteristic of the alloy-environment combination and is the result of rate limiting environmental processes such as mass transport of environmental species up the crack to the crack tip. In stage 3, the rate of crack propagation exceeds the plateau velocity as the stress intensity level approaches the critical stress intensity level for mechanical fracture in an inert environment (K_{Ic}).

3. MECHANISMS

3.1 Types of Mechanisms

There are a large number of different mechanisms which have been proposed to explain the synergistic stress corrosion interaction that occurs at the crack tip and there may be more than one process which causes SCC. The proposed mechanisms can be classed into two basic categories:

1. Anodic Mechanisms
2. Cathodic Mechanisms

That is, during corrosion, both anodic and cathodic reactions must occur and the phenomena that results in crack propagation may be associated with either class of reactions. The most obvious anodic mechanism is that of simple active dissolution and removal of material from the crack tip. The most obvious cathodic mechanism is hydrogen evolution, absorption, diffusion, and embrittlement. However, a specific mechanism must attempt to explain the actual crack propagation rates, the fractographic evidence and the mechanism of formation or nucleation of cracks. A very large number of mechanisms have been proposed and not all of these will be discussed here. This discussion will focus on the viable mechanisms for crack propagation of those that have been proposed and will attempt to group similar mechanisms rather than discuss each proposal individually. To demonstrate that SCC will not occur in the repository, it will have to be demonstrated that none of the proposed and viable mechanisms of crack propagation can occur in any of the expected or reasonably possible

repository environments. This assumes that the scientific community has identified all of the possible mechanisms but this may be accounted for by conducting exposure test to verify the modeling of the SCC behavior.

SCC mechanisms can be divided into two catagories based on the mechanism that they assume causes the breaking of the interatomic bonds at the crack tip. There are basically two different mechanisms for this bond breaking process and these are:

1. Chemical solvation and dissolution
2. Mechanical fracture (Ductile or Brittle)

Item (2) above includes "normal" fracture processes which are assumed to be stimulated or induced by one of the following interactions between the material and the environment:

1. Adsorption of environmental species
2. Surface reactions
3. Reactions in the metal ahead of the crack tip
4. Surface films

All of the proposed mechanisms contain one or more of these processes as an essential step in the SCC process. Specific mechanisms differ in the processes assumed to be responsible for crack propagation and the way that environmental reactions combine to result in the actual fracture process.

3.2 Crack Propagation Mechanisms

As indicated by the discussion above, it is unlikely that a single mechanism of stress corrosion cracking exists, but that there are two or three different operative mechanisms. Many models have been proposed, but only those considered viable will be discussed here and, for the sake of space, the differences between similar but different mechanisms will not be discussed in great detail.

The proposed mechanisms for crack propagation fall into two basic classifications, namely those based on dissolution as the principle cause of crack propagation and those that involve mechanical fracture in the crack propagation process.

3.2.1 Dissolution Models

According to models of this type, the crack advances by preferential dissolution at the crack tip. A number of models have been proposed to account for this process. For

example, preferential dissolution at the crack tip has been attributed to the formation of active paths in the material, stresses at the crack tip and chemical-mechanical interactions[9,10,11,12,13,14].

However, research has essentially eliminated all but one model from serious consideration and recent debate has centered on the details of this model.

Film Rupture: The film rupture model, also referred to as the slip-dissolution model, assumes that the stress acts to open the crack and rupture the protective surface film. Champion[15] and Logan[16], working independently, first postulated that localized plastic deformation at the crack tip ruptures the passivating film exposing bare metal at the crack tip. The freshly exposed bare metal then dissolves rapidly resulting in crack extension. Some investigators[17,18,19] assume that once propagation starts, the crack tip remains bare as the rate of film rupture at the crack tip is greater than the rate of repassivation, figure 6(a). Others[20,21,22,23], assume that the crack tip repassivate completely and is periodically ruptured by the emergence of slip steps, figure 6(b).

Considerable evidence has been found to support these mechanistic models and intergranular corrosion may be considered the low stress limiting case of this mechanism[24]. However, the observation of discontinuous cracking and crack arrest markings (discussed in the proceeding sections) is an indication that crack propagation can and frequently is discontinuous. Also, T-SCC fracture surfaces are flat, crystallographically oriented and match precisely on opposite sides of the fracture surface (indicating very little dissolution during crack advance). As a result, film-rupture and dissolution is accepted as a viable mechanism of I-SCC in some systems, but it is not generally accepted as a mechanism of T-SCC[24].

3.2.2 Mechanical Fracture Models

Mechanical fracture models originally assumed that stress concentration at the base of corrosion slots or pits increased to the point of ductile deformation and fracture[14]. These early proposals assumed that the crack essentially propagated by dissolution and then the remaining ligaments failed by mechanical fracture (ductile or brittle). Swann and Pickering[25], Swann 1965, #R32] proposed a refinement of this approach which is generally known as the corrosion tunnel model.

The Corrosion Tunnel Model: In this model, it is assumed that a fine array of small corrosion tunnels form at

emerging slip steps. These tunnels grow in diameter and length until the stress in the remaining ligaments causes ductile deformation and fracture. The crack thus propagates by alternating tunnel growth and ductile fracture, figure 7. Cracks propagating by this mechanism should result in grooved fracture surfaces with evidence of microvoid coalescence (MVC) on the peaks as illustrated in figure 7(a). This is not consistent with the common fractographic features discussed in the proceeding sections. As a result, Silcock and Swann[26] suggested that the application of a tensile stress results in a change in the morphology of the corrosion damage from tunnels to thin flat slots as shown in figure 7(b). They observed the formation of slots below the dealloyed sponge layer on the {110} type planes in austenitic stainless steels and they found that the formation of these slots required the presence of a tensile stress[26]. The width of the corrosion slots was found to approach atomic dimensions and, as a result, close correspondence of matching fracture surfaces would be expected. Silcock and Swann[26] concluded that T-SCC can be explained in terms of the formation and mechanical separation of corrosion slots.

Adsorption Enhanced Plasticity: Studies of liquid metal embrittlement (LME), hydrogen embrittlement (HE), and SCC have led Lynch to conclude that similar fracture processes occur in each case[27,28,29]. Since chemisorption is common to all three, it was concluded[28] that this process must be responsible for the environmental induced crack propagation. Based on this and the hypothesis that cleavage fracture is not an atomically brittle process but occurs by alternate slip at the crack tip in conjunction with formation of very small voids ahead of the crack. Lynch[27,28,29] proposed that chemisorption of environmental species facilitated the nucleation of dislocations at the crack tip promoting the shear processes responsible for brittle cleavage like fracture [R35-39]. The origin of crack arrest markings by this mechanism is uncertain. Nevertheless, this mechanism promises to explain many similarities between SCC and LME and HE[27,28,29,30,31].

The Tarnish Rupture Model: This model was first proposed by Forty and Humble[32] to explain T-SCC, but was later modified by other workers[33,34,35] to explain I-SCC. In the original model [R40], a brittle surface film forms on the metal which fractures under the applied stress. Fracture of the film exposes bare metal which rapidly reacts with the environment to reform the surface film. The crack propagates by alternating film growth and fracture as shown in figure 8(a). This hypothesis was latter modified[34,35] to explain I-SCC based on the assumption that the oxide film penetrates along the grain boundary ahead of the crack tip

as shown in figure 8(b). Again, crack propagation is composed of alternating periods of film growth and brittle film fracture. Film growth requires transport of species across the film and, as a result, the thickness of the film is limited in the absence of stress[35]. This model predicts crack arrest markings on intergranular fracture surfaces and discontinuous acoustic emission during crack propagation which are not always observed during I-SCC. Also, it assumes penetration of the film into the grain boundary ahead of the crack tip which may not be the case for all systems[37]. At present, there are insufficient experimental results to either confirm or refute this model[34,35].

The Film Induced Cleavage Model: In 1959, Forty[38] presented the hypothesis that dealloying and/or vacancy injection could induce brittle fracture. However, the exact nature of the interactions and how they could induce the observed crack propagation was not thoroughly evaluated. More recently, Sieradzki and Newman[39] have developed a model based on the hypothesis that a surface film could induce cleavage fracture. Their model assumes that (1) a thin surface film or layer forms on the surface, (2) a brittle crack initiates in this layer, (3) the brittle crack crosses the film/matrix interface with little loss in velocity, (4) that once in the ductile matrix the brittle crack will continue to propagate and (5) that eventually this crack will blunt and arrest after which this process repeats itself. This model has the unique ability to explain the crack arrest markings, the cleavage-like facets on the fracture surface and the discontinuous nature of crack propagation.

The hypothesis that a brittle crack will continue to propagate after it has entered the normally ductile matrix is a critical point. This allows a thin surface layer to induce brittle crack propagation over distances much greater than the film thickness. Lin and Thomson[40] critically examined this hypothesis and concluded that a brittle crack can propagate in a ductile matrix if the crack is sharp and is propagating at high velocities before entering the ductile matrix. Dienes et al.[41] developed a computer model for this process and concluded that a surface layer can initiate brittle fracture even if the layer is ductile (depending on lattice mismatch etc.). More research into surface films and brittle fracture is required before this model can be thoroughly evaluated.

Adsorption Induced Brittle Fracture: This model was initially proposed by Uhlig[12] and it is based on the hypothesis that adsorption of environmental species lowers the interatomic bond strength and the stress required for cleavage fracture. This model is frequently referred to as

the "stress-sorption" model and similar mechanisms have been proposed for HE and LME[42]. This model predicts that cracks should propagate in a continuous manner at a rate determined by arrival of the embrittling species at the crack tip. This model does not explain how the crack maintains an atomically sharp tip in a normally ductile material since it includes no provision to limit deformation in the plastic zone. Also, the discontinuous nature of crack propagation is not explained by this model.

Hydrogen Embrittlement: Stress corrosion cracking can in some material-environment combinations be a form of hydrogen induced subcritical crack growth. Because the anodic reaction must have a corresponding cathodic reaction and because the reduction of hydrogen is frequently the cathodic reaction, hydrogen induced subcritical crack growth can be the dominant stress corrosion crack growth process in some materials. Many features of hydrogen induced subcritical crack growth from cathodic hydrogen are very similar to those produced by gaseous or internal hydrogen. The mechanisms of hydrogen damage are covered in the following sections and will therefore not be discussed here. However, there are a few features of hydrogen embrittlement from cathodic hydrogen which are unique from other forms of hydrogen embrittlement which will be summarized.

Once hydrogen has been absorbed by a material, its effect whether from a gaseous or cathodic source is the same. This has been shown for a number of material and a variety of properties. The major differences between gaseous and cathodic hydrogen absorption processes include: (1) cathodic hydrogen absorption the surface as atomic hydrogen (as reduced) while gaseous hydrogen absorbs in the molecular form and must dissociate to form atomic hydrogen. Desorption of loosely bound molecular hydrogen is relatively easy while the dissociation step can, under some circumstances, be the rate determining step. Therefore, the desorption and absorption rates of gaseous and cathodic hydrogen may be substantially different for equal hydrogen activities; (2) the hydrogen activities produced by cathodic hydrogen can be quite large (from the Nernst equation) and are dependent on the reaction rates while gaseous hydrogen pressures are generally quite low; and (3) the surface of the material at a crack tip may be substantially different under electrochemical corrosion conditions from that in the presence of gaseous hydrogen containing substantial other gases such as O_2, CO_2, etc.

Ferritic steels show the most evidence of hydrogen induced subcritical crack growth as a stress corrosion cracking mechanism. The effects of yield strength, impurity segregation, temperature, etc. on the crack growth behavior

of ferritic materials in aqueous environments all follow thetrends of gaseous hydrogen embrittlement. As a example, the crack growth rate of a 3% Ni steel as a function of temperature in water is shown in figure 9(a) while the crack growth rates of 4340 steel in gaseous hydrogen is shown in figure 9(b). The maximum in the crack growth rate at about 20 C with a decrease at higher and lower temperatures is very similar; however, anodic stress corrosion processes become active at temperatures above 100 C for the steel tested in water. Similar trends have been shown for impurity segregation effects on hydrogen induced crack growth of materials where cathodic and gaseous hydrogen produce essentially similar results.

Specific mechanisms of cathodic hydrogen induced subcritical crack growth have not been developed because it has generally been sufficient to merely identify hydrogen as the cause of cracking; however, Latanision and Oppenhauser[43] presented a mechanism in which grain boundaries act as hydrogen recombination poisons and enhance the uptake of cathodic hydrogen. A schematic of this process is shown in figure 10 where Sn and Sb segregation to the grain boundaries of Ni enhance the hydrogen uptake kinetics. This mechanism does not propose a new mechanism by which hydrogen can cause cracking but merely proposes a mechanism by which impurity segregation can enhances hydrogen uptake. There may be circumstances where such a mechanism could tip the scales between an anodic and cathodically driven process or could accelerate cracking to a value which is measurable or of practical significance. However, in a review by Jones[44] on the combined effects of impurity segregation and hydrogen embrittlement, it was concluded that grain boundary impurities behave the same with cathodic and gaseous boundary embrittlement processes but not by enhanced hydrogen uptake. It should be noted that a material with impurities such as S, P, Sb, and Sn segregated to their grain boundaries are more susceptible to all forms of hydrogen whether cathodic, gaseous or internal.

4. CONTROLLING PARAMETERS

The mechanisms which have been proposed for SCC require that certain processes or events occur in sequence for sustained crack propagation to be possible. These requirements explain the plateau region where the rate of crack propagation is independent of the applied mechanical stress. That is, a sequence of chemical reactions and processes are required and the rate limiting step in this sequence of events determines the limiting rate or plateau velocity of crack propagation (Until mechanical overload fracture starts contributing to the fracture process in stage 3.). Figure 11 illustrates a crack tip where crack propagation results

from reactions in metal ahead of the propagating crack. By examining this figure it can be seen that potential rate determining steps include:

1. Mass transport along the crack to the crack tip
2. Reactions in the solution near the crack
3. Surface adsorption at or near the crack tip
4. Surface diffusion
5. Surface reactions
6. Absorption into the bulk
7. Bulk diffusion to the plastic zone ahead of the advancing crack
8. Chemical reactions in the bulk
9. The rate of interatomic bond rupture

Changes of the environment that modify the rate determining step will have a dramatic influence on the rate of crack propagation while alterations to factors not involved in the rate determining step or steps will have little influence if any. However, significantly retarding the rate of any one of the required steps in the sequence could make that step the rate determining step. In aqueous solutions, the rate of adsorption and surface reactions is usually very fast compared to the rate of mass transport along the crack to the crack tip. As a result, bulk transport into this region or reactions in this region are frequently believed responsible for determining the steady state crack propagation rate or plateau velocity. In gaseous environments, surface reactions, surface diffusion and adsorption may be rate limiting as well as the rate of bulk transport to the crack tip[45,46].

Several different environmental parameters are known to influence the rate of crack growth in aqueous solutions. These include but are not limited to:

1. Temperature
2. Pressure
3. Solute species
4. Solute concentration and activity
5. pH
6. Electrochemical potential
7. Solution viscosity
8. Stirring or mixing

Altering any of these parameters may alter the rate of the rate controlling steps either accelerating or reducing the rate of crack propagation. Also, it may be possible to arrest or stimulate crack propagation by altering the rate of an environmental reaction. It is well known and generally accepted that the environment at occluded sites such as a crack tip can differ significantly from the bulk

solution. If an alteration to the bulk environment allows the formation of a critical SCC environment at a crack nuclei, then crack propagation will result. If the bulk environment cannot maintain this local crack tip environment, then crack propagation will stop. As a result, slight changes to the environment may have a dramatic influence on crack propagation while dramatic changes may have only a slight influence.

In addition to the environmental parameters listed above. Stress corrosion crack propagation rates are influenced by:

I. The magnitude of the applied stress or the stress intensity factor
II. The stress state
    1. plane stress
    2. plane strain

III. The loading mode at the crack tip
IV. Alloy composition
    1. Nominal composition
    2. Exact composition (all constituents)
    3. Impurity or tramp element composition
V. Metallurgical condition
    1. Strength level
    2. Second phases present
        a. in matrix
        b. at grain boundary
    3. Composition of phases
    4. Grain size
    5. Grain boundary segregation
    6. Residual Stresses
VI. Crack geometry
    1. Length, width and aspect ratio
    2. Crack opening and crack tip closure

CONCLUSIONS

Stress corrosion cracking is a complex subject and the mechanism or mechanisms that cause failure are still subject of scientific debate. Modeling the container lifetime or susceptibility based on mechanistic models will have to incorporate all viable models for SCC. The factors that control susceptibility are not thoroughly understood and little research has been conducted into the crack initiation process.

References

1. W. R. Cieslak, The Role of Crevice Corrosion in the Stress Corrosion Cracking of Fe-29Ni-17-Co, Corro., 44, (8) 1988, 517-526.

2. W. W. Kirk, F. H. Beck and M. G. Fontana, Stress Corrosion Cracking of Austenitic Stainless Steels in High Temperature Chloride Waters, Physical Metallurgy of Stress Corrosion Fracture, T. N. Rhodin, Interscience Publishers, New York, (1959) 227-243.

3. R. W. Staehle, F. H. Beck and M. G. Fontana, Mechanism of Stress Corrosion of Austenitic Stainless Steels in Chloride Waters, Corro., 15, (7) 1959, 373-381.

4. R. E. Westerman, S. G. Pitman and J. H. Haberman, Corrosion Testing of Type 304L Stainless Steel in TUFF Groundwater Environments, Lawrence Livermore National Laboratory, UCRL-21005, SANL 616-007, November, 1988.

5. K. Tamaki, S. Tsujikawa and Y. Hisamatsu, Development of a New Test Method for Chloride SCC of Stainless Steels in Dilute NaCl Solutions, Advances in Localized Corrosion, H. Issacs, U. Bertocci, J. Kruger and S. Smialowska, 9, NACE, Houston , TX, (1990) 207-214.

6. H. R. Copson, Effect of Compositin on Stress Corrosin Cracking of Some Alloys Containing Nickel, Physical Metallurgy of Stress Corrosion Fracture, T. N. Rhodin, Interscience, New York, (1959) 247-272.

7. M. O. Speidel, Stress Corrosion Cracking of Stainless Steels in NaCl Solutions, Metall. Trans. A, 12A, (5) 1981, 779-789.

8. C. J. Beevers, The Measurement of Crack Length and Shape During Fracture and Fatigue, Chameleon Press Ltd., London, (1980).

9. E. H. Dix, Trans AIME, 137, (11) 1940,

10. R. B. Mears, R. H. Brown and E. H. Dix, Sym. on Stress-Corrosion Cracking of Metals, ASTM-AIME, 1944, 323.

11. E. H. Dix, Trans ASM, 42, 1950, 1057.

12. H. H. Uhlig, New Perspectives in the Stress Corrosion Problem, Physical Metallurgy of Stress Corrosion Fracture, T. N. Rhodin, Interscience, New York, (1959) 1-28.

13. L. Yang, G. T. Horne and G. M. Pound, Effect of Elastic Strain on the Electrode Potential of Metals, Physical Metallurgy of Stress Corrosion Fracture, T. N. Rhodin, Interscience, New York, (1959) 29-46.

14. J. J. Harwood, Stress Corrosion Cracking and Embrittlement, W. D. Robertson, J. Wiley and Sons, Inc., New York, (1956) 1.

15. F. A. Champion, Symposium on Internal Stresses in Metals and Alloys, Inst of Metals, London, (1948).

16. H. L. Logan, Film Rupture Mechanism of Stress-Corrosion, J. Res. NBS, 48, 1952, 99.

17. E. W. Hart, Surfaces and Interfaces II, Syracuse Univ. Press, Syracuse, NY, (1968) 210.

18. H. J. Engel, The Theory of Stress Corrosion Cracking in Alloys, NATO, Brussels, (1971)

19. J. C. Scully, Corro. Sci., 15, 1975, 207.

20. D. A. Vermilyea, J. Electrochem. Soc., 119, 1972, 405.

21. D. A. Vermilyea, Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Based Alloys, National Association of Corrosion Engineers, Houston TX, (1977) 208.

22. R. W. Staehle, The Theory of Stress Corrosion Cracking in Alloys, NATO, Brussels, (1971) 223.

23. R. W. Staehle, Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Based Alloys, National Association of Corrosion Engineers, Houston TX, (1977) 180.

24. E. N. Pugh, Progress Towards Understanding the Stress Corrosion Problem, Corro, 41, (9) 1985, 517-526.

25. H. W. Pickering and P. R. Swann, Corro., 19, 1963, 373.

26. J. M. Silcock and P. R. Swann, Nucleation and Growth of Transgranular Stress Corrosion Cracks in Austenitic Stainless Steels, Environment-Sensitive Fracture of Engineering Materials, Z. A. Foroulis, TMS of AIME, Warrendale, PA, (1979) 133-152.

27. S. P. Lynch, A Comparative Study of Stress-Corrosion Cracking, Hydrogen-Assisted Cracking and Liquid-Metal Embrittlement in Al, Ni, Ti and Fe-based Alloys, Hydrogen Effects in Metals, A. W. Thompson and I. M. Bernstein, TMS, Warrendale, PA, (1981) 863.

28. S. P. Lynch, Cleavage Fracture in Face-Centered Cubic Metals, Metal Sci., 15, (10) 1981, 463-467.

29. S. P. Lynch, Mechanisms of Stress-corrosion Cracking and Liquid-metal Embrittlement in Al-Mg-Zn Bicrystals, J. of Matls. Sci., 20, 1985, 3329-3338.

30. N. S. Stoloff and T. L. Johnston, Acta Metall., 11, 1963, 251-256.

31. C. D. Beachem, A New Model for Hydrogen-Assisted Cracking (Hydrogen "Embrittlement"), Met Trans, 3, (2) 1972, 437.

32. A. J. Forty and P. Humble, Phil Mag, 8, 1963, 247.

33. A. J. McEvily and A. P. Bond, On the Initiation and Growth of SCC in Tarnished Brass, J. Electrochem. Soc., 112, (2) 1965, 131-138.

34. E. N. Pugh, A Post Conference Evaluatio of Our Understanding of the Failure Mechanisms, Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Based Alloys, NACE, Houston, TX, (1977) 37-51.

35. J. A. Beavers, I. C. Rosenberg and E. N. Pugh, The Role of Intergranular Attack in Stress-Corrosion Phenomenon, Tri-Service Conference on Corrosion, MCIC-73-19, (1973) 57-67.

36. T. R. Pinchback, S. P. Clough and L. A. Heldt, Stress Corrosion Cracking of Alpha Brass in a Tarnishing Ammoniacal Environment: Fractography and Chemical Analysis, Metallurgical Transactions A, 6A, (8) 1975, 1479-1483.

37. T. R. Pinchback, S. P. Slough and L. A. Heldt, Stress Corrosion Cracking of Alpha Brass in a Nontarnishing Ammoniacal Environment: Fractography and Chemical Analysis, Metall. Trans. A, 7A, (8) 1976, 1241-1243.

38. A. J. Forty, The Initiation and Propagation of Cracks in the Stress Corrosion of Alpha-Brass and Similar Alloys, Physical Metallurgy of Stress Corrosion Fracture, T. N. Rhodin, Interscience, New York, (1959) 99-120.

39. K. Sieradzki and R. C. Newman, Brittle Behavior of Ductile Metals During Stress-corrosion Cracking, Phil. Mag. A, 51, (1) 1985, 95-132.

40. I.-H. Lin and R. M. Thomson, Dynamic Cleavage in Ductile Materials, J. Mater. Res, 1, (1) 1986, 73-80.

41. G. J. Dienes, K. Sieradzki, A. Paskin and B. Massoumzadeh, Critical Film Properties for Epitaxy, Surf. Sci., 144, 1984, 273-289.

42. N. S. Stoloff, Recent Developments in Liquid-Metal Embrittlement, Environment-Sensitive Fracture of Engineering Materials, Z. A. Foroulis, TMS of AIME, Warrendale PA, (1979) 486-518.

43. R. M. Latanision, O. H. Gastine and C. R. Compeau, Stress Corrosion Cracking and Hydrogen Embrittlement: Differences and Similarities, Environment-Sensitive Fracture of Engineering Materials, Z. A. Foroulis, TMS of AIME, Warrendale PA, (1979) 48-70.

44. R. H. Jones, A Review of Combined Impurity Segregation-Hydrogen Embrittlement Processes, Advances in the Mechanics and Physics of Surfaces, R. M. Latanision and T. E. Fischer, Scientific and Technical Book Service, (1986)

45. D. P. Williams and H. G. Nelson, Embrittlement of 4130 Steel by Low-Pressure Gaseous Hydrogen, Metall. Trans., 1, (1) 1970, 63-68.

46. R. E. Ricker and D. J. Duquette, The Role of Environment on Time Dependent Crack Growth, Micro and Macro Mechanics of crack Growth, K. Sadananda, B. B. Rath and D. J. Michel, TMS-AIME, Warrendale PA, (1982) 29.

TABLE I

SUBJECT	ALLOY 1	ALLOY 2	ALLOY 3
Common Desgn.	304L	316L	825
UNS Desgn.	S30403	S31603	N08825
Wt. % C	0.03%	0.03%	0.03%
Wt. % Mn	2.00%	2.00%	1.00%
Wt. % P	4.50%	4.50%	*
Wt. % S	3.00%	3.00%	3.00%
Wt. % Si	1.00%	1.00%	0.50%
Wt. % Cr	18.00-20.00%	16.00-18.00%	19.5-23.5%
Wt. % Ni	8.00-12.00%	10.00-14.00%	38-46%
Wt. % Mo	*	2.00-3.00%	2.0-3.5%
Wt. % N	0.001% max	0.001% max	*
Wt. % Ti	*	*	0.6-1.2%
Wt. % Cu	*	*	1.5-3.0%
Wt. % Al	*	*	.02% max
Tensile Str. (ann)	483 MPa	483	586
Yield Str. (ann)	170 MPa	170	241
Elongation	40%	40%	30%
Reduction in Area	40%	40%	No Spec.

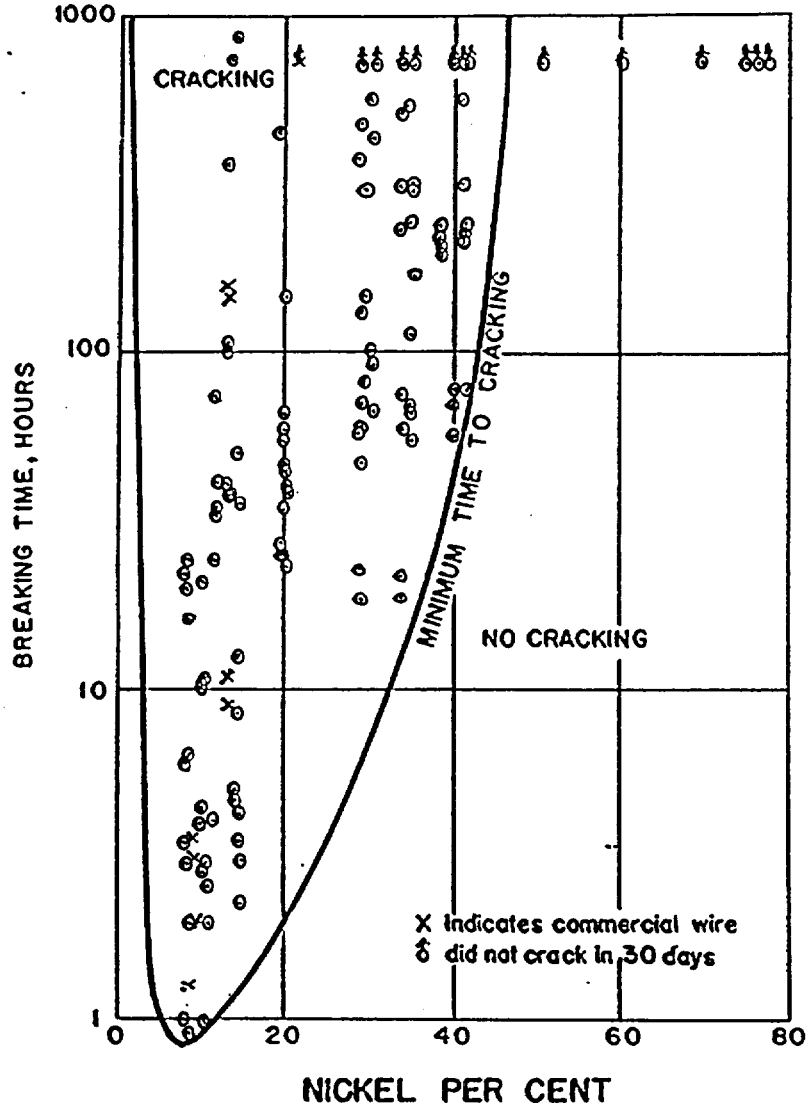


Figure 1a. The influence of nickel content on the time to failure of Fe-Ni-Cr curves in boiling 42% magnesium chloride[6].

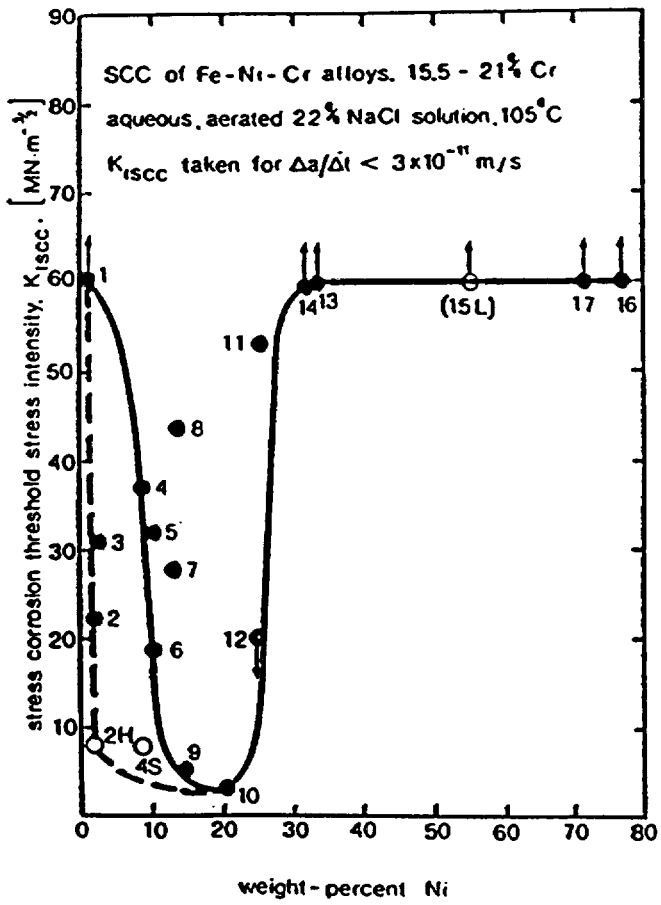


Figure 1b. The effect of nickel content on the threshold stress intensity for SCC of Fe-Ni-Cr alloys in 22% sodium chloride at 105 C.

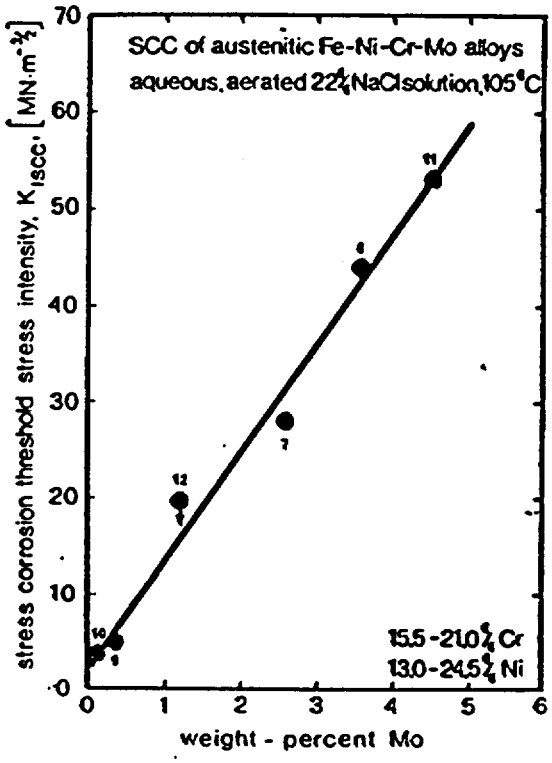


Figure 2. Effect of molybdenum content on the threshold stress intensity for SCC for Fe-Ni-Cr alloys in 22% sodium chloride at 105 C[7].

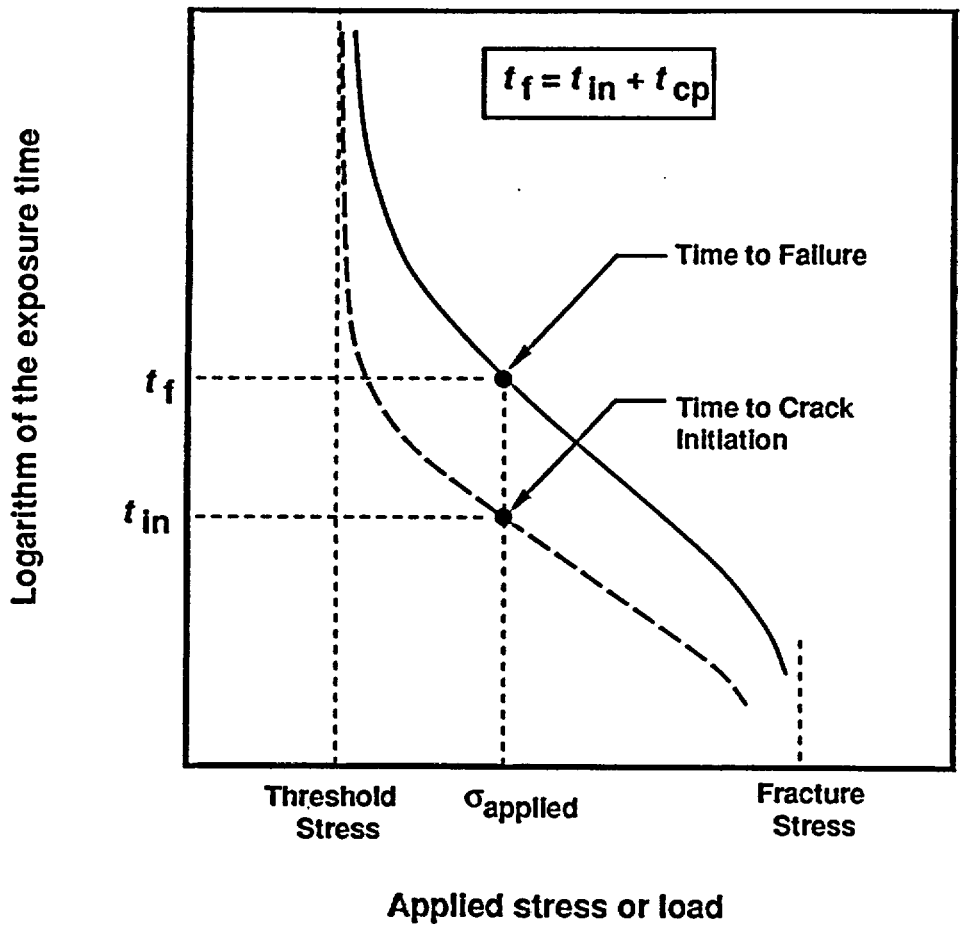
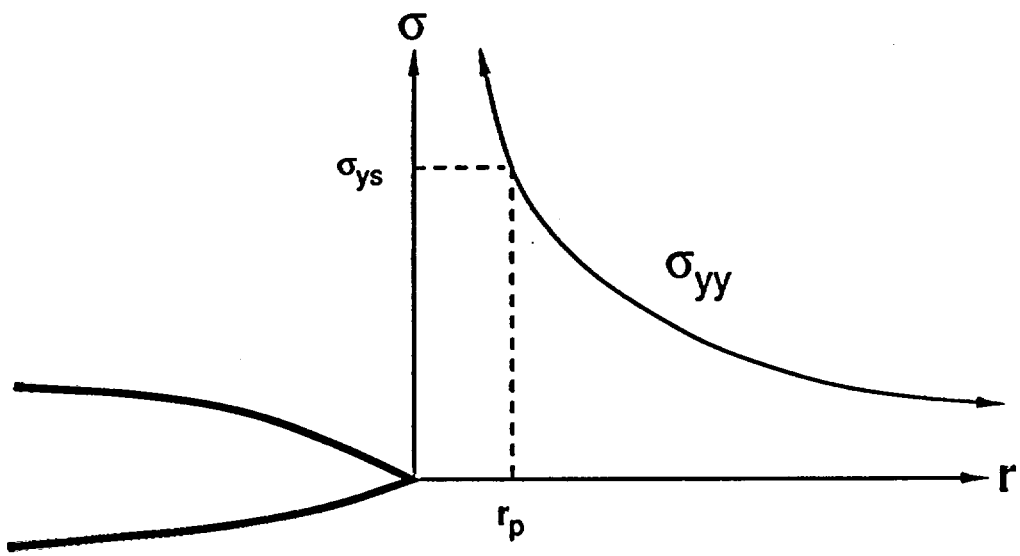


Figure 3. Schematic of the time to failure for smooth samples as a function of the applied stress.



$$\sigma_{yy} = \frac{K}{\sqrt{2\pi r}} \cos\frac{\theta}{2}\left[1+\sin\frac{\theta}{2}\sin\frac{3\theta}{2}\right]$$

$$K = Y\sigma\sqrt{\pi a}$$

Y = Crack geometry and shape factor

Figure 4. Stress normal to the crack plane as a function of distance ahead of the crack tip for linear elastic fracture mechanisms.

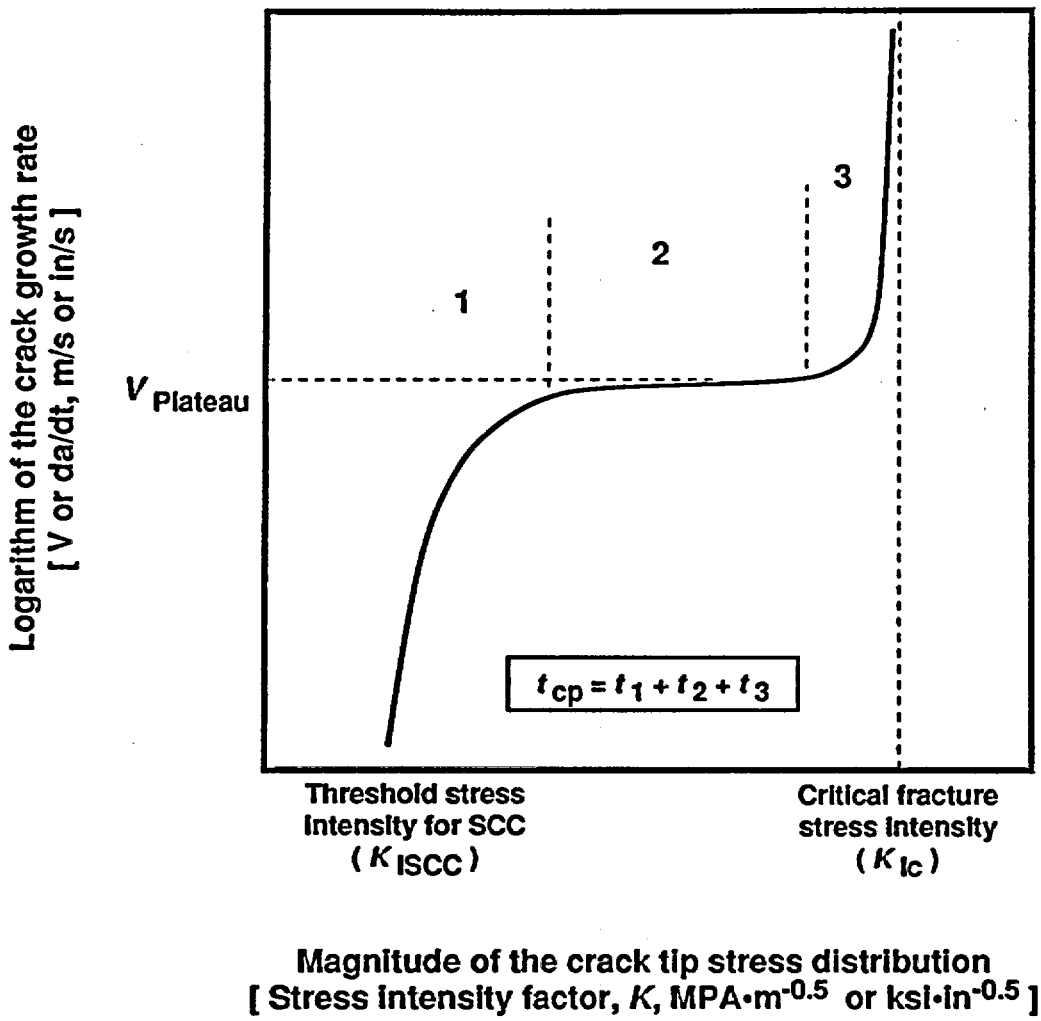


Figure 5. Schematic of a typical crack growth rate vs. stress intensity curve.

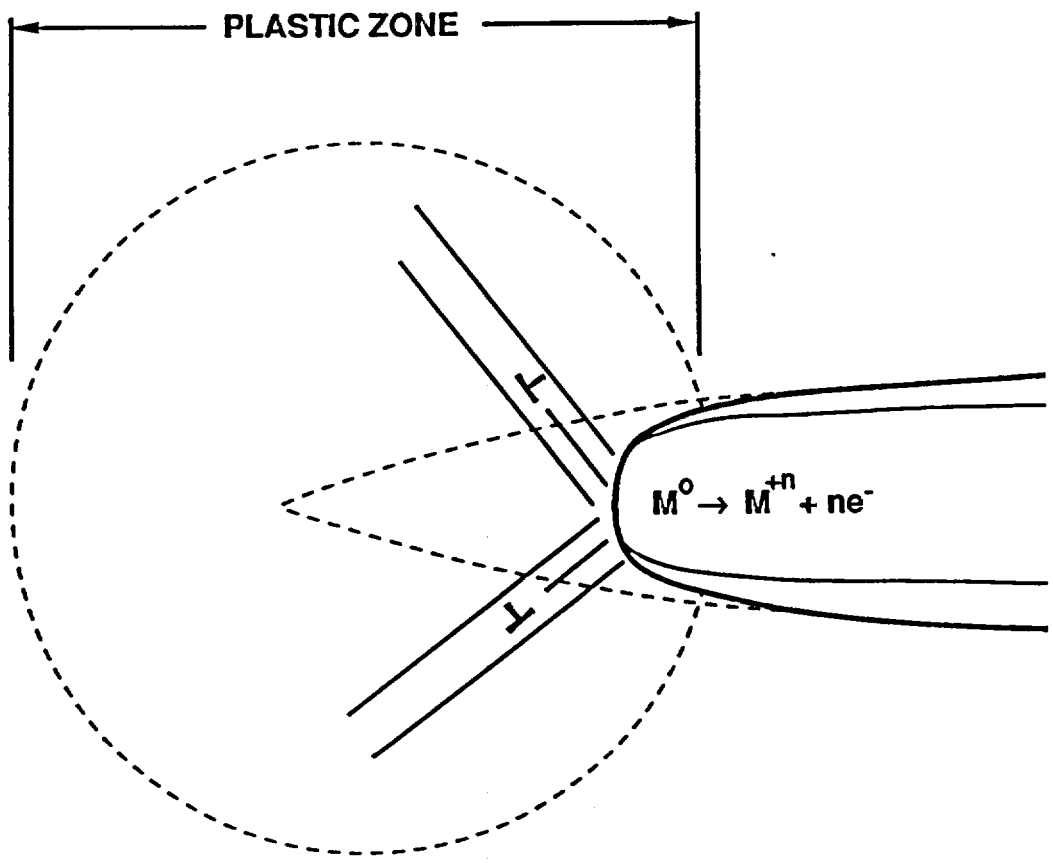


Figure 6a. Schematic representation of the film-rupture model as envisioned by Logan[16].

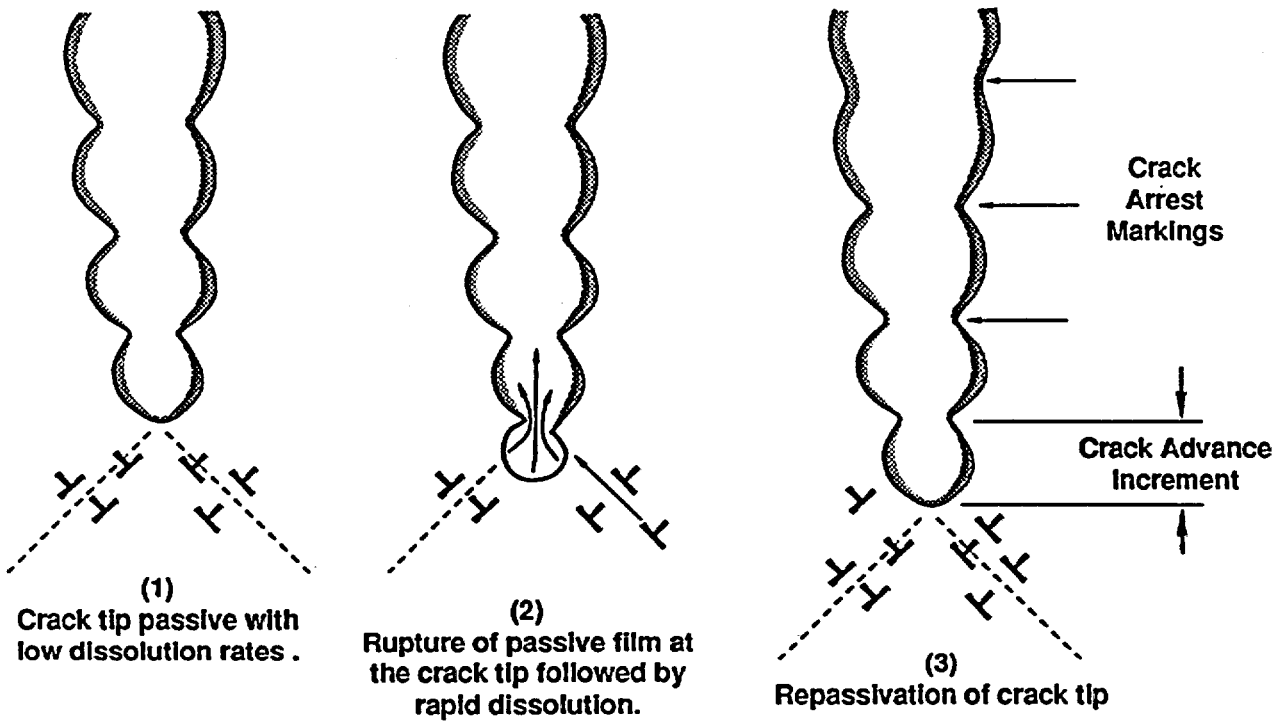


Figure 6b. Schematic representation of crack propagation by the film-rupture model, as suggested by Staehle[3].

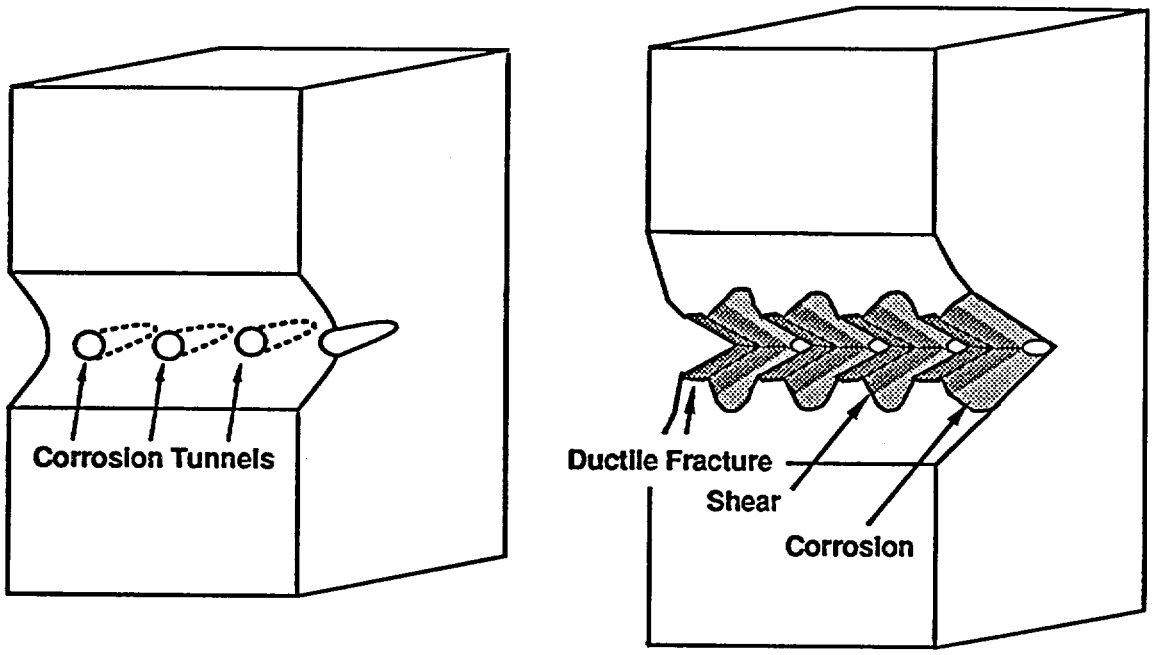


Figure 7a. Schematic of tunnel model showing the initiation of a crack by the formation of corrosion tunnels at slip steps and ductile deformation and fracture of the remaining ligaments.

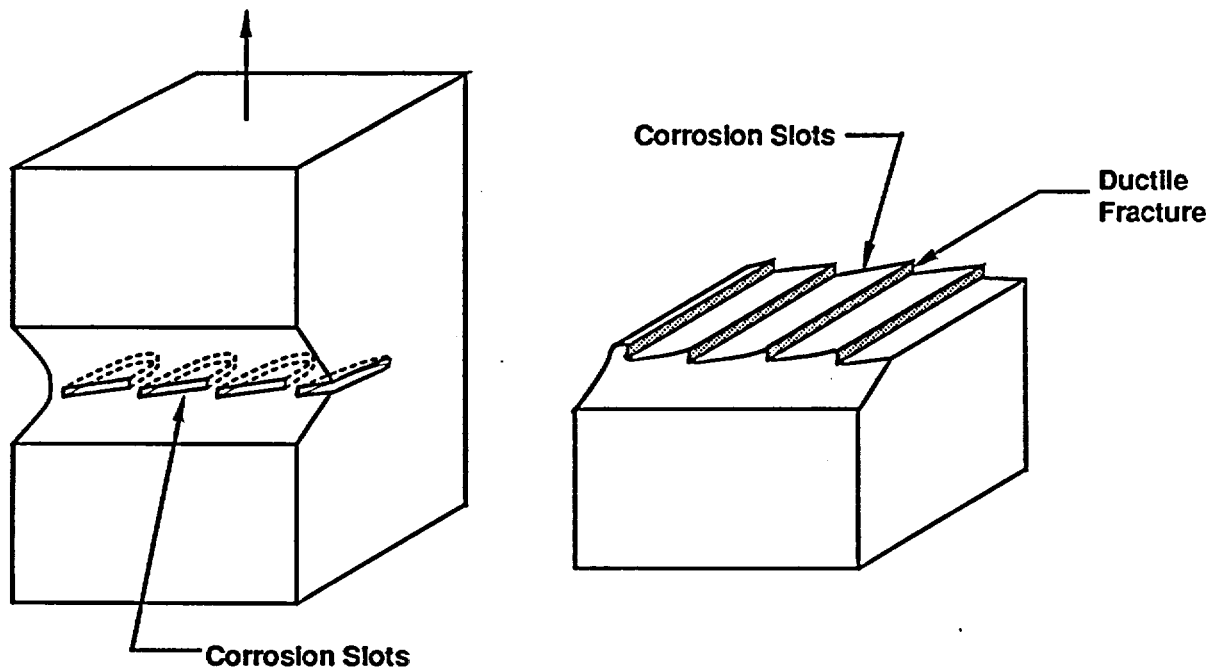


Figure 7b. Schematic diagram of the tunnel mechanism of SCC and flat formation as proposed by Silcock and Swann[26].

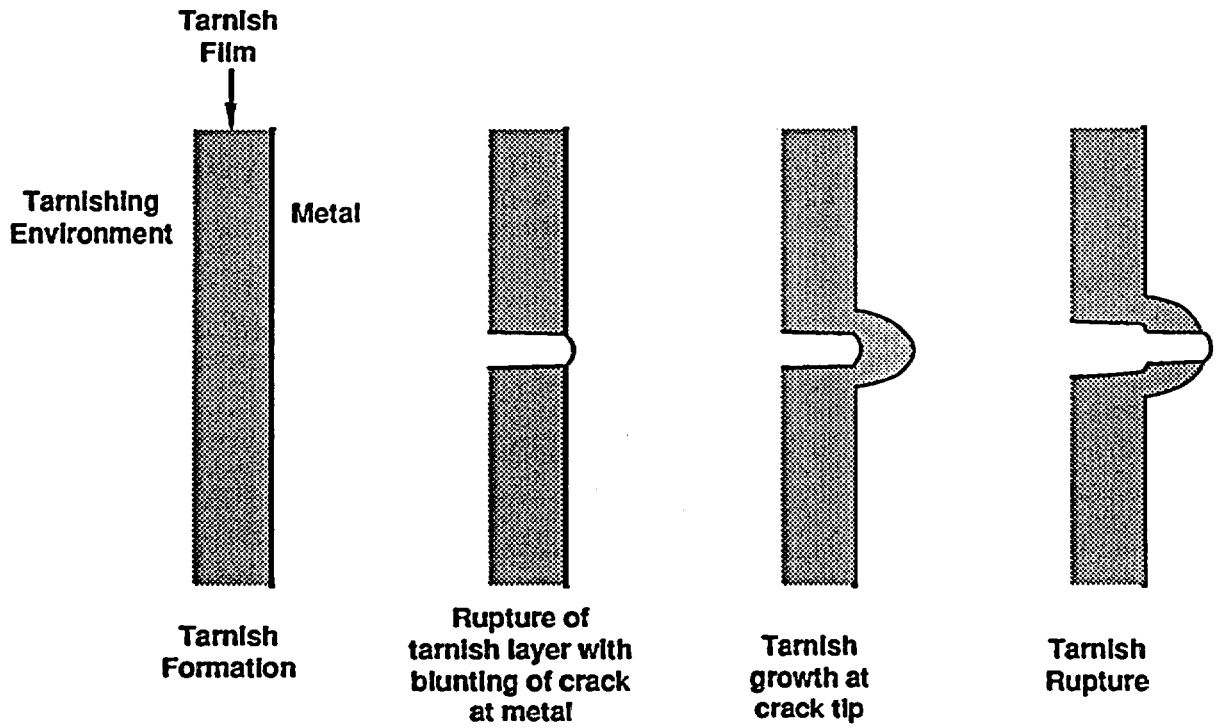


Figure 8a. Schematic diagram of the tarnish rupture model for SCC as proposed by Forty and Humble[32].

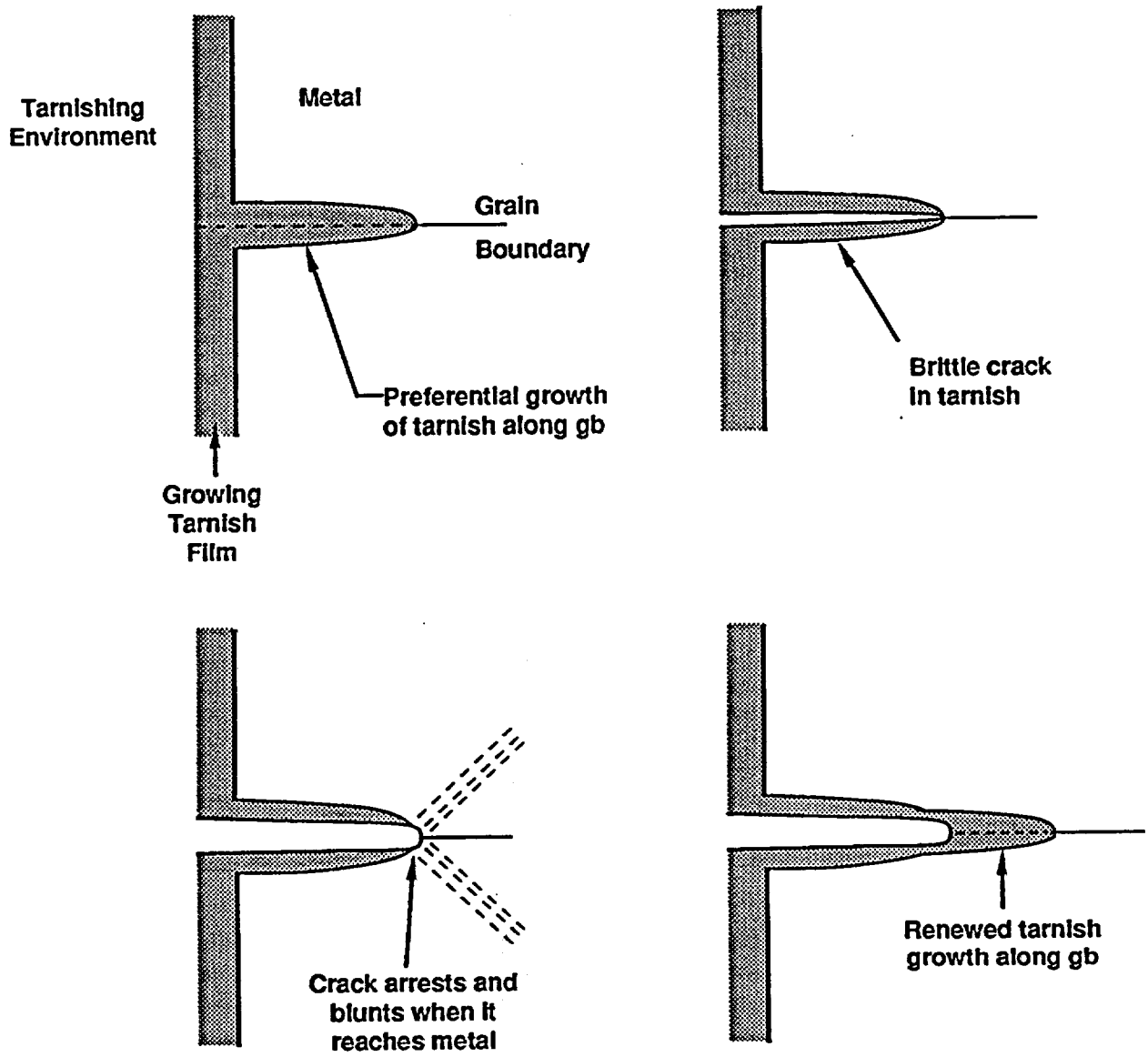


Figure 8b. Schematic diagram of the modified tarnish rupture model of SCC for systems with intergranular oxide film penetration ( ).

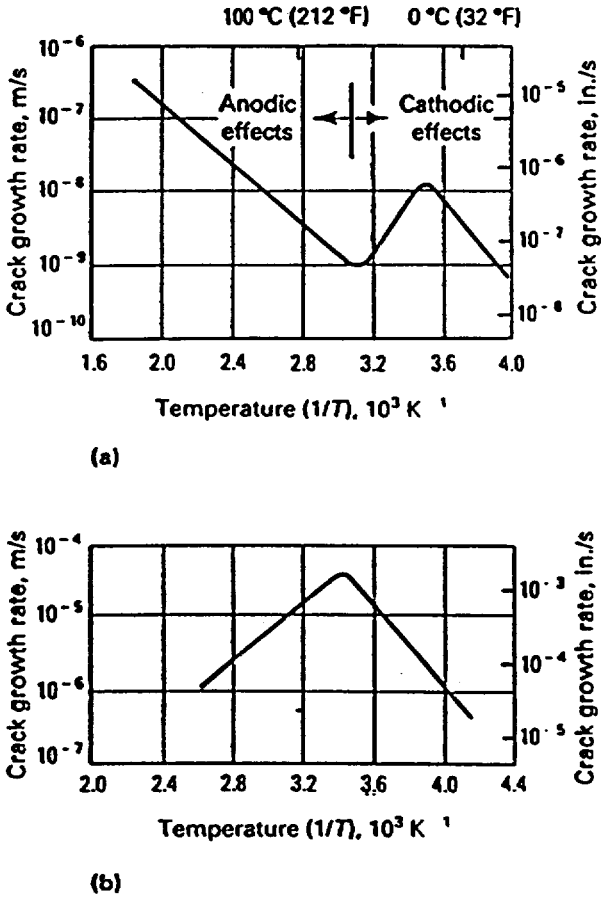


Figure 9. The crack growth rate as a function of temperature for (a) a 3% Ni steel in water[7] and (b) a 4340 steel in gaseous hydrogen[45].

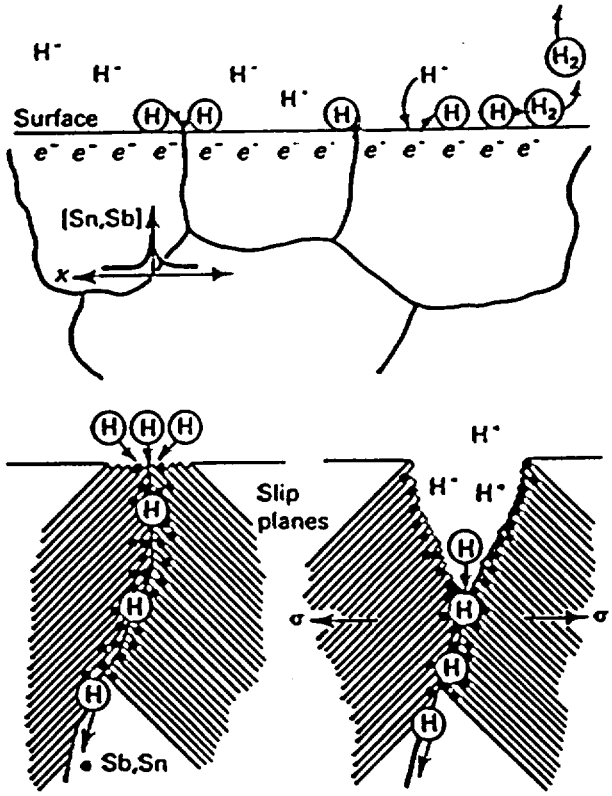


Figure 10. Proposed mechanism for enhanced hydrogen uptake as a result of impurity segregation (Sn, Sb) to the grain boundaries[43].

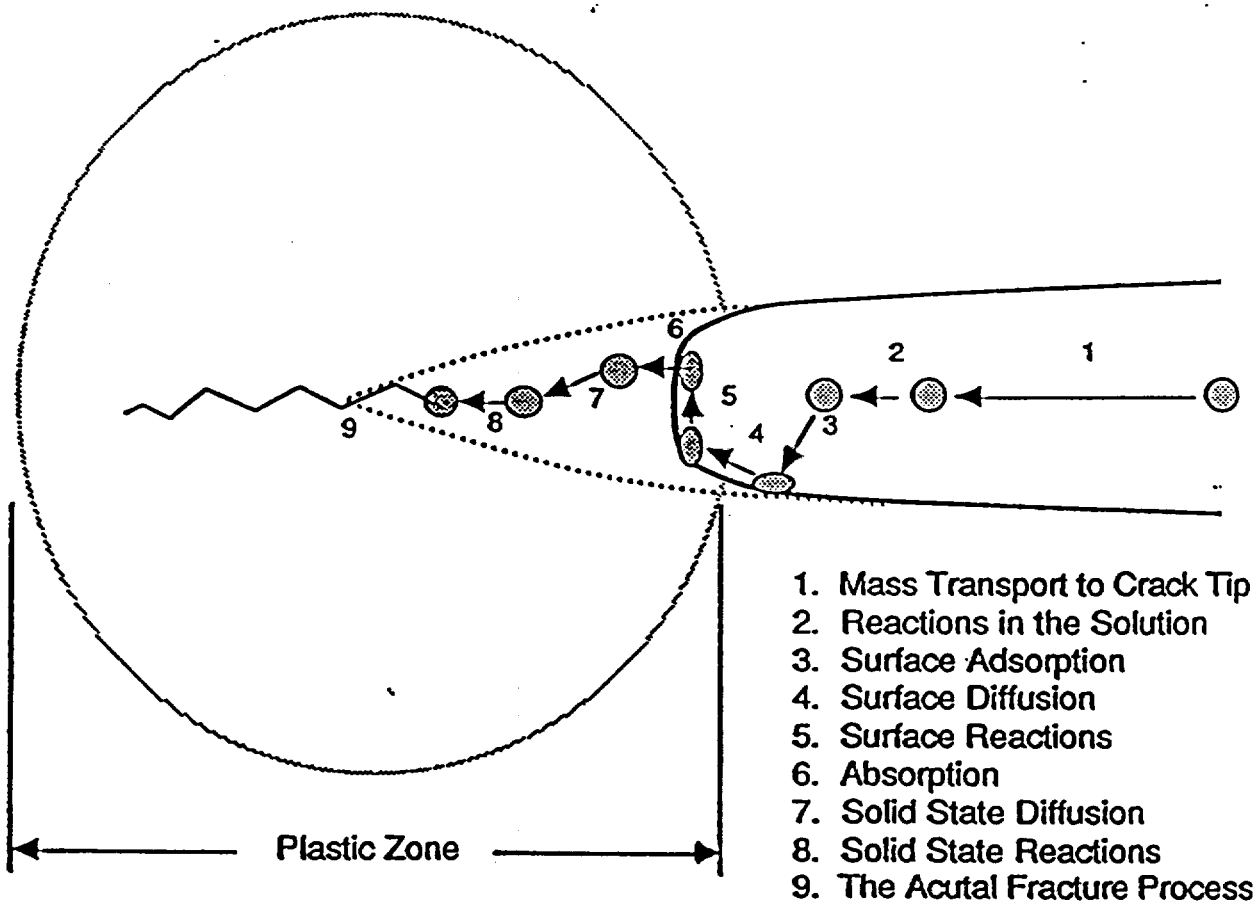


Figure 11. A schematic of the processes which may be rate limiting for environmentally induced crack propagation. To include all possibilities, on internal embrittlement mechanism was assumed.

MECHANISMS OF INTERNAL CORROSION OF ZIRCALOY-2 AND -4 SPENT FUEL RODS

I. INTRODUCTION

The bulk of nuclear fuel cladding is made of the zirconium alloys, Zircaloy-2 and -4. Approximately three percent of the cladding in temporary storage is made of stainless steel (Types 304, 304L, 348 and 316)[1,2]. A discussion of cladding failure modes and repository conditions in a tuffaceous environment has been given previously[2] and is recommended reading although some of the material is included in this paper. Failure mechanisms for stainless steel, essentially those of localized corrosion relating to cracking, pitting and changes in the metal such as sensitization, will be discussed only briefly in this paper.

Zircaloy-4 cladding is used in pressurized water reactors (PWR) and Zircaloy-2 is used in boiling water reactors (BWR). Both of these alloys consist of over ninety-eight percent zirconium. The Zircaloy-4 differs from Zircaloy-2 by having a lower nickel content and an increased iron content. More information on corrosion and other aspects of these alloys can be found in other publications[3-9]. The Zircaloy cladding is a tube that is less than 1 mm thick, and UO_2 pellets are contained within the tubes. Most failures of Zircaloy nuclear fuel cladding until now have been internal resulting from mechanical, chemical and nuclear reactions.

The nuclear waste presently planned for storage consists of approximately ninety percent spent fuel. This means that eighty seven percent of the nuclear waste will be clad with Zircaloy. It is not known whether credit can be given to this cladding for containment of radionuclides in long term nuclear waste storage. An understanding of the corrosion and degradation mechanisms of the Zircaloy will be invaluable in making the determination of whether the Zircaloy cladding can be included in the engineered barrier to help meet the radionuclide release requirements.

The radionuclide release requirements as established by the Nuclear Regulatory Commission (NRC) and state that "nuclear waste containment shall be substantially complete for a period of 300 to 1000 years"[10]. The NRC also requires that after the complete containment period is over, 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 the repository. The Environmental Protection Agency (EPA) has environmental

radiation protection standards for management and disposal of nuclear fuel high level and transuranic waste[11]. The Department of Energy (DOE) has established guidelines for recommending sites for nuclear waste repositories[12].

II. PURPOSE

This paper will discuss some mechanisms involved in previous failures to the extent that the failure mechanisms are known. It is hoped that this information will be useful for assessing corrosion and making predictions of the long term durability of Zircaloy cladding in a tuff repository. Other information will be given on the metallurgical aspects of the cladding, and the effects of use in the reactor and the condition after removal from the reactor and temporary storage. This should provide knowledge of the materials, their corrosion susceptibility under various conditions and the state of the cladding and spent fuel that is planned for storage.

III. SCOPE

This paper includes information on radionuclide containment requirements, previous cladding failures, causes of failures, corrective measures taken by the nuclear industry and discussions of potential modes of internal failures that should be considered for long term repository storage. Also included are descriptions of some of the spent fuel cladding rods analyzed by the Materials Characterization Center (MCC) for use as Approved Testing Materials (ATMs). References are given for most of this information.

IV. BODY OF THE REPORT

A. Materials

Characteristics of materials for structural use in the reactor and for nuclear fuel cladding include[13]:

a. High melting point
b. High mechanical strength
c. Corrosion resistance
d. High thermal conductivity and heat transfer properties
e. Resistance to thermal stress and creep
f. Free from serious radiation damage
g. Nonactivating
h. Able to retain fission products
i. Low absorption cross section if used in a thermal reactor
j. Easy to fabricate
k. Abundant and reasonably priced

Realistically, a material may not have all of these attributes so the material selection may be a compromise. Aluminum which meets a number of these requirements is unsatisfactory due to its excessive corrosion in high temperature water. Cladding materials considered for use in supercritical reactors include high nickel alloys, and an iron alloy with 16 percent chromium and 20 percent nickel[14].

1. Zircaloy-2 and Zircaloy-4

Zirconium (Zr) alloys meet a number of these requirements, especially the high corrosion resistance to the water coolant and the low neutron absorption cross section. The absorption cross section for hafnium free zirconium is 0.18 b compared to 2.43 b for iron and 4.5 for Ni[8]. The cladding is exposed to temperatures of 400 C in normal reactor operation, and the Zircaloys seem to be satisfactory for the temperature and the conditions. If temperatures reach 675 C, the Zircaloy will react with the uranium oxide (UO_2), but this would occur only under accidental conditions. Radiation affects the mechanical properties of the Zircaloys causing an increase in yield strength and a decrease in ductility.

The compositions for the Zr alloys most commonly used for cladding are given in Table 1.

Table 1. Composition of Zirconium Alloys Used for Cladding

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.

Zircaloy-2 and -4 are the most used alloys and will be the ones discussed in this paper. Zr-2.5Nb is not as corrosion resistant as Zircaloy-2 and -4 except in high temperature steam above 400 C (750 F). Zr-2.5Nb has been used in smaller amounts but would be more useful if higher and prolonged service temperatures were required due to its superior mechanical properties and corrosion resistance in deoxygenated environments[9]. More information is needed on the localized corrosion behavior of Zr-2.5Nb as well as on Zircaloy-2 and -4.

The zirconium alloys listed in Table 1 are low alloys and consist of approximately ninety eight percent zirconium. Many of the properties of these low alloys will be similar to those of zirconium. The alloying elements shown in Table 1 are from a group of elements which are known to stabilize the beta form of

zirconium, and these elements are added in small amounts as strengtheners. The precipitates, $Zr(Fe,Cr)_2$ in Zr-4 and $Zr(Fe,Cr)_2$ and $Zr_2(Fe,Ni)$ in Zr-2 form as a result of these alloying additions. Zirconium has a close packed hexagonal crystal structure which transforms to a body centered cubic crystal structure at 870 C (1600 F). The hexagonal form, alpha, is stabilized by Al, Sb, Sn, Be, Pb, Hf, N, O and Cd. The cubic form, beta, is stabilized by Fe, Cr, Ni, Mo, Cu, Nb, Ta, V, Th, U, W, Ti, Mn, Co and Ag.

Wrought forms of zirconium and its low alloys exhibit strong anisotropy and develop a preferred crystallographic orientation during processing. This can be important in the formation of hydrides since specific crystallographic sites are more favorable for hydride formation.

Zirconium is pyrophoric, and pieces with a high surface area to volume ratio will ignite easily. Larger pieces form a protective surface oxide film and have good high temperature oxidation resistance.

Zirconium and its low alloys are highly reactive and obtain their excellent corrosion resistance to various environments by the formation of a protective oxide surface film. The protective visible oxide film changes to a thick loose white nonprotective film at higher temperatures beyond 280 C and especially above 425 C[3,15,16,17].

2. Stainless Steel Nuclear Fuel Cladding

Stainless steels used in cladding were of types 304, 304L, 316 and 348[2]. Stainless steels have good corrosion resistance but are subject to stress corrosion cracking (SCC) in high temperature water in the presence of oxygen and the halogens. SCC appears not to have been a problem for stainless steel in BWR but it would be a problem in higher temperature operations. Stainless steels have high strength, another desirable property of cladding[18]. Mechanical properties of stainless steel, like those of the Zircaloys, are affected by radiation, and the yield point increases and the ductility decreases. Unfortunately, stainless steel has a relatively high neutron cross section and requires an initial fuel enrichment when it is used. Stainless steel is not recommended for use with natural uranium. Stainless steel, like the Zircaloys appears to have suffered no detrimental effects from storage after being removed from the reactors. Discussion of stainless steel in this paper will be limited and most of the discussion in this paper will be on the topic of Zircaloy.

B. Environments

The environment and all associated parameters such as water, oxygen, chemistry, and temperature, etc. play an important role in the rate of corrosion and the type of corrosion which occurs. The environment can cause severe and disastrous corrosion or it can react with the metal to produce protective films, etc. that slow the corrosion process or essentially prevent further corrosion from occurring.

1. Environments of Previous Failures

Previous failures of cladding have occurred under conditions of use in the nuclear reactors. The cladding and contained fuel have been exposed to high temperatures and pressures and various levels of neutron irradiation in the reactor core and have been cooled with flowing water. Soluble fission products or corrosion products from pipes or structural materials could be present in this water. The fuel rods are held in place with fixtures. Temperatures will be between 250 C to 350 C (480 F to 660 F) at pressures of approximately 7MPa (1000 psi) for BWRs and 15 MPa (2200 psi) for PWRs[19].

Some spent fuel rods will be from reactors where the burnup level has been moderate, 2600 GJ/kgM (30 MWd/kgM) and other rods will be from reactors where the burnup level has been high, 3700 GJ/kgM (43 MWd/kgM)[20,21]. Increased amounts of fission gas have been present in some of the high burnup spent fuel rods, but this is not always the case. The interior surface of the spent fuel is exposed to fission products that are produced during the burnup of the fuel. Radiation can cause changes in the surface and chemical reactions of the Zircaloy and can produce microstructural defects.

After removal from the reactor, the spent fuel usually is stored in pools of deionized water to await permanent storage, and some of the materials have been stored for ten or twenty years. No degradation resulting from this storage has been reported, but a comprehensive study of the condition of the stored fuel rods would be prudent.

2. Anticipated Repository Environments

The conditions in a tuff repository have been reviewed previously[2], and much of the information here is taken from the report on Zircaloy cladding corrosion[4]. The tuff repository is located in the Topopah Spring Member of the Paintbrush Tuff at Yucca Mountain, Nevada. The tuff is in unsaturated devitrified zones with twelve percent porosity and contains five volume percent water[2,22]. Oxygen is expected to be present, and water flow has been stated to be 6 to 8 mm per year.

Radiation present will be gamma and will be approximately 10^4 rads per hour. Repository temperatures will change with changes in storage design. Some calculations show a fuel centerline temperature of 330 C which decreases to 100 C after one hundred years[2] and other calculations show a centerline temperature of 350 C[22]. Another report[5] indicated maximum temperatures expected in the repository for the fuel for ten year old waste with 44 kW/acre are around 325 C. This temperature will drop to just over 200 C after 100 years, and the temperature will approach 100 C after 700 years where is will remain or drop only slightly for well over 100 years. The repository will not pressurize after closing, and the water will boil off leaving a residue of salts.

C. Failure Modes and Mechanisms

Failure rates have been less than 0.01 percent for light water reactors (LWR)[23]. Failure rates in earlier times in BWRs were around one percent. Less than 0.002 percent of Zircaloy fuel rod failures, under reactor conditions, are caused by waterside corrosion. The failure rate percentages are small but the numbers of failed fuel rods can be significant since there can be multi-thousands of rods per fuel assembly. The failures until this time have been initiated internally. Failures which occurred from 1969 through 1977 have been summarized[2,24]. Some of the types of failures and associated mechanisms that have been reported will be discussed.

1. Cladding Collapse

Cladding collapse is a failure which occurred in fuel for PWRs prior to 1973. Cladding collapse resulted from high temperature creep of the cladding, and the cladding collapsed around the pellets instead of remaining a straight rod. This problem was overcome by putting a small positive pressure of helium (He) gas in the fuel rods. Caution must be exercised here, and all air must be removed before filling with the He. Failure to remove all air would leave oxygen, water and other elements available for reactions with the cladding and the fuel.

2. Stress Corrosion Cracking

Stress corrosion cracking (SCC) is a form of localized corrosion that occurs in the presence of a corroding environment and a tensile stress. SCC is considered a mode of internal fuel rod failure for simplicity, but there are a number of different mechanisms of SCC and more than one mechanism can be involved with a given material in a given environment. The chemistry inside the cladding is important as well as corrosion or other degradation means, either inside or outside of the cladding, that would alter the wall thickness of the cladding. (SCC) is one

failure mode[25] that is responsible for failure in pellet/cladding interactions. Time to failure for fuel rods in the reactor has been considered to be a function of the hoop stress, h, the iodine concentration, I_2, the temperature, T, and the fluence, F.

A model was developed[25] to include, in addition to these factors, the effects of as fabricated defects, crack initiation and crack growth, and an extensive study was conducted on unirradiated and irradiated Zircaloy tubing exposed to iodine under constant and changing hoop stresses. The hoop stress, s,is equal to pr/t where p is the pressure in MPa, r is the radius of the tube in meters, and t is the wall thickness of the tube in meters[3]. Laboratory tests indicated a threshold stress value, below which smooth Zircaloy specimens were immune to attack. It was found that cracks initiate at inhomogeneities at the inner surface of the tubing, and it has been shown that crack formation rather than crack propagation is the dominating factor in iodine induced SCC of Zircaloy[26]. Both the threshold stress and the time to failure are lower in the irradiated Zircaloy, and the predictions are better for the irradiated material than for the unirradiated material.

Crack formation appears to be associated with the penetration of iodine into the Zircaloy, and below the threshold stress, penetration does not occur. Local strain rather than local stress was considered to govern iodine penetration at the crack tip. Irradiation increases the yield strength and reduces the ductility of Zircaloy and causes dislocation channeling and the creation of slip steps at the surface and at grain boundaries. These slip steps serve as sites for iodine penetration. Cracks initiate in smooth specimens at iodine concentrations of approximately 10^{-6} g/cm^2, and there is an inverse linear dependence of t_f on iodine concentrations above this level[27,28]. The formation of zirconium iodides may occur beyond this level[29], and other works indicate that increases beyond approximately 10^{-4} g/cm^2 have no further effect on SCC, and this may be due to the iodine reaching a saturation level[26-28].

Other studies[30] involving effects of crystallographic orientation of the surface (surface texture) and microstructure on the propagation of stress corrosion cracks in an iodine environment showed that texture had a strong effect of the stress needed for fracture and on the fracture path. The main mode of crack propagation in Zircaloy is transgranular cleavage near the basal plane. As the number of basal poles that are parallel to the crack direction increases, the stress intensity, K, necessary for crack opening or propagation, decreases.

Other modes of crack propagation may also accompany cleavage or may precede the transgranular mode at lower stress levels, and these include fracture along grain boundaries, tearing along grain boundaries and fluting. Flutes are ductile channels

between widely spaced cleavage planes, and probably occur as a result of plastic deformation.

It must be noted that some research investigations conducted on unirradiated Zircaloy in iodine vapor outside of the reactor did not achieve a cladding failure at temperatures of 100 C and 300 C and for times of 550 days[31a](Peehs et al). Other studies offer the possibility that cadmium in combination with cesium could be the cause of the failure[5,28,31-35]. Other work demonstrated that Zircaloys undergo SCC in CsI both in unirradiated and irradiated environments[36]. Unirradiated specimens, coated with CsI, were stressed at elevated temperatures and cracked. Fractography analyses[37] revealed that the cracks were caused by SCC and not by delayed hydride cracking (DHC). Specimens exposed in the reactor also underwent SCC. Care was taken not to have any water in the system since the water could have caused DHC instead of SCC. It was concluded that SCC would occur in the Zircaloy if a mechanism were present to transport the I to the Zircaloy surface. One mechanism for this transport might be provided by ionic diffusion in a fission product oxide melt in the fuel clad gap, but it was stated that the more probable cause was radioloysis of the CsI to release volatile I. Another study[38] showed an influence of I on mechanical properties and SCC of Zircaloy-4 at temperatures below 700 C.

Fission gas release is measured for the Approved Testing Materials (ATMs) which are being prepared and characterized by the Materials Characterization Center (MCC). Experiments[40], dealing with two rods of ATM-103 exposed under similar conditions, showed that the fission gas release from the two rods differed by 0.2% versus 14%, and that the rod with the higher fission gas release had a lower threshold stress, 200 versus 275 MPa. There was more Cs deposited on the inner surface oxide in the case of the higher fission gas release and this thinner oxide had more cracks than did the other rod with the lower fission gas release. It is possible that these rods did not have identical power exposures even though conditions appeared to be similar. Recent analyses by the MCC have shown that higher power levels of operation result in higher fission gas release and that there can be variations in the fuel rods from the top of the rod to the middle and to the bottom[40].

3. Hydrogen Embrittlement

The uptake of hydrogen into Zircaloy results in embrittlement. In earlier years, 1969 to 1977, failure from hydriding was one of the principal modes of cladding failure[24,2]. A source of hydrogen was the water left in the fuel, and this was corrected by drying the fuel. There are other sources of hydrogen such as that present in the coolant or that which might be generated from other corrosion processes. The amount of hydrogen that is

soluble in Zircaloy at room temperature is 20 ppm. Hydrogen in the outer cladding surface can be absorbed from the reactor coolant to a concentration of 20 to 40 ppm for a BWR and to 100 to 200 for a PWR. When temperatures are lowered or at reactor shutdown, the excess hydrogen precipitates out as hydrides. At concentrations of hydrogen exceeding amounts that can be absorbed, hydride precipitates will form. The crystallographic orientation for the precipitates is in the basal plane. Analysis of fuel rods of ATM 106[41] showed that hydrogen content in the upper half of the rod was greater than in the lower half, and the areas with increased hydrogen content correlated with the same areas that had increased oxide. The hydrides were oriented longitudinally around the circumference of the tube as shown in Figure 1 (Figure 4.26)[41] from a peak power region specimen·

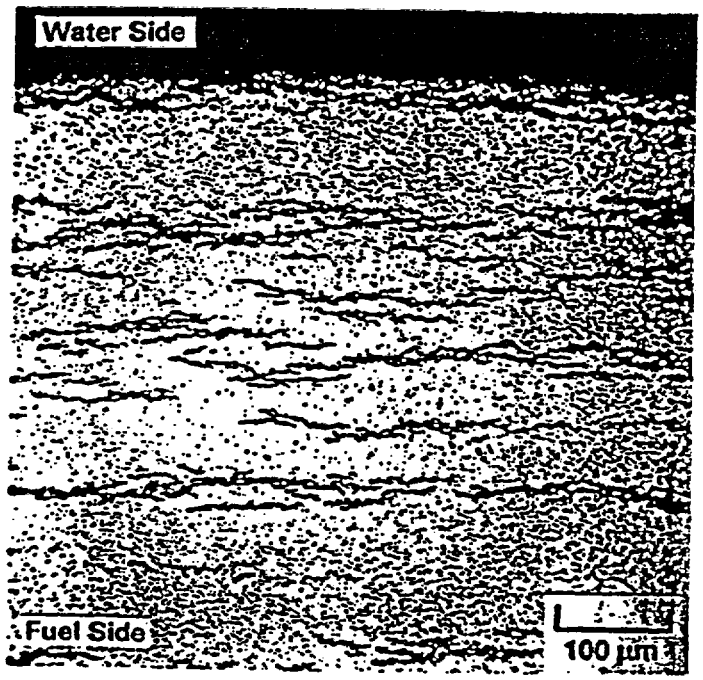


Figure 1. Etched Cladding of Transverse Sample 106-NB107-G from the Peak-Power Region[41]

4. Fretting Corrosion

Fretting occurs when two surfaces in contact experience small amplitude relative oscillatory motion. The motion and force of fretting destroys the protective film that gives a metal such as Zircaloy its corrosion resistance. The reformation of this film in air or other oxic media will follow, and this is corrosion. Fretting corrosion can be destructive if the removal and reformation of this film occur repeatedly. Fretting corrosion involves wear and corrosion. Particles or oxide removed from the surface is wear debris and may serve as an abrasive to increase

the wear rate. If the wear debris is soluble, increased wear will not be a problem and chemical reactions will play a larger role. Fretting corrosion is an important consideration for materials such as zirconium alloys that depend on a surface film for corrosion protection. Fretting corrosion would be a problem

if cladding rods or spacers, or other structures were rubbing against each other. Fretting-corrosion of Zircaloy-2 pressure tubes was observed after less than two years[14,42,43]. Fretting-corrosion may be less of a problem for the inner surface of the cladding.

D. Effects on Corrosion of Environmental Factors

Zirconium and its alloys, Zircaloy-2 and -4 are reactive and obtain their corrosion resistance from the formation of a protective surface oxide film. The formation and stability of this film will be influenced by various environmental factors including but not exclusive of others, temperature, chemical ions, hydrogen, stress, oxidation and radiation. Effects on corrosion of these factors will be discussed here in a general way and only in terms of corrosion of the inner wall of the cladding tube or corrosion of the outer wall, such as thinning of the outer wall, that would affect the mechanism of internal failure.

1. Temperature

The Zircaloy-2 and -4 cladding available for long term storage will have been exposed to high temperatures. The water coolant temperature for boiling water reactors is in the range of 250 C to 350 C at a pressure of 7 MPa (1000 psi) for light water reactors (BWRs) and 15 MPa (2200) for pressurized water reactors (PWRs)[45]. It has been generally accepted that corrosion of Zircaloy at these temperatures usually is uniform, but this is not accurate, and more corrosion studies and developmental work on the cladding alloy would be useful[45]. This may be especially true for the PWRs where increased temperature and higher pressure can combine and can result in a form of attack termed nodular corrosion[45].

Nodular corrosion and its relation to crud induced localized corrosion (CILC) have been discussed previously[3,46], and CSLC always occurs on the outside of the cladding. Nodular corrosion, which precedes CILC, could occur in the interior of the older cladding tubes that had remaining small amounts of water. Heat treating at a temperature of 825 C causes precipitates present in the Zircaloy to reprecipitate at the grain boundaries and improves nodular corrosion resistance. One mechanism proposed for this improvement was based on the fact that uniformly distributed precipitates increase the cathodic potential of the

base metal and promote migration of hydrogen ions through the oxide resulting in nodular attack[47]. Another study suggests that the fine precipitates are substantially dissolved after on cycle of irradiation and that this mechanism is not correct and that nonuniform distribution of precipitates cannot be responsible for the improved nodular corrosion resistance [48]. More recent studies indicated that the mechanism involved in nodular corrosion is local solute depletion[46]. The occurrence of nodular corrosion and/or CILC on the outside of the cladding could cause the tube wall thickness to become thinner and also could be a source of embrittling hydrogen that would change the hoop stress and make conditions more favorable for an internal SCC or HE cracking failure.

2. Ions

Ions present within the interior of the cladding will play an important role in the mechanisms of the cladding failure. Some examples of the effects of ions on cladding corrosion were discussed in the above sections. Iodine ions or radionuclides was one of these, and I^- enhances the stress corrosion susceptibility. Cesium may line the inner wall of the cladding and interact with the iodine to cause SCC. Hydrogen that is produced from the radiolysis of water and from other oxidation reactions enters the cladding as an embrittling agent. Ions of iron, nickel and copper are detrimental to the protective oxide of the outer surface of Zircaloy and cause nodular corrosion and CILC. These ions would play the same role internally if water or other corrosive environments were present. There probably are other radionuclides produced which can be important in the corrosion resistance of the inner cladding wall.

3. Hydrogen

Effects of hydrogen on internal cladding corrosion are primarily due to the embrittling of the metal that results from hydrogen being absorbed into the structure. Hydrogen also reacts at specific crystallographic sites to produce a hydride precipitate which has a needle like shape and can serve as a stress raiser as well as an embrittled area to promote cracking.

Electrochemically, hydrogen can prevent passivation resulting in a shifting of the potential away from the noble direction and intensifying local reactions, but this should not be a problem in the absence of water.

4. Stress

SCC and its occurrence internally in fuel cladding have been discussed in a previous section. Stress has a strong effect on the corrosion resistance of metals and alloys such as zirconium

and the Zircaloys that obtain their inertness from the presence of a surface film. An applied stress, either static as in SCC of a dynamic stress, eventually will cause a shift in the substrate structure sufficient to rupture the protective film or will cause the protective film to rupture due to its inherent stiffness. Once the stress has caused the initiation of local failure, the stress enhances the continued breakage of the oxide film and the propagation of the crack.

5. Oxidation

A visible surface oxide forms on zirconium at 200 C that is protective but at temperature of 425 C, a thicker, loose white scale develops which is not protective. The oxidation of zirconium and Zircaloy-2 and -4 usually is divided for broad general considerations, into two stages, the pretransition stage and the post transition stage. A protective oxide forms and corrosion rates diminish with time up to 280 C or above which is a transition temperature. At the transition temperature, the protective black oxide changes to a gray or white oxide that is thicker and the corrosion rate becomes linear with time. Oxidation of zirconium and Zircaloy have been discussed previously and numerous references were cited[3,5].

The inner cladding wall with its protective oxide faces the UO_2 fuel pellets although there usually is a small space between them. There is no reaction of the UO_2 fuel and the Zircaloy cladding until 600 C. The affinity of U and Zr for oxygen appear to be similar. The free energy of formation for the oxides is as follows[49].

$Zr^{+4} + O_2 \rightarrow ZrO^2$ F = -1.04 kJ/mole (-248 Kcal/mole)

$U^{-2} + O_2 \rightarrow UO_2$ F = -1.03 kJ/mole (246.6Kcal/mole).

6. Radiation

Effects of radiation are numerous. Radiation causes the production of iodine which is considered by many to be a source of the SCC problems associated with internal cladding failures. Other radionuclides such as Cs are produced and accumulative gases can cause pressure on the inside of the cladding. Radiolysis of any water present results in hydrogen being available to embrittle the material and to promote sites of local attach wither by cracking or by a form of nodular corrosion.

V. CONDITION OF INTERNAL CLADDING WALL PRIOR TO REPOSITORY STORAGE

Studies of spent fuel that has been stored, and analysis of selected spent fuel for Approved Testing Materials (ATMs) will provide information on the condition of the spent fuel prior to repository storage. A literature review conducted regarding failure mechanisms of Zircaloy cladding under dry storage conditions indicated three potential failure modes; creep rupture, delayed hydride cracking and fuel side SCC 50.

A. Approved Testing Materials

ATMs are being developed by the Materials Characterization Center (MCC) at the Pacific Northwest Laboratories. These ATMs will serve as a source of well characterized spent fuel to be used for testing in the U. S. Department of Energy Office of Civilian Radioactive Waste Management (OCWRM) program.

B. Characterization of the ATMs

The MCC conducts extensive studies and analyses of the spent fuel rods that are to become ATMs. The MCC characterization of the ATMs[51] includes discussions and/or sampling for the following;

1. Fuel rod, assembly and reactor descriptions
2. Irradiation and decay histories
3. unusual incident description
4. Fission gas release
5. Transverse and longitudinal ceramography/metallography
6. Burnup distribution
7. Gross and spectral axial gamma scanning
8. Calculations of the axial radionuclide distribution
9. Chemical overchecks of the axial radionuclide distributions.

Additional characterization will be carried out in the various categories as needed. Calculations and measurements of the radial radionuclide distributions also will be made. Transmission electron microscopy studies also will be conducted on some specimens.

C. Source of the ATMs

These ATMs will consist of a number of spent fuel rods from reactors with different burnups or power levels from different locations in the United States. The spent fuel ATMs now being characterized by the MCC are given in Table 1.

Table 1. Summary of Spent Fuel ATMs Being Characterized by the MCC[41]

No.of ATM	Fuel Type	Reactor	Expected Burnup Level	Expected Gas Release, %	Fission Rods
101	PWR	H. B. Robinson No. 1	Moderate, 2600GJ/kgM (~30 MWd/kgM) segments	<1	9 as 27 1.2 m
103	PWR	Calvert Cliffs No. 1	Moderate 2600 GJ/kgM	<1	176 full length
104	PWR	Calvert Cliffs No. 1	High, 3715 GJ/kgM (~43 MWd/kgM)	<1	128 full length
105	BWR	Cooper	Moderate 2400 GJ/kgM (~28MWd/kgM)	<1	98 full length
106	PWR	Calvert Cliffs No. 1	High, 3700 GJ/kgM (~43 MWd/kgM)	~10	20 full length

D. Analyses of the ATMs Claddings' Internal Surface

The spent fuel rods were sectioned by the MCC and studies were made on the cladding and on the spent fuel. Some microscopic studies were performed on the same samples. Other specimens had the spent fuel removed for measuring radionuclide content of the cladding, and some of the fuel samples were prepared and studies using transmission electron microscopy. This gave much useful structural and chemical information on the spent fuel, but this will not be presented here in this discussion of the interior of the cladding material.

1. Cladding Inner Surface Oxide

The report on the spent fuel ATM-103 gave the following description of the oxide on the interior of the cladding surface. "A uniform oxide layer was not present over the entire length of the interior cladding surface of Sample 103-MLA098-N taken from the peak-power region ;instead, localized islands of oxide were present as illustrated in Figure 2 (Figure 4.17)[40]. The Zircaloy cladding is partially thinned at the same location as the deposit buildup on the interior cladding surface. The buildup is rough

in comparison to the smoothness of the cladding interior wall where there is no reaction product. The oxide layers were essentially negligible on the cladding interior surfaces of the two longitudinal samples taken near the bottom of Rod MLA098. The interior surface of the cladding of Sample 103-MLA098-Z near the bottom of the rod is shown in Figure 3 (Figure 4.18)[40] for comparison with the localized interior oxide layers shown in Figure 2 (Figure 4.17)[40] for a sample near the middle of the rod."

The middle of the rod represents a peak-power region while the bottom of the rod would be in a lower power region. The oxide formation on both the external and internal surfaces of the cladding varies with the magnitude of power the rod experienced. Figure 4[41] shows an 8 um thick oxide layer was present on the exterior of the cladding from the middle or peak-power region, and Figure 5[40] shows a 3 to 4 um thick oxide layer that was present on the cladding exterior surface near the bottom of the rod. The oxide on the exterior cladding surface, especially from those exposed to peak-power, appeared to be composed of two layers as seen in Figure 5. In corresponding locations, the interior cladding surface as shown in Figure 2, has localized reaction areas where as much as 6 um of the cladding wall is removed.

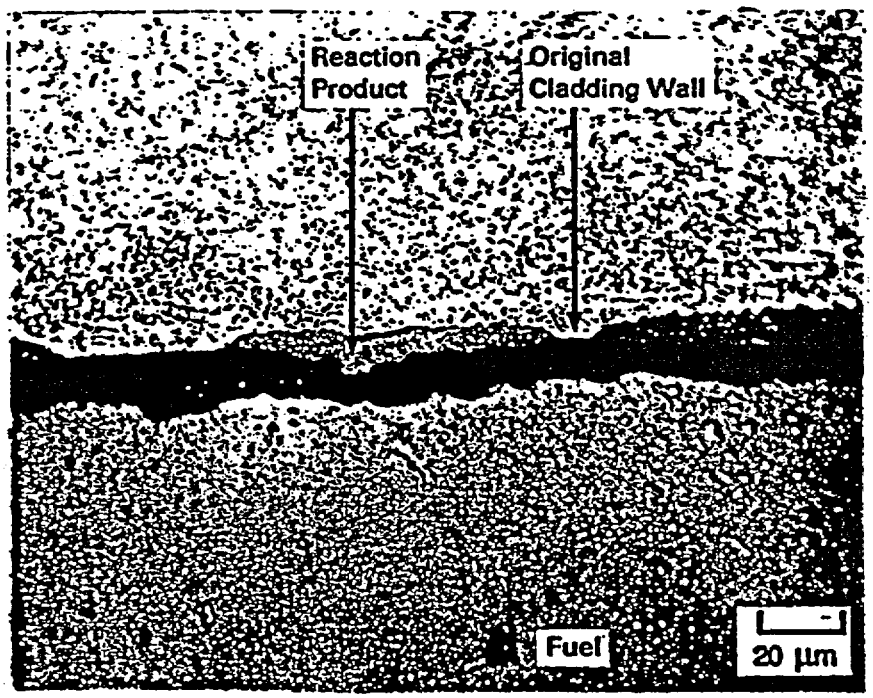


Figure 2. Interior Cladding Surface of As-Polished Sample 103-MLA098-N[40] from Peak-Power Region.

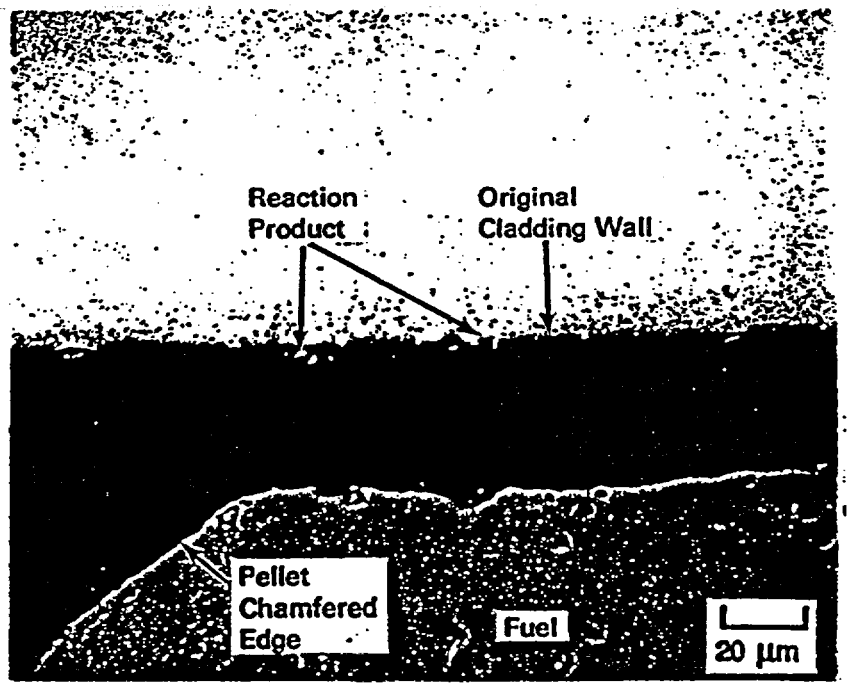


Figure 3. Interior Cladding Surface of As-Polished Sample 103-MLA098-Z[40] from Lower End of Rod at ~82 % of Peak Power.

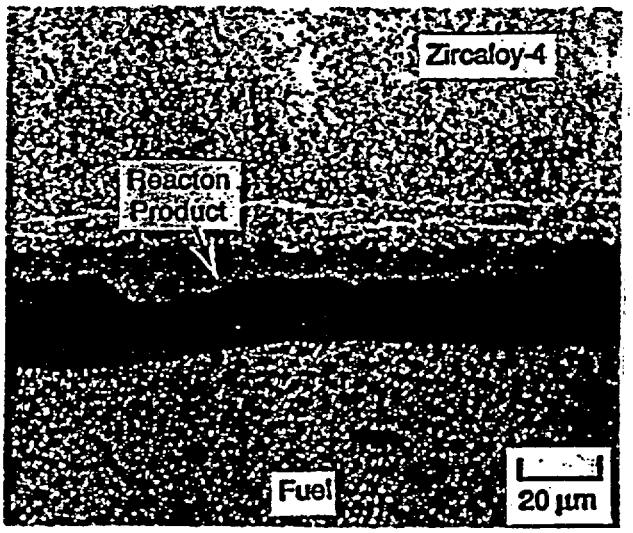


Figure 4. Interior Cladding Surface of As-Polished Sample 106-NBD107-O[41] from the Peak Power Region.

Figure 5 shows an 8 um thick oxide layer was present on the exterior of the cladding from the middle or peak-power region. This layer will be 3 to 4 um thick on the cladding exterior surface near the bottom of the rod. the oxide on the exterior cladding surface, especially from those exposed to peak-power, appeared tp be composed of two layers as seen in Figure 5. In corresponding locations, the interior cladding surface as shown in Figure 2, has localized reaction areas where as much as 6 um of the cladding wall is removed.

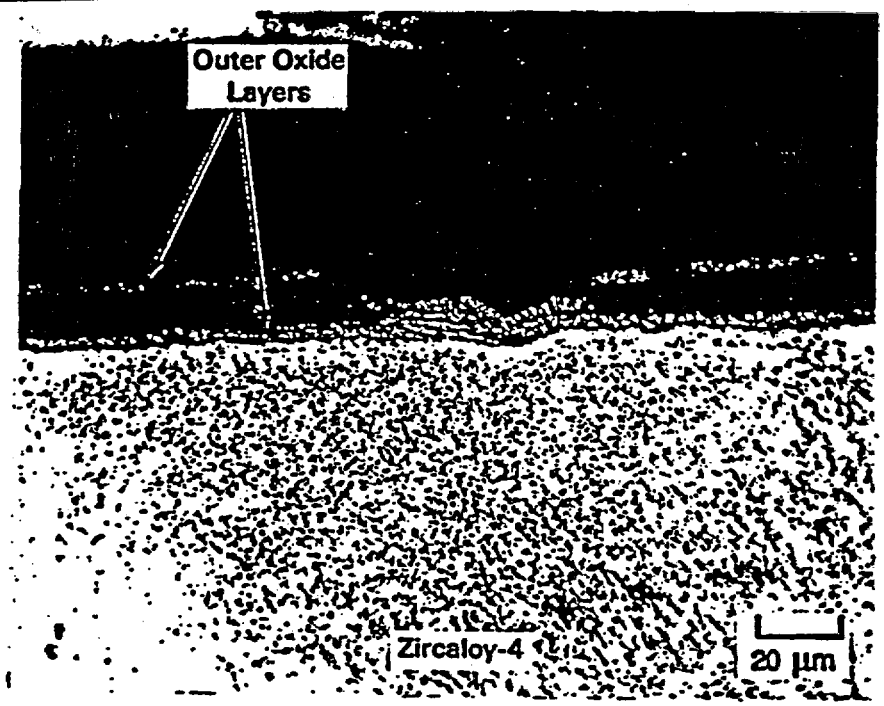


Figure 5. Exterior Cladding Surface of As-Polished Sample 103-MLA098-N[40].

2. Radionuclides on Inner Cladding Wall

The ATM-103 cladding was analyzed both on the exterior and interior surfaces for ^{135}Cs, ^{137}Cs and ^{129}I. The Cs concentrations were relatively constant on the exterior, the Cs concentration on the interior surface generally followed the power profile of the fuel, decreasing at both ends of the rod. This does not follow the temperature profile which increases from the bottom to the top.

3. ^{14}C Available From Spent Fuel

The analysis of ATM 106[41] for ^{14}C involved burning a sample of spent fuel or cladding in pure oxygen, collecting the CO^2, and measuring the ^{14}C by scintillation counting. The uncertainty for both the analysis of the spent fuel and for the cladding for a single analysis was 5.6%. There was wide scatter in the results analyses of five sections of cladding taken from different locations along the length of the rod, and this was believed to be due to measurement uncertainties or to variations in the of nitrogen impurity levels assumed to be in the cladding. These analyzed concentrations were 120% of the predicted concentrations (using ORIGEN2, a computer program for predicting the radionuclides and amounts present). Another work reported on fuel rod specimens irradiated at Turkey Point and in the H. B. Robinson reactor (ATM-106 may be from the H. B. Robinson reactor.), and showed relatively high ^{14}C solution activities of 2660 and 946 pCi/ml. The scatter again was attributed to possible nitrogen being present in the as fabricated cladding. These tests indicated that a portion of the ^{14}C originated from the bare cladding hulls. Higher ^{14}C activity was present in the sealed tests that in the unsealed tests, and it was stated the some ^{14}C from the unsealed tests may have escaped into the atmosphere as CO^2.

The ^{14}C in the ATM-103 cladding ranged from 10 to 150 percent of that predicted by ORIGEN2. This discrepancy, again, was attributed to measurement uncertainties or to uncertainties for the assumed nitrogen content at the start of irradiation.

V. SUMMARY AND CONCLUSIONS

This paper has presented the reason that the long term durability of the zirconium alloy, Zircaloy, is in question, and this is to know whether credit can be taken for the Zircaloy cladding controlling or reducing radionuclide release for time periods of 300 to 1000 years in a nuclear waste storage facility. Some of the properties of Zircaloy that make it a suitable material for nuclear fuel cladding were given. The cladding failure rate appears to have been low, and most appeared to have initiated from the internal side of the cladding tube. Some cladding failures that have occurred were discussed, as well as other types of corrosion and associated environmental effects. some information was presented on the Materials Characterization Center's analyzed specimens of spent nuclear fuel cladding, and this provided an opportunity to see the condition of some of the material that would be placed in the nuclear waste storage repository.

Some points of information that are useful to consider in determinations of the corrosion resistance and durability of Zircaloy spent fuel cladding are as follow.

1. In terms of long term durability of the cladding, the significance of the oxide layer formation on both the inner and exterior surfaces of the cladding is difficult to assess. The double layer of oxide indicates that the cladding exposure may have been in the post transition oxidation region, and that some thinning of the cladding wall occurred.

2. Localized thinning of the cladding wall also has occurred as indicated by the reactions at the inner cladding wall.

3. Changes in the wall thickness will affect the hoop stress and this increases the probability that stress cracking will occur.
4. Hydrogen is present in the cladding, and seems to be increased in areas of increased oxidation.

5. The presence of Cs and I on the inner wall of the cladding affect susceptibility to cracking.

6. Past records and documented information on Zircaloy cladding failures that have occurred either in nuclear reactor service or in storage should be reviewed.

7. The know mechanisms of internal cladding failures discussed in this paper such as localized corrosion due to radionuclide products such as Cs and I, cracking due to effects of hydrogen, effects of oxidation and wall thinning and others should be addressed in more detail.

8. In view of these analyses of the spent fuel cladding, it is useful to know how well the cracked cladding will contain the radionuclides. Some studies of this question have been conducted by the Department of Energy (DOE)[51], and results showed that with cracks and holes provided some containment of the radionuclides when compared with bare fuel. More quantitative data are needed.

REFERENCES

1. Woodley, R. E., The Characteristics of Spent LWR Fuel Relevant to Its Storage in Geologic Repositories, Hanford Engineering Development Laboratory, Hanford, Washington, HEDL-TME 83-28, October, 1983.

2. Soo, P. and Gause, E., Review of DOE Waste Package Program, Brookhaven National Laboratory, Upton NY 11973, NUREG/CR-2482, BNL-NUREG-51494, Vol. 7, April, 1984.

3. Fraker, Anna C., Corrosion of Zircaloy Spent Fuel Cladding in a Repository, NISTIR, 1989.

4. Hillner, Edward, Corrosion of Zirconium-Base Alloys-An Overview, in An Overview of Zirconium in the Nuclear Industry, American Society for Testing and Materials (ASTM) Special Technical Publication (STP) 633, 211-235, 1977.

5. Rothman, A. J., Potential Corrosion and Degradation Mechanisms of Zircaloy Cladding on Spent Fuel in a Tuff Repository, Attachment 10 to MRB-0418, JUCID-20172, Contract W-7405-Eng-48, Lawrence Livermore National Laboratory, Livermore, CA 94555, 1984.

6. Yau, T. L. and Webster, R. T., Corrosion of Zirconium and Hafnium, Am. Soc. for Metals Handbook, Ninth Ed., Vol. 13, 707-721, 1987.

7. Schemel, John H., Introduction to Zirconium and Its Alloys, and Corrosion Resistance of Zirconium and Its Alloys, am. Soc. for Metals Handbook, Ninth Ed., Vol. 3, 781-791, 1980.

8. Fontana, M. G. and Greene, N. D., Corrosion engineering, McGraw-Hill Series in Materials Science and Engineering, McGraw-Hill Book Co., New York, 2nd Ed., 179-180, 389, 1978.

9. Cox, B. Oxidation of Zirconium and Its Alloys, Advances in Corrosion Science and Technology, 5, M. G. Fontana and R. W. Staehle, Eds., Plenum Press, 173-391, 1976.

10. Title 10 Code of Federal Regulations (CFR) Part 60-Disposal of High Level Radioactive Wastes in Geologic Repositories: Section 60.113(a)(1)(ii)(B), United States Nuclear Regulatory Commission, 1988.

11. Title 40 CFR Part 191-Environmental Radiation Protection Standards for Management and Disposal of Spent Nuclear Fuel, High Level and Transuranic Radioactive Wastes, United States Environmental Protection Agency, 1987.

12. Title 10 CFR part 960-General Guidelines for the Recommendation of Sites for Nuclear Waste Repositories, United States Department of Energy, 1988.

13. Murray, Raymond L., Introduction to Nuclear Engineering, Prentice Hall, Inc., Englewood Cliffs, NJ, 152-181, 1961.

14. Berry, Warren, Corrosion in Nuclear Applications, John Wiley & Sons, Inc., NY, 66, 1971.

15. Knights, C. F. and Perkins, R., Effect of Applied Tensile Stress on the Corrosion Behavior of Zircaloy-2 in Steam and Oxygen, J. Nucl. Mat., Vol. 36, 180-188, 1970.

16. Woolsey, I. S., and Morris, J. R., Study of Zircaloy-2 Corrosion in High Temperature Water Using Ion Beam Methods, Corrosion, Vol. 37, No. 10, 575-585, 1981.

17. Bryner, J. S., The Cyclic Nature of Corrosion of Zircaloy-4 in 633 C Water, J. Nucl. Mat., Vol. 82, 84-101, 1979.

18. Tong, L. S. and Weisman, Joel, Thermal Analysis of Pressurized Water Reactors, An AEC monograph, Published by American Nuclear Society, 66-70, 1970.

19. Machiels, A. J., Corrosion of Zircaloy-Clad LWR Fuel Rods, Am. Soc. for Metals Handbook, Ninth Edition, Vol. 13., Corrosion, 945-948, 1987.

20. Barner, J. O., LWR Spent Fuel Testing Materials for Radionuclide Release Studies, PNL-4686, Pacific Northwest Laboratory, Richland, Washington, 99352, 1984.

21. Guenther, R. J., Blahnik, D. E., Campbell, T. K., Jenquin, U. P., Mendel, J. E., Thomas, L. E. and Thornhill C. K., Characterization of Spent Fuel Approved Testing Material - ATM-103, PNL-5109-103, UC 70, Pacific Northwest Laboratory, Richland, Washington, 99352, 1988.

22. McCright, R. D., and others, UCRL-89988, Selection of Candidate Canister Materials for High Level Nuclear Waste Containment in a Tuff Repository, Lawrence Livermore National Laboratory, 1983.

23. Nishimura, S., Evaluation of Crack Growth Rate and Variation of Initiation Time for Stress Corrosion Cracking in Zircaloy-2 Cladding Tube, Am. Nuc. Soc. Meeting, New Orleans, Louisiana, June, 1984.

24. Garzarolli, F., von Jan, R., and Stehle, H., Main Causes of Fuel Element Failure in Water-Cooled Power Reactors, Atom., Energy Rev., 17,31, 1979.

25. Miller, A. K., Ocken, H. and Tasooji, A., Iodine Stress Corrosion Cracking of Zircaloy: Laboratory Data, A Phenomenological Model, and Predictions of In-Reactor Behavior, J. Nucl. Mater., 99, 254-268, 1981.

26. Jones, R. L., Yaggee, F. L., Stoehr, R. A. and Cubicciotti, D., J. Nucl. Mater. 82, 26, 1979.

27. Tucker, R. P., Kreyns, P. H. and Kearns, J. J., WAPD-TM-1248, Bettis Atomic Power laboratory, West Mifflin, PA, 1976.

28. Peehs, M., Stehle, H. and Steinberg, E., Out-of-Pile Testing of Iodine Stress Corrosion Cracking in Zircaloy Tubing in Relation to the Pellet-Cladding Interaction Phenomenon, in Zirconium in the Nuclear Industry (Fourth Conf.), American Society for Testing and Materials(ASTM), Philadelphia, PA, ASTM STP 681, 244-260, 1979.

29. Cubicciotti, D., Jones, R. L. and Syrett, B. C., EPRI NP-1329, Electric Power Research Institute, Palo Alto, CA, 1980.

30. Knorr, D. B. and Pelloux, Effects of Texture and Microstructure on the Propagation of Iodine Stress Corrosion Cracks in Zircaloy, Metallurgical Transactions A, 13A, 73-83, 1982.

31. Peehs, M., Kuhnel, R. and Kaspar, G., Discussion of Spent LWR Fuel Properties in Relation to Actual Long Term Storage Concepts, Proc. Intnl. ENS/ANS Conf. on New Directions in Nuclear Energy with Emphasis on the Fuel Cycle, Brussels, Belgium, April 26-30, 1982.

32. Syrett, B. C., Cubicciotti, D., and Jones, R. L., Embrittlement of Zircaloy-4 by Liquid Cesium at 300 C, in Zirconium in the Nuclear Industry, A. L. Lowe, Jr., and G. W. Parry, Eds., American Society for Testing and Materials, Philadelphia, PA, ASTM STP 633, 281-294, 1977.

33. Shann, S. H. and Olander, D. R., Stress Corrosion Cracking of Zircaloy by Cadmium, Iodine and Metal Iodides, J. Nucl. Mater. 113, 234-248, 1983.

34. Grubb, W. T., and Morgan, M. H., A Survey of the Chemical Environments for Activity in the Embrittlement of Zircaloy-2, in Zirconium in the Nuclear Industry (Fourth Conf.) American Soc. for Testing and Materials, STP 681, 145-154, 1979.

35. Atrens, A., Dannhaeuser, G., and Baero, G., Stress-Corrosion-Cracking of Zircaloy-4 Cladding Tubes, - Part 1. Threshold in the Presence of Iodine, J. Nucl. Mater., 126, (2) 91-102, 1984.

36. Cox, B., Surette, B. A., and Wood, J. C., Stress Corrosion Cracking of Zircaloys in Unirradiated and Irradiated CsI, J. Nucl. Mater., 138, (1), 89-98, 1986.

37. Dannhaeuser, G., and Baero, G., and Atrens, A., Stress-Corrosion-Cracking of Zircaloy-4 Cladding Tubes- Part 2. Cs/Cd Mixtures and Fractography, J. Nucl. Mater., 126, (2) 103-110, 1984.

38. Hofman, P., and Spino, J., Stress Corrosion Cracking of Zircaloy-4 Cladding at Elevated Temperatures and Its Relevance to Transient LWR Fuel Rod Behaviour, J. Nucl. Mater., 125, (1), 85-95, 1984.

39. Yaggee, F. L., Mattas, R. F. and Neimark, L. A., EPRI NP-1557, Electric Power Research Institute, Palo Alto, CA, 1980.

40. Materials Characterization Center, Approved Testing Material, ATM 103, Pacific Northwest Laboratories, Richland, Washington, 1988.

41. Materials Characterization Center, Approved Testing Material, ATM-106, Pacific Northwest Laboratories, Richland, Washington, 1988.

42. Doman, D. R. and Pankaskie, P. J., "In-Reactor Monitoring of Zircaloy-2 PRTR Pressure Tubes, Part II, May and June, 1962", USAEC Report HW-74731, August, 1962.

43. Winegardner, W. K., "Fretting Corrosion in the Plutonium Recycle Test Reactor", USAEC Report HW-80021, March, 1964.

44. Wilson, C. N., Summary of Results from the Series 2 and Series 3 NNWSI Bare Fuel Dissolution Tests, UCRL-21013. Westinghouse Hanford Company, Pacific Northwest Laboratories, Richland Washington, November, 1987.

45. Machiels, A. J., Corrosion of Zircaloy-Clad LWR Fuel Rods, ASM Metals Handbook, Ninth Edition, Corrosion, Vol. 13, 944-948, 1987.

46. Cheng,B. and Adamson, R. B., Mechanistic Studies of Zircaloy Nodular Corrosion, Am. Soc. for Testing and Mater., 7th Internl. Conf. on Zirconium in the Nuclear Industry, Strasbourg, France, June 24-27, 1985.

47. Urquhart, A. W., Vermilyea, D. A. and Rocco, W. A., J. Electrochem. Soc., 125, 199, 1978.

48. Cheng, B. Adamson, R. B., Bell, W. L. and Proebstle, R. A., Corrosion Performance of Some Zirconium Alloys Irradiated in the Steam Generating Heavy Water Reactor -- Winfrith, Proc. Internl. Sympos. in Nuclear Power Systems -- Water Reactors, Myrtle Beach, SC, NACE/AIME/ANS, 274, 1984.

49. Chase, M. W., Jr., Davies, C. A., Downey, J. R., Jr., Frurip, D. J., McDonald, R. A. and Syverud, A. N., JANAF Thermochemical Tables, J. Phy. and chem. Ref. Data, Vol. 14, Supplement No. 1, 1985.

50. Pescatore, C., Cowgill, M. G. and Sullivan, T. M., Zircaloy Cladding Performance Under Spent Fuel Disposal Conditions, BNL52235, Nuclear Waste Management, DOE/OSTI-4500-R75, May - October, 1989, Brookhaven National Laboratories, Upton, NY 11973, April 1990.

51. Wilson, C. N. and Oversby, V. M., Radionuclide Release from PWR Fuels in a Reference Tuff Repository Groundwater, UCRL-91464, Waste Management 85 Conference, Tuscon, AR, March 25-29, 1985.