



UNITED STATES DEPARTMENT OF COMMERCE  
National Bureau of Standards  
Gaithersburg, Maryland 20899

April 15, 1988

Mr. Charles Peterson  
Technical Review Branch  
Division of High-Level Waste Management  
Office of Nuclear Materials Safety and Safeguards  
U.S. Nuclear Regulatory Commission  
Washington, DC 20555

Re: Monthly Letter Status Report for March 1988 (FIN-A-4171-7)

Dear Mr. Peterson:

Enclosed is the March 1988 monthly progress report for the project  
"Evaluation and Compilation of DOE Waste Package Test Data"  
(FIN-A-4171-7). The financial information is reported separately.

Sincerely,

Charles G. Interrante  
Program Manager  
Corrosion Group  
Metallurgy Division

Enclosure

Distribution:

NMSS PM (1)  
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A 4171  
WM-11  
NH 14

Monthly Letter Report for March 1988

Published April 1988

(FIN-A-4171-7)

Performing Organization: National Bureau of Standards (NBS)  
Gaithersburg, MD 20899

Sponsor: Nuclear Regulatory Commission (NRC)  
Office of Nuclear Materials Safety and Safeguards  
Washington, DC 20555

Task 1 -- Review of Waste Package Data Base

Status of database and of reviewable documents

- 792 Documents in HLW database.
- 53 Completed reviews in HLW database (taken from Vol. 1 to 3).
- 25 Nearly completed reviews from Vol. 4 being readied for database entry.
- 24 Reports currently under review for tuff.
  - 3 Identified and not yet assigned.
- 11 Reports currently under review for glass.
  - 2 Under consideration for review for glass.

During the month of April the NBS will reconsider all papers previously listed for review. Each will be classified by a system to be determined. For example, papers currently having highest review status (Category 1), review when time permits (Category 2) and file with cross reference(s) to other similar report(s) (Category 3). Completed reviews are currently listed in the NBS HLW database as to relevance: 1-entered into database, 2-no review necessary, 3-non-critical review, 4-critical reviews.

As part of our search for documents relevant to the waste package and in addition to documents received directly from NNWSI, the NBS uses a service called Dialog Selective Dissemination of Information (SDI) to search the files of two data sources, the National Technical Information Service (NTIS) and DOE Energy. During the month of March, Dialog SDI

bibliographic updates were received from NTIS and DOE Energy database files. Selected items taken from the list of citations furnished by this search are currently under consideration for review and they are listed in section titled WASTE FORM DEGRADATION (see p. 5). Also enclosed is the search strategy used for these searches. It is attached for general information (see p. 16, Attachment B).

In response to an NRC request for information on the availability of any of the 90 papers presented at the MRS Symposium 1987, Symposium P on the Scientific Basis for Nuclear Waste Management, it has been established that while these papers largely are available only in the published proceedings, authors can make selected papers available to us. Therefore, several papers from this symposium are currently undergoing review at the NBS.

Appended to this report are the following three Draft Reviews not previously submitted (see p. 8, Attachment A).

1. UCRL-92891, "LWR Spent Fuel Characteristics Relevant to Performance as a Wasteform in a Potential Tuff Repository," June 1985.
2. DP-MS-83-110, "Solidification of Savannah River Plant High-Level Waste," November 1983.
3. DP-MS-86-48, "Processing of Transuranic Waste at the Savannah River Plant," March 1987.

#### STATUS OF REVIEWS OF NNWSI REPORTS

NNWSI -- Reports identified for review this month.

Three reports were identified for review during this period. Two of them deal with dissolution of spent fuel and the third considers the interaction of groundwater with tuff.

The first report describes the dissolution of spent fuel in J-13 groundwater using a computer simulation, EQ3/6 code version 3245 (Bruton, 1987). The results, based on available data, indicate that the dissolution of uranium is limited by the presence of  $\text{SiO}_2$  in solution. The results are compared with experimental studies.

A two-year laboratory experiment simulating the dissolution of bare spent fuel in J-13 water is summarized in the second report (Wilson, 1987). Using copies of slides, the concentrations of radionuclides are shown as a function of time (up to 240 d). At 25 and 86° C, uranium concentrations decrease with time, and these concentrations are affected by the type of container used.

The third report describes 66-day laboratory tests of the dissolution of tuff in J-13 water. The concentrations of the components of tuff are shown as a function of time at different temperatures in J-13 water and

distilled water. Photomicrographs and electron diffraction patterns are shown.

1. Bruton, C. J. and Shaw, H. F., "Geochemical Simulation of Reaction Between Spent Fuel Waste Form and J-13 Water at 25°C and 90°C," UCRL-96702, November 1987.
2. Wilson, C. N., "Recent Results from NNWSI Spent Fuel Leaching/Dissolution Tests," UCRL-21019, SAN-662,-027, April 1987.
3. Knauss, K. G., Beiriger, W. J., Peifer, D. W., and Piwinski, A. J., "Hydrothermal Interaction of Solid Wafers of Topopah Spring Tuff with J-13 Water and Distilled Water at 90, 150, and 250°C, Using Dickson-Type, Gold-Bag Rocking Autoclaves," UCRL-53645, September 1985.

NNWSI -- Review is continuing on the following 24 reports.

1. UCRL-94708, "Carbon-14 in Waste Packages for Spent Fuel in a Tuff Repository," October 1986.
2. UCRL-94633, "Experimental Study of the Dissolution Spent Fuel at 85°C in Natural Groundwater," December 1986.
3. UCRL-95962, "Hydrogen Speciation in Hydrated Layers on Nuclear Waste Glass," January 1987.
4. UCRL-94658, "Integrated Testing of the SRL-165 Glass Waste Form," December 1986.
5. UCRL-91258, "Leaching Savannah River Plant Nuclear Waste Glass in a Saturated Tuff Environment," November 1984.
7. ANL-84-81, "NNWSI Phase II Materials Interaction Test Procedures and Preliminary Results," January 1985.
8. HEDL-TME 85-22, "Results from Cycles 1 and 2 of NNWSI Series 2 Spent Fuel Dissolution Tests," May 1987.
9. UCRL-94363, "Hydrological Properties of Topopah Spring Tuff - Laboratory Measurements," December 1985.
10. UCRL-53761, "Waste Package Performance Assessment: Deterministic System Model Program Scope and Specification," October 1986.
11. HEDL-7540, "Technical Test Description of Activities to Determine the Potential for Spent Fuel Oxidation in a Tuff Repository," June 1985.
12. HEDL-SA-3627, "Predicting Spent Fuel Oxidation States in a Tuff Repository," April 1987.

13. UCRL-53702, "Spent Fuel Test - Climax: An Evaluation of the Technical Feasibility of Geologic Storage of Spent Nuclear Fuel in Granite," March 1986.
14. UCRL-53767, "Geomechanics of the Spent Fuel Test - Climax," July 1987.
15. UCRL-53795, "Reaction of Vitric Topopah Spring Tuff and J-13 Ground Water under Hydrothermal Conditions Using Dickson-Type, Gold-Bag Rocking Autoclaves", November 1986.
16. UCID-21044, "Progress Report on the Results of Testing Advanced Conceptual Design Metal Barrier Materials Under Relevant Environmental Conditions for a Tuff Repository", December 1987.
17. UCRL-15976, SANL-522-006, "Microstructural Characteristics of PWR Spent Fuel Relative to its Leaching Behavior", April 1985.
18. UCRL-97562, "Impact of Phase Stability on the Corrosion Behavior of the Austenitic Candidate Materials for NNWSI," October 1987.
19. UCRL-21005, SANL 616-007, "Corrosion Testing of Type 304L Stainless Steel in Tuff Groundwater Environments," December 1987.
20. UCRL-96703, "Geochemical Simulation of Dissolution of West Valley and DWPF Glasses in H-13 Water at 90°C," November 1987.
21. UCRL-96555, Rev. 1, "Thermodynamic Data Bases for Multivalent Elements: An Example for Ruthenium," November 1987.
22. UCID-21190, "Plan For Glass Waste Form Testing For NNWSI", September 1987.
23. UCRL-92311, "Gamma Radiation Effects on Corrosion, I. Electrochemical Mechanisms for the Aqueous Corrosion Process of Austenitic Stainless Steels," February 1985.
24. UCRL-97936, "Effect of Ionizing Radiation on Moist Air Systems," December 1987.

#### WASTE FORM DEGRADATION

A review of PNL-5157, "Final Report of the Defense High-Level Waste Leaching Mechanisms Program," Chapter 3, "Environmental Interaction," is expected to be available in May. Chapter 4, "Dissolution of Specific Radionuclides," is expected to be completed in July. Chapter 5, "Radiation Effects," is expected to be completed in April. Chapter 6, "Phenomenological Models of Nuclear Waste Glass Leaching" will be assigned when a suitable reviewer is available.

WASTE FORM DEGRADATION -- Documents under consideration.

1. PNL-6353, "Comprehensive Data Base of High-Level Nuclear Waste Glasses: September 1987 Status Report: Volume 1, Discussion and Glass Durability Data," December 1987.
2. PNL-6353, "Comprehensive Data Base of High-Level Nuclear Waste Glasses: September 1987 Status Report: Volume 2, Additional Appendices," December 1987.

WASTE FORM DEGRADATION -- Review is continuing on the following 11 reports.

1. "Long Term Leach Behavior of West Valley HLW Glasses," P. B. Macedo, et al., ANS Spectrum, 1986.
2. "Leach Mechanisms of Borosilicate Glass Defense Waste Forms -- Effects of Composition," A. Barkatt, et al., Waste Management '86: Waste Isolation in the U.S.-Technical Programs and Public Education, March 1986.
3. "Chemical Determination of West Valley Waste Form Products," D. M. Oldman, J. R. Stimmel, and J. H. Marlow, March 1987.
4. PNL-5157, "Final Report of the Defense High-Level Waste Leaching Mechanisms Program," August 1984.
5. "Physical Chemistry of Glass Surfaces," J. Non-Cryst. Solids, 1978.
6. DP-MS-83-135, "Process Technology for Vitrification of Defense High-Level Waste at the Savannah River Plant," Paper for presentation in the proceedings of the American Nuclear Society Meeting on Fuel Reprocessing and Waste Management, August 1984.
7. DP-MS-86-96, "Process and Mechanical Development for the Savannah River TRU Waste Facility," Paper proposed for presentation at the American Nuclear Society International Meeting, Spectrum '86, September 1986.
8. PNL-4382, "Materials Characterization Center's Workshop on Leaching Mechanisms of Nuclear Waste Forms," May 19-21, 1982.
9. "Large Scale Leach Testing of DWPF Canister Sections," Proceedings of the Materials Research Society Symposium, "Scientific Basis for Nuclear Waste Management X," December 1986.
10. "Waste Glass Leaching: Chemistry and Kinetics," Proceedings of the Materials Research Society Symposium, "Scientific Basis for Nuclear Waste Management X," December 1986.

11. "Method for Showing Compliance with High-Level Waste Acceptance Specifications," Waste Management '86: Waste Isolation in the U.S. Technical Programs and Public Education, Volume 2, High-Level Waste, March 1986.

TASK 2 -- Identification of Additional Data Required and Identification of Tests to Generate the Data

NBS lead workers are continuing their studies concerning the types of additional data and verification tests needed to demonstrate that the DOE waste package designs will meet the performance objectives of 10 CFR 60.

Conclusions, results, and recommendations for the work reviewed to date are given in each review form under the heading GENERAL COMMENTS OF REVIEWER.

TASK 3 -- Laboratory Testing

The work on each of the three projects reported below is on schedule with the work statements listed in their respective proposals. The work conducted in March 1988 is reported below. Work conducted in previous months was reported earlier.

Title of Study: Evaluation of Methods for Detection of Stress Corrosion Crack Propagation in Fracture Mechanics Samples.

Principal Investigator: Charles Interrante

Work in February and March was temporarily halted to conduct training of laboratory support staff necessitated by recent reorganization within the NBS HLW Program brought about from a reduction in the level of effort. Training Courses taken by support staff, Advanced Revelation for use in the database and C programming language for use in the laboratory, further reduced the amount of time that could be spent on this project. Mr. Harrison will be working half time on the HLW program, and this time will be split between database activities and laboratory testing activities, so slower progress can be expected in this program in the future months. However, the laboratory testing apparatus is constructed and software for conducting the test is largely developed, so in this data gathering phase of the work, these curtailments in support staff are not as detrimental as they would be in the preliminary phase.

Data generated in February were reviewed. While data were considered to represent results of a preliminary test of the apparatus using a live test specimen, analysis of the data was required before further tests were conducted. As part of this analysis some software development was done to compute stress intensity from displacement and load.

Title of Study: Effect of Resistivity and Transport on Corrosion of Waste Package Materials.

Principal Investigator: Edward Escalante

The corrosion measurements indicate that in the simulated soil environments, the highest corrosion of steel did not occur in the lowest resistivity environment, as might be expected. In general, the greatest corrosion occurred at a resistivity of 150 to 600 ohm cm. Other factors are overriding the effect of a low resistivity media, and among these is the effect of oxygen transport which we are now evaluating. The next phase of this experiment will incorporate changes in experiment design based on our experiences.

Title of Study: Pitting Corrosion of Steel Used for Nuclear Waste Storage  
Principal Investigator: Anna C. Fraker

The work on this project has been completed, and the report has been written. A draft copy of the report is included in Attachment D. The report is being reviewed and will be submitted in final form after the review is completed.

Title of Study: Corrosion Behavior of Zircaloy Nuclear Fuel Cladding  
Principal Investigator: Anna C. Fraker

The work on this project is continuing and additional anodic polarization measurements are being made. Some parameters of the testing such as the rate of stepping the applied potential and the solution pH will be changed to obtain more information regarding the corrosion behavior of Zircaloy in 95°C simulated J-13 well water.

#### TASK 4 -- General Technical Assistance

Dr. C. Interrante participated in an international workshop on Corrosion of Waste Containers on February 9-10, 1988 in Winnipeg, Manitoba, Canada. A trip report is enclosed (see p. 18, Attachment C).

E. Escalante and A. Fraker attended an NRC/DOE Workshop on NRC Draft Point Papers on the Consultation Draft Site Characterization Plan (CDSCP) for the Yucca Mountain, Nevada Site at the NRC, White Flint Building, Rockville, MD, on March 23, 1988.

C. Interrante and E. Plante attended a meeting on "Tektite Glass as a Natural Analogue for Nuclear Waste Glass," at the NRC, White Flint Building, Rockville, MD, on March 30, 1988. Drs. John O'Keefe (NASA/Goddard Space Flight Center) and Aaron Barkatt (Catholic University of America, Vitreous Laboratory) reported their findings and lead discussion.

NBS Review of Technical Reports on the High Level Waste Package  
for Nuclear Waste Storage

DATA SOURCE

(a) Organization Producing Data

Westinghouse Hanford Company (CNW, REE and REW) and Lawrence  
Livermore National Laboratory (VMO).

(b) Author(s), Reference, Reference Availability

Wilson, C. N., Einziger, R. E., Woodley, R. E., and Oversby, V. M.,  
"LWR Spent Fuel Characteristics Relevant to Performance as a  
Wasteform in a Potential Tuff Repository", UCRL-92891, June 1985.

DATE REVIEWED: 12/14/87; Revised 3/2/88.

TYPE OF DATA

Literature review of leach studies from PWR spent fuels and oxidation of  
spent fuel.

MATERIALS/COMPONENTS

None given.

TEST CONDITIONS

None given.

METHODS OF DATA COLLECTION/ANALYSIS

None given.

AMOUNT OF DATA

None given.

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

KEY WORDS

Literature review, spent fuel leaching, laboratory, air, J-13 water, deionized, high temperature, basic (alkaline) solution (pH >7), neutral solution (pH = 7), spent fuel, spent fuel oxidation, <sup>237</sup>Np, <sup>239</sup>Pu .

GENERAL COMMENTS OF REVIEWER

This report is essentially a review of the related HLW reports cited below which have been previously reviewed and are included in the NBS data bank. In addition, new observations, not described, state that examination of partially oxidized spent fuel particles and ion microprobe data on spent fuel, which was partially oxidized using <sup>18</sup>O<sub>2</sub>, support previous data suggesting grain boundary oxidation as the initial stage in the oxidation process. No data are given.

RELATED HLW REPORTS

Wilson, C. N., and Oversby, V. M., "Radionuclide Release from PWR Fuels in a Reference Tuff Repository Groundwater," UCRL-91464, March 1985.

Einzigler, R. E., and Woodley, R. E., "Low Temperature Spent Fuel Oxidation Under Tuff Repository Conditions," HEDL-SA-3271FP, 1985.

APPLICABILITY OF DATA TO LICENSING:

[Ranking: key data ( ), supporting data (X)]

(a) Relationship to Waste Package Performance Issues Already Identified

Report relates to NNWSI ISTP issue, 2.3.2, what is the solubility of the waste form under the range of potential repository conditions?

(b) New Licensing Issues

(c) General Comments

NBS Review of Technical Reports on the High Level Waste Package  
for Nuclear Waste Storage

DATA SOURCE

(a) Organization Producing Data

E.I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken,  
South Carolina 29808.

(b) Author(s), Reference, Reference Availability

Maher, R., Shafranek, L. F., and Stevens, W. R., "Solidification of Savannah River Plant High-Level Waste," paper presented to a meeting of the American Institute of Chemical Engineers, Washington, DC, DP-MS-83-110, November 1983.

DATE REVIEWED: 8/17/87; Revised 3/30/88.

TYPE OF DATA

(1) Scope of the Report:

Review paper describing technology and engineering for immobilizing large volumes of high-level liquid radioactive nuclear wastes in a borosilicate glass disposal form at a concentration ratio of 30 to 1.

(2) Failure Mode or Phenomenon Studied:

High-level defense waste immobilization.

MATERIALS/COMPONENTS

Defense radioactive waste materials, borosilicate glass waste immobilization form, stainless steel containment canisters.

TEST CONDITIONS

(1) State of the Material being Tested:

High-level defense waste radionuclide materials, present as metal oxide and salts, present as a liquid sludge.

(2) Specimen Preparation:

Radwaste will be physically and chemically treated to separate various nuclide forms and fractions, then combined either with cementitious materials or with glass forming frit and melted for immobilization.

### (3) Environment of the Material being Tested:

Sludge is stored in a sealed liquid radioactive environment. Processing will take place within the sludge containment environment. Further sludge processing, melting, canister filling, and canister decontamination will occur in the DWPF facility. Long-term canister storage will be in deep mine repositories.

#### METHODS OF DATA COLLECTION/ANALYSIS

Data in paper is of a general design nature, collected from referenced sources.

#### AMOUNT OF DATA

Twenty one figures listed, consisting of process flow charts, process materials, or photographs of DWPF facilities or equipment:

- Figure 1. Source of Radioactive Wastes at Savannah River, (flow chart)
- Figure 2. Radioactive Liquid Waste, (photographs)
- Figure 3. Actual Waste Sludge, (photograph)
- Figure 4. Salt in Waste Tank, (photograph)
- Figure 5. New Waste Storage Tank, (cutaway schematic)
- Figure 6. Waste Tank Farm, (aerial photograph)
- Figure 7. Defense Waste Processing Facility, (flow chart)
- Figure 8. Shielded Cells, (photograph)
- Figure 9. Large Slurry-Fed Melter, (photographs)
- Figure 10. Inside Sludge Removal Demonstration Tank Before Sludge Removed, (photograph)
- Figure 11. Inside Sludge Removal Demonstration Tank Most Sludge Removed, (photograph)
- Figure 12. Inside Sludge Removal Demonstration Tank After Sludge Removal, (photograph)
- Figure 13. Glass Waste Canister, (photograph)
- Figure 14. Defense Waste Processing Facility, (artists drawing)
- Figure 15. DWPF Building 221-s - Level 1, (schematic)
- Figure 16. DWPF Melter Off-Gas System, (photograph)
- Figure 17. Off-Gas Line Cooler, (photograph)
- Figure 18. DWPF Building 221-S - Section C, (schematic)
- Figure 19. Interim Storage Building, (artists drawing)
- Figure 20. Glass Storage Building Section B - B, (schematic)
- Figure 21. Saltstone Monolith Cross Section, (schematic)

#### UNCERTAINTIES IN DATA

Only general process design data presented.

#### DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

KEY WORDS

Process design, facility design, Savannah River Plant, air, ambient temperature, ambient pressure, basic (alkaline) solution, stainless steel, defense high level waste (DHLW); solidification, high-level waste; waste form, sludge, slurry, salt, liquid, saltcake, waste tank, borosilicate glass, DWPF, repository, joule heating, stainless steel canister, off-gas, decontamination.

GENERAL COMMENTS OF REVIEWER

Paper presents general overview of DWPF history, design, development, and operations.

APPLICABILITY OF DATA TO LICENSING

Ranking: key data ( ), supporting data (X)

(a) Relationship to Waste Package Performance Issues Already Identified

Related to ISTP issues 2.7.2, how will the waste package design ensure that the radioactive wastes will be in solid form in a sealed container?, 2.7.3, how will the waste package design ensure that particulate waste forms will be consolidated (for example, by incorporating into an encapsulating matrix) to limit the availability and generation of particulates?

(b) New Licensing Issues

(c) General Comments on Licensing

NBS Review of Technical Reports on the High Level Waste Package  
for Nuclear Waste Storage

DATA SOURCE

(a) Organization Producing Data

E.I. du Pont de Nemours & Co., Savannah River Laboratory,  
Aiken, South Carolina 29808.

(b) Author(s), Reference, Reference Availability

Daugherty, B. A., Salizzoni, L. M., and Mentrup, S. J., "Processing  
of Transuranic Waste at the Savannah River Plant," paper proposed  
for presentation at the Waste Management '87 meeting, Tucson, AZ,  
DP-MS-86-48, March 1987.

DATE REVIEWED: 8/17/87; Revised 3/30/88.

TYPE OF DATA

(1) Scope of the Report:

General background and review of the design of the transuranic (TRU) waste  
processing facility (TRWF) at the Savannah River Plant.

(2) Failure Mode or Phenomenon Studied:

TRU waste processing and immobilization.

MATERIALS/COMPONENTS

Transuranic waste containing both combustible and non-combustible  
materials in sludge and resin form contained within 55-gallon drums and  
carbon steel boxes.

TEST CONDITIONS

(1) State of the Material being Tested:

Transuranic waste containing both combustible and non-combustible  
materials in solid, sludge and resin form.

(2) Specimen Preparation:

(3) Environment of the Material being Tested:

Air, earthen burial, waste preparation area (WPA), deep geological  
repository.

METHODS OF DATA COLLECTION/ANALYSIS

General design information.

AMOUNT OF DATA

Figures

1. The Process Flow, (schematic)
2. Waste Preparation Cell, (schematic)

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

KEY WORDS

Design, Savannah River Plant, field, air, earth, ambient temperature, ambient pressure, transuranic waste (TRU), Waste Isolation Pilot Plant (WIPP), deep geological repository, TRU Waste Facility (TWF), remote operation, hydrogen explosion, sand filters, high-efficiency particulate air (HEPA) filters, verification, solidification, Waste Certification Facility (WCF).

GENERAL COMMENTS OF REVIEWER

Good general overview of transuranic waste facility (TRWF) planned for the Savannah River Plant.

APPLICABILITY OF DATA TO LICENSING

Ranking: key data ( ), supporting data (X)

- (a) Relationship to Waste Package Performance Issues Already Identified

Related to ISTEP issues 2.7.2, how will the waste package design ensure that the radioactive wastes will be in solid form in a sealed container?, 2.7.3, how will the waste package design ensure that particulate waste forms will be consolidated (for example, by incorporating into an encapsulating matrix) to limit the availability and generation of particulates?

- (b) New Licensing Issues
- (c) General Comments on Licensing

## AUTHOR'S ABSTRACT

The Department of Energy (DOE) has instituted a national program to isolate defense TRU waste in a deep geological repository, the Waste Isolation Pilot Plant (WIPP), in Galsbad, New Mexico. Since 1972, the highly toxic and long half-life transuranic (TRU) waste at the Savannah River Plant (SRP) has been stored on above-grade concrete pads in 55-gallon drums, large carbon steel boxes, and concrete culverts. As part of the national program, a major project is planned at SRP to retrieve and process this waste. This project, the TRU Waste Facility (TWF), will provide equipment and processes to retrieve TRU waste from 20-year retrievable storage and prepare it for permanent disposal at the WIPP. This project is an integral part of the SRP Long Range TRU Waste Management Program to reduce the amount of TRU waste stored at SRP. The TWF is designed to process 15,000 cubic feet of retrieved waste and 6,200 cubic feet of newly generated waste each year of operation. This facility is designed to minimize direct personnel contact with the waste using state-of-the-art, remotely operated equipment. In support of the TWF, a remote size-reduction and material handling process is being cold-tested at the Savannah River Laboratory. The process consists of a large, low-speed shredder and material handling system, a remote worktable, bagless transfer system, and a robotically controlled manipulator.

SDI006, UD 8807, SER. DD016

File(s) searched:

File 6:NTIS - 64-88/ISS07  
(COPR. 1988 NTIS)

Sets selected:

Set	Items	Description
1	4	WASTE(W)PACKAGE?
2	3	CANISTER?
3	34	CORROSION
4	19	LEACHING
5	51	GLASS
6	3	VITRIFICATION
7	102	S3-S6/OR
8	2	HIGH(W)LEVEL(W)WASTE?
9	134	RADIOACTIVE(W)WASTE?
10	21	NUCLEAR(W)WASTE?
11	2	(S1 OR S2) AND S7 AND (S8 OR S9 OR S10)
12	0	ANNA FRAKER RM. B-106 BLDG. 223 X6009
13	0	JILL RUSPI

Prints requested (\* indicates user print cancellation) :

Date Time Description  
05mar 23:14EST PR 11/5/1-25 (items 1-2)

Total items to be printed: 2

16

Attachment B

SDI103, UD 8805, SER. DD017

File(s) searched:

File 103:DOE ENERGY - 83-88/MAR (ISS05)

Sets selected:

Set	Items	Description
1	7	WASTE(W)PACKAGE?
2	18	CANISTER?
3	247	CORROSION (1974 DEC)
4	57	LEACHING (1974 DEC)
5	215	GLASS (1974 DEC)
6	12	VITRIFICATION (1974 DEC)
7	497	S3-S6/OR
8	22	HIGH(W)LEVEL(W)WASTE?
9	345	RADIOACTIVE(W)WASTE?
10	64	NUCLEAR(W)WASTE?
11	9	(S1 OR S2) AND S7 AND (S8 OR S9 OR S10)
12	0	ANNA FRAKER RM. B-106 BLDG. 223 X6009
13	0	JILL RUSPI

Prints requested ('\*' indicates user print cancellation) :

Date Time Description  
15mar 19:32EST PR 11/5/1-25 (items 1-9)

Total items to be printed: 9

17

Notes taken by C. Interrante at the Workshop on Waste Container Corrosion  
held February 9-10, 1988 in Winnipeg, Manitoba, Canada

### Introductory Remarks

Proceedings Chairman Dick Shoesmith of the Atomic Energy of Canada Limited (AECL) indicated that this is the second workshop on waste container corrosion. A transcription of the first workshop was given to us and Shoesmith indicated that the proceedings of this second workshop would also be transcribed. Accordingly, copies of all slides and overhead projections were requested by the Chairman. I obtained a copy of the transcript of the first workshop.

The Canadian program uses candidate materials of Ti-, Cu-, and Ni-base alloys. The most pressing problem is development of models to predict failure of the container, and this was a motivation for holding this second workshop. By 1991 the Canadian program hopes plan to have a definitive plan.

M. Molecke and N. R. Sorenson of Sandia National Laboratories (USA) spoke on the WIPP facility in New Mexico which is largely (>90%) NaCl. Both Ti and stainless steel (SS) canisters are being tested. The SS canister uses an overpack of carbon steel. High-Mg brine has been injected into one of the Ti canister emplacements to accelerate the rate of corrosion (to simulate longer times). Some of the SS canister emplacements have had brine injected to surround their overpac materials.

### Speakers on Titanium

M. Molecke, Sandia National Laboratories

Titanium Grade-12 (Ti, 0.3 Mo, 0.8 Ni, 0.10 Fe, 0.14 O<sub>2</sub>) or Ti-code 12 was characterized as having many advantages for a salt repository environment. What concerns exist regarding the susceptibility to local corrosion attack?

1. Crevice corrosion -- Westerman's observations
2. Hydrogen sorption and its effects
3. Smear iron from shipping, etc., may be a problem.

In response to my questions, the speaker characterized Ti as being a suitable material to use either as an overpac for stainless canisters (for a Savannah River's Defense Waste) or possibly as the primary container for the tuff repository. This view was punctuated by his understanding that sensitivity to local attack may have to be resolved. G. Kass, Lawrence Livermore National Laboratories (LLNL) pointed out that tuff and salt are widely different media and the use of titanium in tuff may be questionable. Nevertheless, a further look at the suitability of titanium-alloys is warranted for the tuff environment.

N. R. Sorenson, Sandia National Laboratories

$\gamma$ -radiation has minor to nil effects. There is no evidence of SCC, or crevice corrosion (using metal-to-metal crevices and optical determinations of attack).

R. A. Oriani observed H uptake of 60 ppm (and beyond). Uptake was smaller with radiation than without.

Environmental cracking (SCC and HE) -- anodic potentials have no effect on susceptibility to SCC. [Ed. This may not be true and needs to be qualified].

Cathodic potentials at sufficiently high overpotentials, do give decreases in reduction in area (R.A.) and time to failure ( $t_f$ ). Microstructurally, the H goes into the  $\beta$  phase, which is the minor constituent, and the  $\beta$  phase is transformed with the addition of hydrogen. Up to 400 or 500 ppm, no transformation and no effects of embrittlement are observed. Transverse notched specimens are more sensitive than longitudinal ones. Ti-code 6 weldments performed like those that had not been smeared (with iron).

My question -- Hydrogen uptake influences mechanical properties only at higher uptake levels, and these occur at longer exposures; I understand a hydride layer forms at long times of exposure. Can you predict the limiting value for uptake?

Answer: The limiting value is an open question.

R. E. Westerman, Battelle Memorial Institute asked about work on hydrogen induced delayed failure of Ti-code 12.

B. Ikeda, Atomic Energy of Canada Limited, White Shell

Ikeda characterized Ti as a passive metal that is subject to local corrosion if passive layers are broken. Needed are understandings of corrosion mechanisms, crevice corrosion susceptibility, H uptake levels, effects of radiation, rates of corrosion (uniform), and estimates of long-term damage by crevice and hydrogen effects.

The iron content seems to govern the propensity for activation or passivation of the Ti alloys:

Ti-Code 12 (0.02 wt% Fe) undergoes activation and crevice corrosion.

Ti-Code 2 (0.13 Fe) undergoes passivation and no crevice corrosion, except for a local (near-surface only effect); this crevice corrosion has been observed to be self limiting.

An active but oxygen-starved system was regarded as unacceptable for a repository because slow crevice corrosion might proceed in this system. An acceptable system is one demonstrated to repassivate.

Factors affecting these behaviors were discussed: availability of oxygen, chloride concentration,  $\gamma$ -radiation, time and temperature of exposure.

A uniform corrosion allowance of 3 mm would give a predicted lifetime of  $>10^4$  y.

Film breakdown (mechanical or chemical) can lead to hydrogen embrittlement or crevice corrosion.

I asked, "Is there any metastability in the microstructure of the as-welded canister that would give you pause in interpreting what would happen during the repository life of the canister?" Answer -- based on the time-temperature (t-T) needed for transformation, Shoesmith felt it very unlikely that repository conditions would lead to transformation. I pointed out that the problem might not be that simple, e.g., the repository conditions of long times might permit diffusion induced grain-boundary migration and chemistry changes, and these may promote unfavorable effects at longer times.

R. E. Westerman, Battelle National Laboratories

Ti-code 12 was studied (scoping tests) to determine if hydrogen embrittlement would pose a problem for this material as the SRP alternate overpac material. These studies revealed a crevice corrosion, the oxide of which initiated under a spacer of alumina ( $Al_2O_3$ ). This was unexpected in an irradiation field in the high-Mg brine used in these studies. In further experiments, using  $Al_2O_3$ -to-metal and metal-to-metal couples, all specimens showed at least some of this corrosive attack, with a noticeable 0.1 mm maximum being observed in the tests. The attack progressed periodically, but only along the specimen surface. An anoxic condition was used as the starting point for the tests; no oxygen was allowed to enter the system. Effects of the concentration of magnesium [Mg], and of radiation (with vs without) were not explored.

Hydrogen analyses showed that ~10 ppm H was absorbed over about an 18-month exposure; this is much less absorption than that which was observed by Oriani. In addition in these 18-month tests, sand blasted specimens absorbed about 20 ppm. Measurements of uptake were taken away from (not within) the crevice corrosion region.

Scoping exposure tests of OFHC Cu, 90-10 Cu-Ni and 70-30 Cu-Ni were also done. Increased temperature lead to increased corrosion rates. These studies led to the conclusion that copper and its alloys deserve consideration for use in brine repository environments, e.g.,  $<7$  mm/y maximum observed average corrosion rate was observed in 3-month tests conducted at  $150^\circ C$ .

## Speakers on Copper

### G. Kass, Lawrence Livermore National Laboratories

Kass characterized the U. S. tuff site at Yucca Mountain as one that will be above the water table, in a region 300 to 200 ft below the earth surface, and in this region, little water (5 L/y/container, as an upper bound), which has neutral pH and 10 ppm each  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{O}_2$ , and 20 ppm  $\text{SO}_4^-$ . No external pressure (lithostatic or hydrostatic) is expected.

Candidate alloys -- Of Copper (CDA102), 7% Al Bronze (CDA613), and 70/30, Cu-Ni (CD715) were specified and briefly characterized. They might be used at up to a 3-cm thickness. "Hydrogen sickness" fracture is due to bubble formation within pure copper, and it can be readily prevented. These three materials are each single (alpha) phase materials. The CDA715 has a potential miscibility gap that has been predicted but not found; in it  $\alpha_1 + \alpha_2$  would form. Creep might be a problem in pure copper. Corrosion rates in J-13 water, with and without radiation, were characterized as negligibly small. Peroxide, formed from  $\gamma$ -radiation, is broken down by the Cu, which serves as a catalyst.

Assurance that a level of 80 ppm  $\text{NH}_3$  (or other nitrogen-bearing species) will not obtain in the repository is a must; otherwise, cracking problems may be of serious concern. The  $\gamma$  Flux is  $10^4$  rd/h at first in the repository and  $10^2$  after a few decades. None of the candidates have shown SCC susceptibilities in one-year tests of U-bend specimens.

Advantages of these materials were enumerated. Their disadvantages must be evaluated in relation to the repository requirements. Fabrication problems are of concern, especially for the closure weld of a 7% Al bronze container.

Stability of microstructures and embrittlement tendencies of weldments will be studied.

Strategy -- Evaluate thermal aging effects on welds and look at SCC susceptibilities of these materials. Reversing d.c. crack growth technology will be used: fracture mechanics (FM) specimens (precracked) will have  $K_I$  applied of ~7 to 15 ksi/in and a crack rate of  $2 \times 10^{-7}$  in/h will give 300y life. I mentioned our acoustic method and its greatly improved sensitivity for crack extension measurements and the speaker indicated interest in communicating with us on results of these studies.

An alumina liner, inside a metal jacket, will be explored as a means of having a "thermodynamically safe" container material that would be inert to any environmental effects. SiC whiskers may be embedded in the Alumina matrix. The concept is to provide two independently viable barriers that would furnish the 300y or more protection required by law. Lars Werme (Sweden) indicated that, in the Swedish program, ceramics were considered and discounted after considerations of cost of the ceramics and after

other cracking considerations. By end of FY89, a prime choice and at least one back-up material will be selected and studied.

The Swedish use of Cu is different in two important aspects. The Swedes have a reducing environment and thus no corrosion, and the  $\gamma$  Flux will be only a few percent of that for the U.S. case, due to the self shielding of the Swedish design.

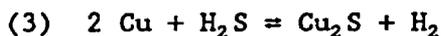
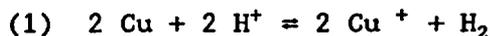
L. Werme, Swedish Nuclear Fuel and Waste Management Co. (SKB)

Werme briefly reviewed both the copper and steel canister materials that are being studied in a program which extends from 1987 through 1990.

Manufacture (fabrication) of a copper container\* is more of a problem than that of a steel container. Inorganic reactions are not a problem in the Swedish repository. Sulfates, are expected to become reduced to sulfides, (perhaps by inorganic species) and this is favorable in relation to sulfate corrosion. Electron Beam (EB) welding will be used. Total attack after  $10^6$  years, is a function of wall thickness but, even for 10 mm walls, only 1.1 mm uniform corrosion is expected. When a pitting factor is used, only 5.5 mm corrosion allowance is needed. The water contains 2 mM (milimolar) (1 mM  $\approx$  70 ppm) bicarbonate, and perhaps 10 mM sulfate, and 6 to 7 x  $10^3$  chloride, with nitrates  $<1/2$  ppm. [Nitrates, if they became concentrated, could be a problem if radiation effects product nitrites]. They assume that mass transport will bring oxidants to the repository and that all oxidants brought to the repository will result in corrosion. Their present efforts are aimed at (1) understanding pitting of Cu in reducing conditions, (2) exclusion of creep failure at low strains (10 to 20 MPa is max expected stress), and (3) use of the hot isostatic pressing (HIP) process for filling the canister with copper. Oxygen in or on the copper powder is a problem, so you almost have to atomize the powder into the canister, so this is a serious concern.

A natural analog is available to the Swedes, a 96.3% Cu bronze cannon that was 200 y old, had never been fired and was found beneath the Baltic Sea, sitting vertically, in clay (illite, montmorillonite kaolinite). In this low-oxygen environment, the measured corrosion produces an estimate of  $< 10 \mu\text{m}$  corrosion in  $10^5$  y.

In pure  $\text{H}_2\text{O}$ , Cu was characterized as being thermodynamically stable under anaerobic conditions. The reactions cited are given below:



Equation 3 can lead to pit initiation, but this might better be called general corrosion because propagation as a pit would be limited by transport considerations.

\*They plan to have 800 watts/container and a temperature of container wall of  $-80^\circ\text{C}$ , which is just a bit lower than the temperature of the fuel itself.

Fraser, King, AECL, Canada.

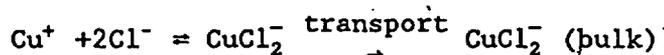
Corrosion of Cu (OFHC) at 100-150°C for the expected canadian environment would include uniform corrosion, possibly pitting, not likely SCC.

They have one molar chlorides and the chance for copper chlorides to form, so pitting in sulfide-containing solutions is an observed reality. Copper chloride complexes are formed in neutral solutions. Their system has the potential for having oxidants present. Many unanswered questions were raised on the pitting question. These are being studied.

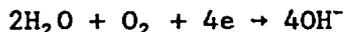
On uniform corrosion, the rate was observed to decrease monotonically (in autoclave studies), and with a proper buffer, corrosion of  $<1 \mu\text{m/y}$  can be expected.

From a mechanistic, rather than rate-measurements, view point the rate-determining step for this corrosion is being studied using rotating-disk-electrode measurements.

At the anode --  
 $\text{Cu} = \text{Cu}^+ + e$



At the cathode transport of oxygen from the bulk solution limits the reaction at the metal surface:

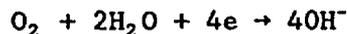


These studies indicate the following:

- 1) The anodic reaction is transport controlled.
- 2) The cathodic reaction is kinetic controlled [i.e. charge transfer kinetics].

Anodic polarization studies indicate that the rate of the surface reactions (electron transport) also governs the anodic reaction, so joint kinetic/transport control is indicated.

Cathodic polarization reactions are again dependant on rotation rate and the results indicate that at  $E \geq -450 \text{ mV}_{\text{SCE}}$  a complex mechanism obtains. At  $-450 > E > -800 \text{ mV}_{\text{SCE}}$  reduction of oxygen is under joint transport/kinetic control



At  $E_{\text{SCE}} \geq -900$ , pure transport control obtains:



Studies involving variation of  $i_{\text{corr}}$  with rotation rate lead to the conclusion that the overall rate determining step is under joint kinetic/transport control.

They believe that at  $E_{corr}$  the cathodic reaction is under kinetic control; and the anodic reaction is mostly under transport control. The overall slowest step is the transport control of the anodic reaction (it gives the least current, when compared with the computed values for the other possibilities).

At what concentration of oxygen  $[O_2]$  does the anodic transport  $i_{anodic} = i_{cathodic}$  (transport):

Answer:  $\sim 5 \times 10^{-9} \text{ mol} \cdot \text{dm}^{-3}$  (or 0.2 ppb)

In deaerated solutions:  $[O_2] \approx 10^{-6}$  or 10's ppb, in the lab.

From radiolysis products:

$[H_2O_2] = 10^{-7}$  to  $10^{-8} \text{ mol} \cdot \text{dm}^{-3}$

$[O_2] = 10^{-9}$  to  $10^{-11} \text{ mol} \cdot \text{dm}^{-3}$

Thus, from radiation, reactions will never be limited by the rate of supply of oxygen, under the Canadian conditions.

Under their simulated disposal conditions, their studies were expected to indicate a mass transport (of copper from the copper surface) process limits the rate of corrosion. After actual (limited) studies, a value of effective diffusivity  $D$  of  $< 5 \times 10^{-7}$  was computed as a preliminary estimate for the copper species that is actually being transported during this corrosion.

W. Brehm (BNL) summarized that basalt studies of copper were conducted at 50, 100, 150, and 200°C in a saturated (air-steam). Weight-loss measurements were made.

In other tests in mud, groundwater was sparged with Argon to keep anoxic conditions inside the autoclaves. Radiation was used as a controlled variable. Grande Ronde No. 4 groundwater was used in the tests. The results of the anoxic mud-packing tests indicated that much data scatter was obtained, generally uniform corrosion, no (high-aspect-ratio) pitting. Chalcocite ( $Cu_2S$ ) was present on the surface of 200°C test specimens, where corrosion was greater than that observed at 150 to 50°C: 39  $\mu\text{m}/\text{y}$  at the higher temperatures and  $\sim 13 \mu\text{m}/\text{y}$  at the lower temperatures. No radiation effects were observed in the reducing medium used.

The results of air-steam tests of copper alloys indicated that no general pitting was observable and fairly modest corrosion rates were measured. Linear corrosion was observed at all temperatures and the maximum thickness loss was 0.13 mm/25 mo for copper. The Cupro-nickel corroded less and was maximum of 0.045 mm/25 mo and they observed accelerated corrosion at 250 to 300°C. Surface film morphology was different under irradiated conditions. The packing tended to unexpectedly promote weight loss of the copper-base alloys, perhaps it absorbed moisture and thus provided a more aggressive environment near the surface of the copper.

[Ed. Results of these tests suggested to me that perhaps the laboratory conducted the tests at NBS on the effects of diffusivity and resistivity of the soil (environment) should consider copper and these observations.]

It was noted that the sulfate present in basalt (as an impurity) at least in part reacted on the copper to produce  $H_2S$ , which seemed to clearly be noticeable when specimens were examined after the exposure studies.

Radiation at  $>100$  Rd/h increased the corrosion rate in air-steam ( $50^\circ C$  dew pt.) studies of Cu and of Cu-Ni conducted at  $250^\circ C$ . This phenomena has not been explained. This observation was also observed for the A27 and A387 steels studied.

Kim Lam, Ontario Hydro Research Division

Factors that enhance copper corrosion were briefly presented. The remarks were based on the following references:

W. D. Robertson et al., JES, 105, 569(58)

B. C. Syrett, Corrosion, 33, 257(77)

In sulfide environments, some localization of corrosion (called pitting) was shown to have been observed. It led to a surface roughness in short-term experiments. This "pitting" tended to be centered on (originated at) grain boundaries. The crystallography (grain orientation effects) affected the behavior, and pitting at the grain boundaries spread widely to the exposed surfaces of the grains, so the localization was not as pronounced as it would have been if the behavior was what one might normally call pitting, i.e. local attack with a pronounced aspect ratio. The depth of pits was no greater in long-time experiments, when compared with the depth of the general corrosion over the same time. A ratio of 15 was reported for a pitting factor  $\equiv$  depth of pit/depth of uniform corrosion. Over a one-year period, maximum corrosion rates of  $\sim 105 \mu m/y$  were observed. This was for aerated slurries saturated with sulfides.

Speakers on Iron and Steel

W. DeBruyn, Studiecentrum voor Kernenergie/Centre d'études de l'énergie nucléaire, Belgium

Corrosion of container materials under clay repository conditions were discussed:

Ferrous Materials: C-steels, cast irons.

Corrosion Resistant Materials:

AISI 304, 316, 430 stainless steels,

Al alloys,

Ni-base alloys,

Ti and Ti 0.2-Pd.

Studies of corrosion allowance materials were done in wet clay. Corrosion rates of 50-150  $\mu\text{m}/\text{y}$ , solid clay (2-50  $\mu\text{m}/\text{y}$ ) and initially high rates of corrosion abated to lower levels after about one month. In corrosion resistant materials, SCC was observed in 316 and 304, and local attack observed was in all except the Ti alloys.

Interactions between clay and the materials of interest are being studied in tests conducted at RT, 90 and 170°C, for both humid- and dry-clay environments. Both large tubes and C rings are being tested. An underground laboratory (-225 m or ft?) below the surface and in a clay bed containing 15 percent water. Linear polarization resistance and electrical resistance (corrosometer probes) measurements are aimed at the evaluation of corrosion rates, and especially those that can be measured during the critical operational phase of the repository. The effects on the environment, which are a result of drilling, emplacement, etc., are being studied in attempts to predict return to steady-state conditions; this requires about one to two months. This is done using Eh, pH measurements.

Gamma-irradiation tests at  $10^5$  rd/h at up to 1000 h are being conducted and have already shown  $\text{H}_2$  production values and various effects on materials. Electrochemical laboratory tests are used to develop a database for estimation of parameters related to container performance. Short-term tests conducted under "equilibrium" conditions will be extrapolated to very long times to make performance predictions. Under my questioning, the so called "equilibrium" conditions were actually the steady-state conditions obtained after the two-month or so disturbance had past. Thus, kinetic data, and not necessarily anything that would be sound justifiable, extrapolations, were intended.

George Marsh, United Kingdom Atomic Energy Authority

All of their work is done on C-steel, some of it sponsored by Swedish nuclear interests. The UK has a policy of 50-y storage, and only generic types of low-cost studies are being supported by the government in the UK.

Pitting in carbonate-bicarbonate-chloride solutions was discussed. The aim is really to come up with deterioration rates predicted from the various local and general attack mechanisms by which container materials might fail.

Predictions of general corrosion rates based on mathematical models derived from various kinetic considerations were compared with experimental results. This was done for steel in a relatively impermeable (to oxygen) bentonite environment with and without radiation at 20, 50, and 90°C. Transport of oxygen is slow and occurs under diffusion control in this case. Frightening levels of  $\text{H}_2$  production are expected and this now is reason for reconsideration of the approach taken. Some pitting attack was

observed in 90°C tests that inadvertently gave convective flow of oxygenated water in the vicinity of the test coupons.

The passive period was predicted, assuming that oxygen was abundantly present at one boundary of the bentonite present in the bore hole. This approach was regarded as more favorable, in that it permits predictions to be made with less extrapolation.

Pit growth experiments were made potentiostatically in an aqueous electrolyte using a PTFE cell. These results were used to estimate expected container pitting. Two statistical distributions on pit depths were analyzed using experimental results to determine correlation coefficients with assumed limited pit depths. The best fit was generally that for an "unlimited distribution". This type of analysis was used to estimate expected behavior (probability of failure). The maximum penetration in 125 y was 165 mm. When a general attach allowance of 67 mm is added to this for 875 y at repository temperature a total corrosion allowance is estimated (to be 232 mm).

To avoid SCC, stress relief at 550°C was suggested, so as to decrease residual stress to 50 percent of the Y.S. This was criticized as too high a temperature for the fuel to withstand. U.S. regulations permit 350°C maximum. It was suggested that local Y.S.-level stresses should be expected in any realistic, full-size structure. Thus, residual stress may present some problems here.

On the question of hydrogen effects, the equation leading to the highest fugacities of hydrogen ( $f_{H_2}$ ) was given as  $3Fe + 4 H_2O \rightarrow Fe_3O_4 + 4H_2$ .

From this reaction, one obtains the following:

<u>Temperature</u>	<u>Partial Pressure</u>	<u>H Content in Steel.</u>
25°C	$H_2 = 736 \text{ atm.}$	$9 \times 10^{-3} \text{ wppm}$
100°C	$H_2 = 1365$	0.125 wppm.

Thus, the expected maximum hydrogen content in steel would be only 0.125 wppm, and these modest levels would not cause embrittlement of C steel.

When S is present, higher levels of  $P_{H_2}$  would be expected, perhaps an order of magnitude higher than those indicated here. [But, I would caution that sulfides can be very serious promoters of hydrogen absorption and the effects of any S present should be very carefully examined].

#### R. Westerman, Battelle Memorial Laboratories

Westerman reported on SRP on a cast mild steel (A 216-Grande W) for a proposed 10-cm-thick-wall container. Inside the container, is a canister that holds the waste form. This steel has a specified  $C_{max} = 0.25$  wt.percent. It has a pearlite-ferrite microstructure.

The activation energy computed from corrosion rate data is 14 Kcal/mol, which is consistent with the reduction of the water molecule. The corrosion rates in dissolution brine is (by a factor of ~45) much lower than that of the high Mg (inclusion) brine.

The concentrations of magnesium [Mg] is ~300 ppm. and that of the inclusion brine is ~ (notes not complete). There exists an apparently monotonic increase in corrosion rate with Mg content of the brine. The question of the mechanism leading to the increased corrosion rate due to the Mg was studied, with the conclusion that Mg incorporates itself into the protective film and decreases its protectiveness.

"Excess-salt" tests were performed. In these tests, H<sub>2</sub> builds up in sealed inconel canisters (stainless steel parts on this canister lasted only a few days). Brine is added to the salt, and the container is sealed and held at test temperature for times up to 5 y (only 18-month results were presented).

Temperature (90, 150 and 200°C) affected the rates, with higher rates being observed at higher temperatures.

Results of pitting corrosion tests were reported. Anoxic conditions never showed pits under a multiplicity of test conditions. Radiation 10<sup>5</sup> rd/h increased the observed corrosion rates.

Hydrogen permeation studies were made using tubular specimens. The brine flow rate in the autoclave was related linearly to the hydrogen permeation rate. This phenomena was not really understood.

G. Kass (LLNL) -- on 316L, 304L, and alloy 825 candidates materials for the NNWSI program. 304L is the benchmark from which 316L and alloy 825 offer increased resistance to sensitization. If 304L were used, then maximum values of .020 or .015 would be specified on C to "essentially preclude" sensitization.

The metastability of 304L and 316L were recognized, with 304L being more susceptible to martensite transformation. The 825 was presented as a stable austenitic alloy.

Sensitization, due to welding of 304 is likely, but sensitization of 304L and 316L is unlikely if [C] ≤ 0.015 wt. percent, based on BWR Program test results. Sensitization was presented as unlikely in alloy 825. His conclusion -- sensitization is probably a non issue.

In chloride/oxygen SCC tests, using U-bend specimens at 50, 90°C in J-13 H<sub>2</sub>O, high  $\gamma$  flux, water and steam, SCC was found in both 304L and 316L. However, this is expected when >10ppm O<sub>2</sub> is present.

Testing is regarded as being needed for crevice and pitting problems, H-embrittlement susceptibility and fabrication methods must be yet demonstrated, Cl<sup>-</sup> SCC may occur and weld embrittlement may be an issue.

The weld embrittlement of concern is from a high ferrite content in the weld metal, which embrittles (notch toughness decreases sharply) due to sigma phase formation.

The strategy for alloy 825 includes doing tests and literature work on Cl<sup>-</sup> crevice corrosion work.

W. Brehm (Battelle) presented results of air/steam tests and water tests of an A27 cast steel, and a Fe-9Cr-1Mo steel. Tests were conducted at 50 to 200°C in a (Synthetic Grande Ronde #4, BWIP) water-saturated, crushed-basalt (with sodium bentonite) packing, with and without radiation and at various pH levels. Pitting was not regarded to be a problem, based on all tests conducted on the A27 cast steels tested.

E. W. Russel, Lawrence, Livermore National Laboratories

B & W and LLNL are studying various aspects of the fabrication problems for the materials being considered as candidates for NNWSI. The program has 3 phases (1 year each) and this report covered part of the first phase. For each material, fabrication (of the vessel), closure welding, and NDE problems and processes were mentioned. This presentation reviewed various welding processes, such as electron beam, friction welding, etc., and it identified the applicability of these processes to either fabrication or closure welding. The requirements for making the closure weld and an NDE of it in a hot-cell were emphasized.

One consideration is the unknown condition of the fuel. If some of it is wet (despite screening to avoid this), the moisture might lead to problems due to radiation effects within the canister. Thus, one atmosphere Argon is (for now) their choice for the inside of the canister.

Dave Stahl, Science Applications International Corporation addressed the NRC containment and release requirements of 10 CFR 60.113. A definition is needed for the term "substantially complete containment."

Stahl also discussed the dual container concept. The dose rate decreases in relatively few years, from 10<sup>4</sup> rd/h to 10 rd/h. This leads to consideration of dual container (container within a container) concepts. The short-term requirements would be met by the outer container and the long-term requirements would be met by the inner vessel.

<u>Requirement</u>	<u>Outer Container</u>	<u>Inner Container</u>
time	to 300 y	after 300 y
temperature & rad'n	high	low
wetness	mostly dry	mostly wet
metallurgical stability	shorter ~?	long-term
electrochem. activity	anodic	cathodic
environmental interaction	moderate	low
mechanical strength	high	low
oxidation resistance	low	high
gen'l corrosion resistance	low	high
local corrosion resistance	low	high

Nava Garisto (AECL) made some remarks on modeling as applied to repository problems. Specifically she discussed problems associated with the Canadian planned usage of copper and titanium.

A hole in the container is regarded as a local site that limits ingress of H<sub>2</sub>O. In all cases, her discussion centered on representing mathematically (modeling) the science as it is presently understood.

Brian Ikeda (AECL) -- made some remarks on modeling of the results of immersion tests. A matrix of tests conducted on Titanium tested over a 2 y period with several variables (Cl<sup>-</sup> content, temperature, time); the tests will yield results (penetration rates) for both uniform-corrosion and crevice-corrosion rates. Wt. changes would be used only to correlate with other wt. loss data, metallography would be used to estimate directly the penetration depth in areas having crevice corrosion and pitting attack. These penetrations would then result in empirical estimates of corrosion rate predictions as a function of time. Also needed would be estimates (by QTM) of the areas affected by local attack, in relation to total areas. The way in which this data is used to "model" was not clear to this writer.

F. King (AECL) spoke briefly on corrosion processes considered in copper-base materials in clay. Uniform corrosion (controlled by the rate of transport of anodic corrosion products) and pitting attack (accounted for by a simple pitting factor) would be used to model for short-term failures. Pitting factor = 5.

$$\text{Rate} = \frac{\text{atomic mass}}{\text{density}} D_{\text{Cu}} \cdot \frac{\Delta C}{\Delta x}$$

where e.g.  $\Delta C = 10^{-4} \text{ mol} \cdot \text{cm}^{-3}$  (at the highest estimated)

$\Delta x = 25 \text{ cm}$ , and

$D_{\text{Cu}} = 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ .

Container life is thus computed simply as

$$\text{Penetration time} = \frac{\text{thickness-sorption allowance}}{\text{Rate} \times \text{Pitting factor}} = \sim 5000\text{y.}$$

The sorption allowance is the calculated amount of copper that would be sorbed by the surrounding clay. It is of the order of 3 mm copper removed from the surface of the container. This approach (sorption allowance) is considered to be conservative in that an alternative effect of the clay is to act as a diffusion barrier in transport processes needed to corrode the copper.

The reaction  $\text{Cu} + 2\text{Cl}^- \rightleftharpoons \text{CuCl}_2^-$  describes corrosion of the copper, which is limited by  $C_0$ , the concentration of  $\text{CuCl}$  at the copper/buffer boundary at steady state.

The rate controlling step is the transport of a species of copper through the buffer. The next two steps that might control would be (secondly) the oxygen transport and (lastly) kinetic control of oxygen reduction.

W. Brehm (Battelle) -- indicated that models

1. Must consider effects of gradients (temperature,  $\gamma$  levels, Concentrations),
2. Must treat upsets or worst cases, and
3. Must identify a range of possible mechanisms.

He also asked "Is the effect of radiation not only to just furnish more of the species, but also to change the corrosion mechanisms?" Is there a threshold."

A list of workshop attendees is attached in this report.

## Corrosion Behavior of Low Carbon Steel in High pH Aqueous Media

Anna C. Fraker and Jonice S. Harris

## Introduction

The purpose of this work was to study the corrosion behavior and local corrosion susceptibility of low carbon steel in simulated ground water at a pH of 9.75 and a temperature of 95 C. These studies were conducted as part of a program to evaluate materials for long term nuclear waste storage. The canister storage materials should remain intact for 300 to 1000 years as part of a design which would limit release of radionuclides at all times up to 10,000 years to no more than one part in  $10^5$  of a 1000 year inventory. The test conditions used in the present study typify those of a basalt repository in the state of Washington, but selected aspects of the results are applicable to low carbon steels in other environments of similar composition.

Previous studies of low carbon steel in this environment indicated that pits were occasionally found after testing but stated that pitting would not develop in repository conditions<sup>1</sup>. In general, pitting would not be expected in low carbon steel in aqueous media due to the absence of surface passivation<sup>2,3,4</sup>. Other reports on corrosion of low carbon steel in aqueous media indicated uneven attack over the specimen surface but did not indicate pitting attack<sup>5</sup>.

Modelling studies<sup>6</sup> of pit propagation in low carbon steel showed that pit depth propagation increased with the presence of inert or nonreactive pit walls. It has not been determined that sufficient pit depth and corrosion product accumulation would develop to produce this protective effect assumed in the model.

Modelling of pitting has been discussed<sup>7</sup>, and pitting was related to galvanic corrosion with two distinct electrodes in contact where the pit dissolves rapidly and the rest of the metal is passive and dissolves slowly. The rates of electrochemical processes within the pit and on the surface must be known as well as how these rates are affected by solution composition, temperature, current path and other environmental factors. Most of this information is accessible experimentally<sup>7</sup>.

Still another consideration in studying pitting in metals which do not passivate under specified conditions is pitting at cathodic potentials. Pitting at cathodic potentials has been reported for austenitic stainless steel<sup>8</sup> and for passivated iron<sup>9,10</sup>. The latter work concluded that the pitting potential was a mixed potential with a cathodic dissolution process,



and an anodic dissolution process,  $\text{Fe} > \text{Fe}^{2+} + 2\text{e}$ . Other work indicated that reactions in local cells during anodic and cathodic polarization would be the same<sup>11</sup>. This discussion concluded with the analysis that localized corrosion at cathodic potentials could occur but that it was rare and would not cause serious problems<sup>4</sup>.

Some studies have been conducted of corrosion behavior of carbon steels in tuff repository environments<sup>12</sup>. These studies indicated that AISI 1020 - 1025 and ASTM A-36 did not suffer excessive corrosion in the tuff environment but that more data, increased testing times and studies of galvanic effects were needed.

Roman nails, with a composition similar to A216 low carbon steel which had been buried for 2000 years in Inchtuthil, Perthshire were unearthed and found to be heavily corroded with the remaining material being ferrite with only a small amount of pearlite near the edge<sup>13</sup>. There were areas of localized corrosion but the origin could not be determined due to the overall gross corrosion attack. Approximately 900 nails were found at the burial site, but it is not known whether there were more and some had disintegrated.

The present investigation applied conventional electrochemical techniques to study pitting susceptibility of low carbon steel, and procedures and results are discussed. Electrochemical measurements indicated that pitting would not be occurring. Microscopic examination of corroded specimens indicated overall general uneven surface corrosion with some shallow local attack in the ferritic phase. Since the specimen never passivated, the localized attack was related to preferential surface sites, and not to the usual electrode potential difference and current densities for producing pits of unknown depth and damage. These results indicate that pitting, as classically defined, does not occur in this low carbon steel. The overall general corrosion, thick surface films, and nonpassivating conditions resulted in limited and shallow localized attack.

#### Materials and Methods

The A 27 (ASTM grade 60-30) low carbon steel sheet material was obtained from the Pacific Northwest Laboratory. The composition of A27 steel is given in Table 1.

Table 1. Composition of A 27, ASTM Grade 60-30 Steel

<u>C</u>	<u>Mn</u>	<u>Si</u>	<u>P</u>	<u>S</u>	<u>Mo</u>	<u>Cr</u>	<u>Ni</u>	<u>Fe</u>
0.245	0.69	0.59	0.016	0.018	0.04	0.43	0.20	Bal.

Specimens were cut with a diamond saw. Some specimens were placed in permanent mounts for etching and photographing, and others were mounted in temporary mounts for polishing in preparation for corrosion testing. All specimens were polished through 300 to 600 grit SiC papers and then with 6 um and 1 um diamond paste with a final polish in 0.05 um Al<sub>2</sub>O<sub>3</sub>. Ethanol was used as a wetting agent in the final polish since the steel corroded or etched when water was used for the polishing. Specimens were prepared immediately before testing or were kept in a desiccator for a few days. Specimens for microscopic study were etched with a mixture of 9 parts ethanol to 1 part nitric acid, washed, dried and then studied using the light microscope.

The Grande Ronde No. 4 water was prepared using previously established methods and compositions<sup>14</sup>. The composition of this water was based on ground water samples which previously were collected and analyzed. The pH was adjusted to a value of 9.75 using either 0.10 M HCl or 0.10 M NaOH. Stock solutions are prepared and later diluted as needed for use. The Compositions of the stock solutions are given in Tables 2 and 3. One liter of synthetic Grande Ronde No. 4 water is prepared by adding 25 ml of stock solution A and 25 ml of stock solution B to 900 ml water. After the pH is adjusted, water is added to bring the water level 1 L. The water was placed in the testing flask and brought to a temperature of 95 C before inserting the specimen.

Table 2. Composition of Grande Ronde 4 Basic Stock Solution

<u>Compound</u>	<u>Amount (g)</u>
Na <sub>2</sub> SiO <sub>3</sub> ·9H <sub>2</sub> O	18.2
Na <sub>2</sub> CO <sub>3</sub>	6.40
Na <sub>2</sub> SO <sub>4</sub>	0.239
NaF	1.76
NaOH (50 % solution)	23.0
Water	(Add water to bring volume to 1 liter.)

Table 3. Composition of Grande Ronde 4 Acid Stock Solution

<u>Compound</u>	<u>Amount</u>
KCl	1.05g
CaCl <sub>2</sub> ·2H <sub>2</sub> O	0.323g
HCl	219 ml of 2.0 M HCl
Water	(Add water to bring volume to 1 liter.)

The Cohasset Flow basalt rock and Wyoming bentonite clay were supplied by the Brookhaven National Laboratory. The basalt rock had been collected as large pieces and had to be crushed. This was difficult because the rock was hard and also there was concern regarding contamination by the crushing device. The rock was crushed by a motorized steel rock crusher. Prior to crushing, the rock crusher was washed consecutively with water, acetone and alcohol. There was no apparent contamination of the crushed rock by the crusher.

The corrosion testing involved making cyclic anodic polarization measurements of the A 27 low carbon steel specimens in Grande Ronde No. 4 water at a temperature of 95 C. The pH was approximately 9.75. Some tests were made in Grande Ronde No. 4 water containing a mixture of 75 percent basalt and 25 percent bentonite. The basalt and

bentonite mixture were to fill one half of the testing flask, but the bentonite expanded upon becoming wet and the mixture filled approximately two thirds of the volume of the flask. The solution and mixture were held at temperature for one hour prior to inserting the specimen and beginning the test.

The specimen was placed in the 95 C solution and left at open circuit potential for fifteen minutes prior to making the polarization measurements. The potentiostatic polarization measurements were made by applying a potential to the specimen at the rate of 0.01 V/ 15 sec. All voltages are in reference to a saturated calomel electrode (S.C.E.).

### Results and Discussion

Results of this work showed that the A27 steel was continuously corroding and did not undergo passivation. Specimens showed effects of corrosion in distilled water and in laboratory air. Susceptibility to pitting can be determined for metals which passivate by using a stimulation test such as the test described in the American Society for Testing and Materials (ASTM) F 746, Standard Test Method for Pitting or Crevice Corrosion of Surgical Implant Materials<sup>6</sup>. It was not possible to apply the stimulation test to the A27 low carbon steel. Some results of the tests which were conducted are given.

Passivity. Representative results of the initial open circuit potential and the potential after fifteen minutes are given in Table 4 for exposure in Grande Ronde No. 4 (GR-4) water (Test A) and for GR-4 water plus basalt and bentonite (Test B).

Table 4. Open Circuit Potentials for A27 Low Carbon Steel

<u>Test</u>	<u>Time, min.</u>	<u>Media</u>	<u>pH<sub>i</sub></u>	<u>pH<sub>f</sub></u>	<u>Temp, C</u>	<u>Pot., V</u>
A	0	GR-4 water	9.75		95	-0.46
A	15	GR-4 water	9.75	9.2	95	-0.59
B	0	GR-4 water, basalt, bentonite	8.3		95	-0.769
B	15	GR-4 water, basalt, bentonite	8.3	7.7	95	-0.787

As indicated by the open circuit potential for test A, the A27 steel did not passivate in GR-4 water. The open circuit potential dropped from -0.46 upon immersion to -0.59 after fifteen minutes. This drop in potential occurred due to the absence of a passive film on the surface. The steel also did not passivate in GR-4 water plus basalt and bentonite

as shown in the even lower potentials of  $-0.769$  V initially and  $-0.787$  V after 15 minutes.

Solution pH and Effects of Temperature and Basalt and Bentonite. The initial pH ( $\text{pH}_i$ ) of the GR-4 water was set at 9.75 at 22 C, and decreased with the increasing temperature. The final pH ( $\text{pH}_f$ ) of this water after the anodic polarization test and after the temperature had dropped to at 60 C was 9.2. The pH of GR-4 water plus the basalt and bentonite was lower both at low and high temperatures. The pH of the GR-4 water mixed with the basalt and bentonite was 9.75, and after combining 500 ml of this GR-4 water with 150 g of basalt and 50 g of bentonite, the  $\text{pH}_i$  of the mixture was 8.3. After completion of the anodic polarization measurements, the pH of this mixture at 60 C was 7.7.

Two readily observable effects of adding basalt and bentonite to the test media were an expansion of the test media and a lowering of the pH. The mixture of GR-4 water and basalt and bentonite was made and held at temperature approximately 1 hour prior to running the test. The crushed basalt provided a high surface area ratio/ unit Gr-4 water. Environmental effects resulting from this mixture could change over a longer period of time.

Anodic Polarization. An example of a cyclic anodic polarization curve is shown in Figure 1 where the log of the current density is plotted versus the applied potential. This is an example of the test labeled "A" in Table 4. Arrows on the curve indicate the direction of the applied potential during the test.

This curve shows that no passivation occurred and that the current density increased from the beginning. The current levels off somewhat at high currents due to the presence of a thick film which limits diffusion. This film is constantly breaking up and falling off of the specimen causing sudden rises in the current. This is not a protective film. The reversal of the potential does not show the hysteresis in the current. The increased current in the remaining portion of the curve may be due to increased specimen area as a result of the corrosion during the test.

Figure 2 is a cyclic anodic polarization curve for the test represented by "B" in Table 4. This curve starts from a lower corrosion potential and also shows that no passivation occurred. Here, as in the test of Figure 1, with increasing applied potential, the current reaches a level where it levels off due to the formation of a thick film and limited diffusion. The current level in the remaining portion of the curve is different from that of Figure 1 and is lower. This may indicate increased protectiveness of the film or some reaction of the film with the basalt, bentonite and water mixture.

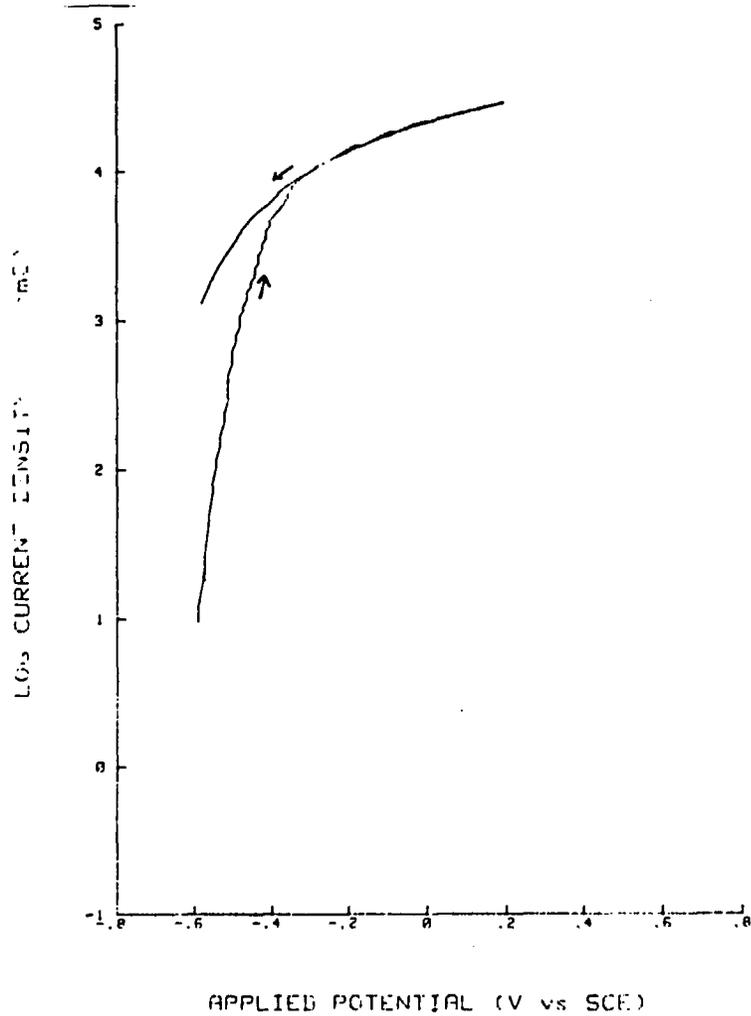


Figure 1. Cyclic anodic polarization curve for A27 steel in GR-4 water at 95°C.

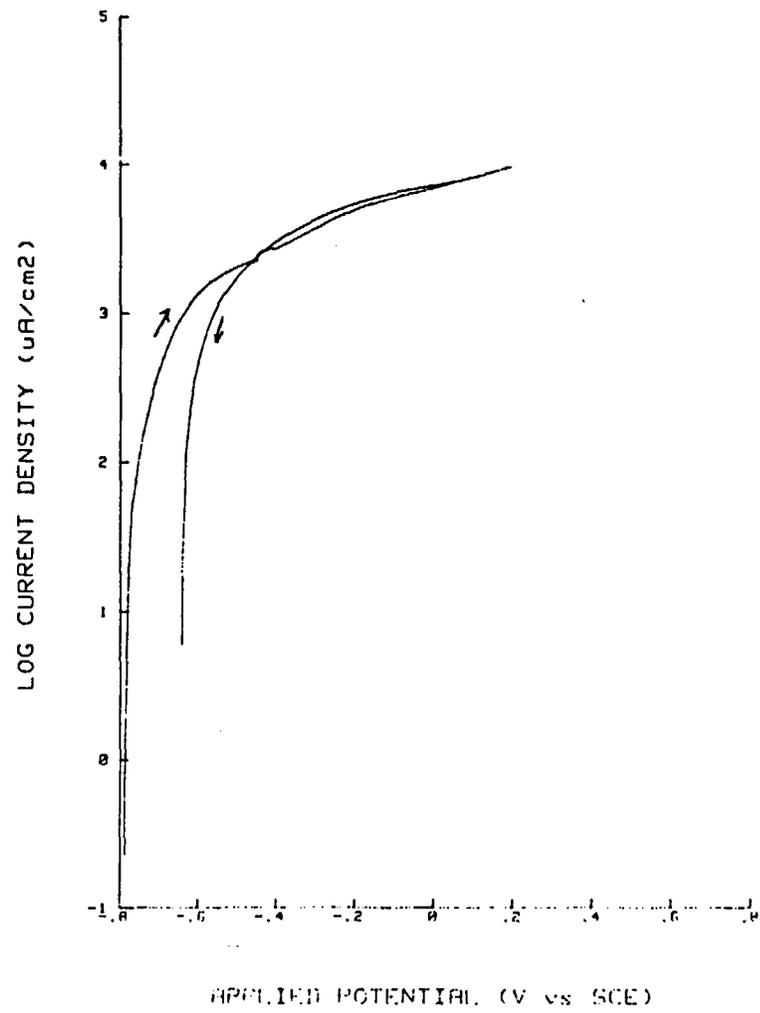


Figure 2. Cyclic anodic polarization curve for A27 steel in GR-4 water with basalt and bentonite at 95°C.

Microstructures. Examples of the microstructure of two uncorroded specimens are shown at two different magnifications in the micrographs of Figures 3 and 4. This microstructure consists of areas of ferrite (labeled f) and pearlite (labeled p). After anodic polarization, the specimen surface becomes uneven and three dimensional in appearance due to the corrosive attack. The pearlite is attacked more severely than the ferrite, as shown in Figure 5. Figure 6 shows an area with some localized attack. These areas, which could be identified as pits, are shallow and crystallographic, but these are not pits in the normal sense of the term.



Fig. 3. A27 steel, uncorroded.

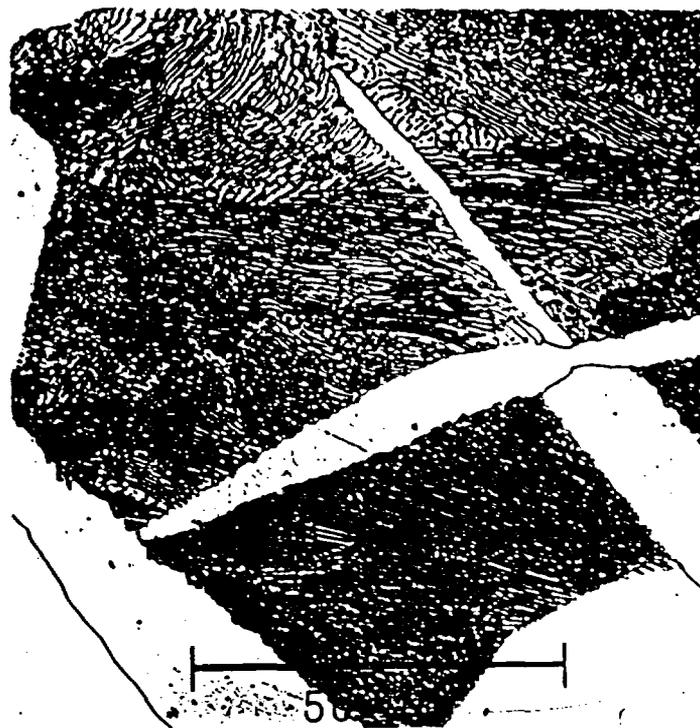


Fig. 4. A27 steel, uncorroded.



Fig. 5. A27 steel, anodically polarized, (cyclic).

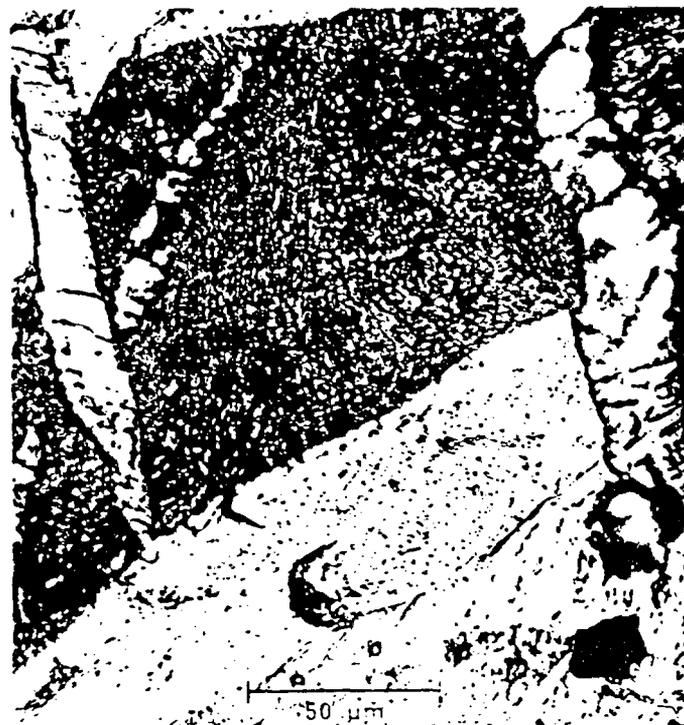


Fig. 6. A27 steel, cathodically polarized.

## Conclusions

Anodic polarization tests were conducted with A27 (ASTM grade 60-30) low carbon steel exposed in 95 C simulated Grande Ronde No. 4 water which had a solution pH ranging from 7.7 to 9.75. The following conclusions can be made from this investigation.

1. A27 ASTM grade 60-30 low carbon steel corrodes to some degree in laboratory air and in distilled water.
2. A27 ASTM grade 60-30 low carbon steel does not passivate in simulated Grande Ronde No. 4 and would not be expected to exhibit pitting corrosion as it is normally defined.
3. Electrochemical electrode potential measurements showed that the open circuit potential decreased after immersion. This indicates that a passive film is not forming and that general (uniform) corrosion was occurring.
4. Localized attack was observed. The localized corroded areas appeared to be crystallographic and were shallow. These areas of localized corrosion are not pits in the classical seise because they are not the result of the local breakdown of a passive film. The exact cause of these features is not known.
5. Thick corrosion product films formed on the surface and occasionally, dropped off. Observation of surfaces under the films revealed an uneven and irregular morphology with preferential attack in the pearlitic regions (grains) of the A27 steel.
6. Effects of adding basalt and bentonite to the simulated Grande Ronde No. 4 water were to increase the volume of the mixture and lower the pH. There may have been additional ions released into the mixture but this was not determined.
7. Increasing temperature lowers the pH of the simulated Grande Ronde No. 4 water.

Additional studies of low carbon steel in various media and for longer times would be useful for determining the materials durability. The irregular surface attack during the general corrosion should be more fully described as well as effects of varying amounts of pearlite in the microstructure, effects of varying ionic species and changing solution pH. The amount and distribution of elements, such as Si, S and P, also should be considered.

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