

December 15, 1989



UNITED STATES DEPARTMENT OF COMMERCE
National Institute of Standards and Technology
(formerly National Bureau of Standards)
Gaithersburg, Maryland 20899

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: Quarterly Progress Report for October, November, December 1989
(FIN-A-4171-0)

Dear Mr. Peterson:

Enclosed is the October, November, December quarterly progress report for the project "Evaluation and Compilation of DOE Waste Package Test Data" (FIN-A-4171-0). The financial information is reported separately.

Sincerely,

Anna C. Fraker ^{12H}

Anna C. Fraker
Metallurgist
Corrosion Group
Metallurgy Division

Enclosures

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Quarterly Letter Report for October, November, December 1989

Published December 1989

(FIN-A-4171-0)

Performing Organization: National Institute for Standards and Technology (NIST)
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

	<u>Current Quarter</u>	<u>Previous Quarter</u>
Number of citations	1131	1122
Number of completed reviews	85	78

Status of Recently Listed Reviewable Documents

Reviewable documents are classified as follows: Category 1 documents are currently being reviewed. Categories 2 and 3 are documents that will be entered into the database with citation information and authors abstracts, and the Category 2 documents are flagged "to review when time permits."

YUCCA MOUNTAIN PROJECT

- 7 Reports currently under review (Category 1).
- 28 Reports to review when time permits (Category 2).
- 2 Reports to file with cross reference(s) to other reports (Category 3).
- 0 Reports identified and not yet categorized.
- 4 Reports received and not yet categorized.

GLASS -- VITRIFIED WASTE FORM

- 0 Reports currently under review (Category 1).
- 4 Reports to review when time permits (Category 2).
- 0 Reports to file with cross reference(s) to other reports (Category 3).
- 0 Reports identified and not yet categorized.

Database searches for (October and November, 1989) include Metadex, NTIS, DOE Energy, Compendex Plus, and Engineered Materials Abstract. Examples of the search conducted for each of these databases are in this report (see p. 9).

STATUS OF REVIEWS OF YUCCA MOUNTAIN PROJECT REPORTS

Yucca Mountain Project -- Reports recently identified for review

Seven reports have been identified for review. The first is on the movement of moisture around the waste container, the second considers the need for tailoring distribution of contained waste in the repository, and the fourth and fifth reports, by the same author, are models of temperature and moisture and the release of radionuclides. Post closure repository conditions are described in the fifth report, and the cladding corrosion is discussed in the sixth report. The last report in this series is a description of the EQ3/6 program.

The role of fractures in the movement of moisture in the variably saturated and fractured rock is the subject addressed in this report. Moisture movement is modeled using LLNL's TOUGH code, and the model considers a semi-infinite vertical fracture with 100% moisture saturation of at the top. The results indicate that much of the moisture is absorbed by the surrounding matrix which has an important influence of moisture velocity along the fracture [Buscheck, 1988].

Nine waste form packaging scenarios are considered in this study of conceptual design of the repository and the waste package. The assumptions used and the effect of variations in these assumptions on the final design are discussed. To maintain the borehole walls above the boiling point of water for the longest period of time requires "tailoring" the physical layout and the amount of heat generated by the canisters [Nelson, 1989].

A model simulating the hydrologic and thermal conditions, versus time, in the vicinity of the waste container is described. The code is based on LLNL's TOUGH numerical model. Results, which are very preliminary because of the uncertainty in the input data, indicate that liquid flow into the borehole is not expected during 2600 years. However, small amounts of water from capillary condensation are expected at the borehole wall at about 200 years [Nitao, 1988a].

A model of radionuclide release rates is described in which effects of absorption by tuff are taken into account. Release rates with and without a backfill are included in this study. The release rate of some radionuclides, such as iodine, show little difference between the two cases, but the release rate of others, such as plutonium, are significantly reduced when a backfill is used [Nitao, 1988b].

Using PANDORA-1, the post-closure performance of the waste packages has been simulated, including individual waste packages, the ensemble of waste packages, and the uncertainty in the performance assessment. Scenarios considered are 1) no significant contact of the waste package with water, 2) contact with dripping water, and contact with the flowing water [O'Connell, 1989].

A corrosion study is described, in which bundles of spent fuel cladding held together with a type 304 stainless steel wrap were exposed to J-13 water for up to 12 months. This study is limited to optical microscopy examination of corrosion on the cladding that occurred after several years of pre-exposure to a reactor environment. No new corrosion was observed [Smith, 1988].

This report, written by the programmers that produced this software, describes the geochemical modeling capabilities of the EQ3/6 computer program. EQ3/6 is made up of several sub-models such as the EQ3NR code that calculates speciation and saturation indices from analytical data. EQ6 calculates reaction paths of equilibrium step processes and kinetic reaction processes. Possible pitfalls in using the software are discussed [Wolery, 1988].

1. Buscheck, T. A. and Nitao, J. J., "Estimates of the Width of the Wetting Zone Along a Fracture Subjected to an Episodic Infiltration Event in Variably Saturated, Densely Welded Tuff", UCID-21579, May 1988.
2. Nelson, T., Russell, E., Johnson, G. L., Morissette, R., Stahl, D., LaMonica, L., and Hertel, G., "Yucca Mountain Project Waste Package Design for MRS System Studies", UCID-21700, April 1989.
3. Nitao, J. J., "Numerical Modeling of the Thermal and Hydrological Environment Around a Nuclear Waste Package Using the Equivalent Continuum Approximation: Horizontal Emplacement", UCID-21444, May 1988.

4. Nitao, J. J., "Simulations of the Near-Field Transport of Radionuclides by Liquid Diffusion at Yucca Mountain -- Comparisons with and without Emplacement Backfill", UCID-21466, July 1988a.
5. O'Connell, W. J., Lappa, D. A., and Thatcher, R. M., "Waste Package Performance Assessment for the Yucca Mountain Project", UCRL-100395, February 1989.
6. Smith, H. D., "Electrochemical Corrosion - Scoping Experiments -- An Evaluation of Results", WHC-EP-0065 (formerly HEDL-7637), September 1988.
7. Wolery, T. J., Jackson, K. J., Bourcier, W. L., Bruton, C. J., Viani, B. D., Knouss, D. G., and Delany, J. M., "The EQ3/6 Software Package for Geochemical Modeling: Current Status", UCRL-08729, July 1988.

Yucca Mountain Project --

Category 1 -- Reports currently being reviewed

1. WHC-EP-0096 (formerly HEDL-7665), "Initial Report on Stress-Corrosion-Cracking Experiments Using Zircaloy-4 Spent Fuel Cladding C-Rings," September 1988.
2. Beavers, J. A. and Thompson, N. G., "Container Corrosion in High Level Nuclear Waste Repositories," - First Semi-Annual Report/Year 2, September 1988 to February 1988.
3. UCID-21466, "Simulations of the Near-Field Transport of Radionuclides by Liquid Diffusion at Yucca Mountain -- Comparisons with and without Emplacement Backfill", July 1988.
4. UCID-21700, "Yucca Mountain Project Waste Package Design for MRS System Studies", April 1989.
5. UCID-21444, "Numerical Modeling of the Thermal and Hydrological Environment Around a Nuclear Waste Package Using the Equivalent Continuum Approximation: Horizontal Emplacement", May 1988.
6. WHC-EP-0065 (formerly HEDL-7637), "Electrochemical Corrosion - Scoping Experiments -- An Evaluation of Results", September 1988.
7. UCRL-100395, "Waste Package Performance Assessment for the Yucca Mountain Project", February 1989.

Category 1 (continued) - Status of Reviews not yet sent to NRC and WERB

Document No.	Assigned to Reviewer	First Draft Completed	Lead Worker	Program Manager
WHC-EP-0096	<u>2/21/89</u>	<u> </u>	<u> </u>	<u> </u>
Beavers, 1988	<u>5/11/89</u>	<u>6/23/89</u>	<u>6/24/89</u>	<u> </u>
UCID-21466	<u>12/18/89</u>	<u> </u>	<u> </u>	<u> </u>
UCID-21700	<u>12/18/89</u>	<u> </u>	<u> </u>	<u> </u>
UCID-21444	<u>12/18/89</u>	<u> </u>	<u> </u>	<u> </u>
WHC-EP-0065	<u>12/18/89</u>	<u> </u>	<u> </u>	<u> </u>
UCRL-100395	<u>12/18/89</u>	<u> </u>	<u> </u>	<u> </u>

Category 2 -- Review as time permits (new entries for this reference data file)

None this quarter.

Category 3 -- File and cross reference

1. UCRL-08729, "The EQ3/6 Software Package for Geochemical Modeling: Current Status", July 1988.
2. UCID-21579, "Estimates of the Width of the Wetting Zone Along a Fracture Subjected to an Episodic Infiltration Event in Variably Saturated, Densely Welded Tuff", May 1988.

OTHER REPORTS ON VITRIFIED WASTE FORM --

Category 1 -- Reports currently being reviewed

None this quarter.

Category 2 -- Review as time permits

None this quarter.

Category 3 -- File and cross reference

None this quarter.

TASK 3 -- LABORATORY TESTING

- A. Title of Study: Evaluation of Methods for Detection of Stress Corrosion Crack Propagation in Fracture Mechanics Samples.
Principal Investigator: Charles Interrante

October, November, December 1989:

During this reporting period, the co-worker on this project, Mr. Stephen Harrison was transferred to another government agency and was not available for consultation after that occurred. Prior to Mr. Harrison's departure Dr. C. Interrante was "schooled" on many aspects of the testing procedures that were known only to Mr. Harrison. This was done in efforts to learn as much as would be needed to interpret data in hand, to complete calibrational studies that must be done to interpret data from the already completed test and to prepare for testing of one additional test specimen, one that was prepared but not tested prior to Mr. Harrison's departure. Near the close of this period, the principal investigator, Dr. Interrante transferred to the Nuclear Regulatory Commission, where he will be stationed henceforth. As a result of these transfers of personnel, this project saw very little or no new results during this reporting period.

What remains for completion prior to reporting on the results of this study are the following activities: (1) Complete the analysis of data now collected and stored on the mainframe computer. (2) Conduct calibration procedures, as needed to interpret the data. (3) Conduct one additional test and in this test correct the errors in either data acquisition or processing that are discovered in step (1). It is anticipated that Dr. Interrante will have the opportunity to do the data analysis and perhaps even to conduct the additional test in the next quarter. In any event, the apparatus for this work will be left intact until completion of these studies is assured.

- B. Title of Study: Effect of Resistivity and Transport on Corrosion of Waste Package Materials.
Principal Investigator: Edward Escalante

October, November, December 1989:

Starting in the second week in October, our laboratory was moved to another location, forcing the cessation of all laboratory efforts. The last laboratory modifications are being made now, completing this move. In the mean time, we have continued to evaluate and prepare the data for reporting.

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

Studies of literature and additional data and specimen analysis in preparation for writing a paper continue. The report that was submitted to NRC earlier will be put in the form of an NIST Internal Report.

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

October - December 1989:

The purpose of this study is to provide information and data on the corrosion behavior of Zircaloy that can be used to determine the long-term durability of nuclear fuel cladding made of this material. This experimental work involves electrochemical measurements made primarily using potentiostatic polarization techniques to study the corrosion behavior of bulk Zircaloy-2 and -4 as well as specimens of cladding tubes made from these two materials. Measurements are made on both the inner and outer walls of the cladding. Measurements have been made in simulated J-13 water, a water that may be typical of that which could be present in the Yucca Mountain, Nevada site.

The work of this period involved preparing and presenting a poster at the Materials Research Society Meeting on November 28, 1989. A trip report regarding this meeting is attached. An eight page paper describing the work was accepted for publication in the proceedings of this meeting. A copy of this paper is attached (see Attachment C).

Two specimens of Zircaloy-2 cladding, one exposing the surface of the inner wall and one exposing the surface of the outer wall, were left in the J-13 water at a temperature of 70 C for six months. Measurements were made on these specimens at 70 C, and the data showed only small changes when the recent curves were compared with the previous ones. There were small decreases in current levels and a positive shift in the corrosion potentials, and both of these changes indicate increased passivity. Measurements will be made at 90 C, a closer visual observation, in situ, will be made, and all results combined with a further analysis of these data for the next report.

Future work will be directed toward investigating of effects of selected halide ions on passivity and localized corrosion of Zircaloy. Other future work involves some measurements of longer term tests, and some additional specimen analysis and tests that can provide a more complete explanation of experimental results already obtained.

TASK 4 - GENERAL TECHNICAL ASSISTANCE

Dr. P. Adams attended the Fourth International Symposium on Ceramics in Nuclear Waste Management on April 24-26, 1989 in Indianapolis, IN. A summary is enclosed (see Attachment A).

Dr. P. Adams attended the SF-12 Vitrification Run External Review at West Valley Demonstration Project held in West Valley, NY on October 31-November 2, 1989. A summary of that review has not yet been received.

Dr. A. Fraker participated in the Materials Research Society 1989 Fall Meeting on November 27-December 2, 1989 in Boston, MA. A trip report is enclosed (see Attachment B).

A response for general technical assistance on the document titled, "Degradation Modes in Candidate Copper-Based Materials for High-Level Radwaste Canisters", by H. K. Manaktala was prepared by Dr. U. Bertocci and sent to Mr. C. Peterson on November 29, 1989.

SDI006, UD 8921, SER. DD016

File(s) searched:

File 6:NTIS - 64-89/ISS21
(COPR. 1989 NTIS)

Sets selected:

Set	Items	Description
1	7	WASTE(W)PACKAGE?
2	8	CANISTER?
3	41	CORROSION
4	19	LEACHING
5	111	GLASS
6	4	VITRIFICATION
7	165	S3-S6/OR
8	6	HIGH(W)LEVEL(W)WASTE?
9	126	RADIOACTIVE(W)WASTE?
10	18	NUCLEAR(W)WASTE?
11	4	(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
06oct 17:22EST PR 11/5/1-25 (items 1-4)

Total items to be printed: 4

SDI008, UD 8910, SER. DA016

File(s) searched:

File 8:COMPENDEX PLUS - 70-89/OCT Copr. Engineering Info
Inc. 1989)

Sets selected:

Set	Items	Description
1	4	WASTE(W)PACKAGE?
2	5	CANISTER?
3	266	CORROSION
4	44	LEACHING
5	312	GLASS
6	6	VITRIFICATION
7	614	S3-S6/OR
8	3	HIGH(W)LEVEL(W)WASTE?
9	53	RADIOACTIVE(W)WASTE?
10	7	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
18oct	17:29EST	PR 11/5/1-20 (items 1-2)

Total items to be printed: 2

10

SDIO32, UD 8911, SER. DD022

File(s) searched:

File 32:METADEx 66-89/NOV
(Copr. 1989 ASM International)

Sets selected:

Set	Items	Description
1	7	HIGH()LEVEL()WASTE? ? OR RADIOACTIVE()WASTE? OR NUCLEAR()WASTE?
2	2085	STEEL? ? OR ZIRCALOY? ? OR TITANIUM? ? OR COPPER
3	3	1*2
4	0	ANNA FRAKER, 223, B-254, X6009

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

Date Time Description
12oct 00:04EST PR 3/5/1-25 (items 1-3)

Total items to be printed: 3

11

SDI006, UD 8922, SER. DD016

File(s) searched:

File 6:NTIS - 64-89/ISS22
(COPR. 1989 NTIS)

Sets selected:

Set	Items	Description
1	0	WASTE(W)PACKAGE?
2	4	CANISTER?
3	40	CORROSION
4	18	LEACHING
5	89	GLASS
6	3	VITRIFICATION
7	140	S3-S6/OR
8	3	HIGH(W)LEVEL(W)WASTE?
9	88	RADIOACTIVE(W)WASTE?
10	17	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
22oct 15:26EST PR 11/5/1-25 (items 1-2)

Total items to be printed: 2

12

SDI293, UD 8911, SER. DD023

File(s) searched:

File 293:ENGINEERED MATERIALS ABS 86-89/NOV
(Copr. 1989 ASM INTERNATIONAL)

Sets selected:

Set	Items	Description
1	4	HIGH()LEVEL()WASTE? ? OR RADIOACTIVE()WASTE? OR NUCLEAR()WASTE?
2	274	STEEL? ? OR ZIRCALOY? ? OR TITANIUM? ? OR COPPER
3	1	S1*S2
4	0	ANNA FRAKER, 223, B-254, X6009

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

Date	Time	Description
24oct	20:14EST	PR 3/5/1-25 (items 1-1)

Total items to be printed: 1

13

SDI006, UD 8923, SER. DD016

File(s) searched:

File 6:NTIS - 64-89/ISS23
(COPR. 1989 NTIS)

Sets, selected:

Set	Items	Description
1	0	WASTE(W)PACKAGE?
2	5	CANISTER?
3	31	CORROSION
4	8	LEACHING
5	72	GLASS
6	9	VITRIFICATION
7	112	S3-S6/OR
8	3	HIGH(W)LEVEL(W)WASTE?
9	55	RADIOACTIVE(W)WASTE?
10	9	NUCLEAR(W)WASTE?
11	0	(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
02nov 23:10EST PR 11/5/1-25 (no items to PRINT)

Total items to be printed: 0

14

SDI103, UD 8918, SER. DD017

File(s) searched:

File 103:DOE ENERGY - 83-89/OCT(ISS18)

Sets selected:

Set	Items	Description
1	7	WASTE(W)PACKAGE?
2	7	CANISTER?
3	216	CORROSION (1974 DEC)
4	43	LEACHING (1974 DEC)
5	109	GLASS (1974 DEC)
6	8	VITRIFICATION (1974 DEC)
7	383	S3-S8/OR
8	13	HIGH(W)LEVEL(W)WASTE?
9	250	RADIOACTIVE(W)WASTE?
10	32	NUCLEAR(W)WASTE?
11	4	(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
04nov 19:20EST PR 11/5/1-25 (items 1-4)

Total items to be printed: 4

15

SDI103, UD 8919, SER. DD017

File(s) searched:

File 103:DOE ENERGY - 83-89/OCT(ISS19)

Sets selected:

Set	Items	Description
1	5	WASTE(W)PACKAGE?
2	7	CANISTER?
3	180	CORROSION (1974 DEC)
4	28	LEACHING (1974 DEC)
5	79	GLASS (1974 DEC)
6	9	VITRIFICATION (1974 DEC)
7	266	S3-S6/OR
8	2	HIGH(W)LEVEL(W)WASTE?
9	141	RADIOACTIVE(W)WASTE?
10	17	NUCLEAR(W)WASTE?
11	2	(S1 OR S2) AND S7 AND (S8 OR S9 OR S10)
12	0	ANNA FRAKER RM. B-108 BLDG. 223 X6009
13	0	JILL RUSPI

Prints requested (* indicates user print cancellation) :

Date	Time	Description
08nov	01:44EST	PR 11/5/1-25 (items 1-2)

Total items to be printed: 2

16

SDI008, UD 8911, SER. DA016

File(s) searched:

File 8:COMPENDEX PLUS - 70-89/NOV Copr. Engineering Info
Inc. 1989)

Sets selected:

Set	Items	Description
1	1	WASTE(W)PACKAGE?
2	3	CANISTER?
3	216	CORROSION
4	38	LEACHING
5	379	GLASS
6	6	VITRIFICATION
7	623	S3-S6/OR
8	3	HIGH(W)LEVEL(W)WASTE?
9	25	RADIOACTIVE(W)WASTE?
10	8	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

17

Prints requested (** indicates user print cancellation) :

Date Time Description
15nov 21:47EST PR 11/5/1-20 (items 1-2)

Total items to be printed: 2

SDI006, UD 8924, SER. DD016

File(s) searched:

File 6:NTIS - 64-89/ISS24
(COPR. 1989 NTIS)

Sets selected:

Set	Items	Description
1	0	WASTE(W)PACKAGE?
2	3	CANISTER?
3	27	CORROSION
4	5	LEACHING
5	42	GLASS
6	4	VITRIFICATION
7	73	S3-S6/OR
8	2	HIGH(W)LEVEL(W)WASTE?
9	44	RADIOACTIVE(W)WASTE?
10	4	NUCLEAR(W)WASTE?
11	1	(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

18

Prints requested (** indicates user print cancellation) :

Date . Time Description
17nov 19:05EST PR 11/5/1-25 (items 1-1)

Total items to be printed: 1

SDI103, UD 8920, SER. DD017

File(s) searched:

File 103:DOE ENERGY - 83-89/OCT(ISS20)

Sets selected:

Set	Items	Description
1	2	WASTE(W)PACKAGE?
2	12	CANISTER?
3	79	CORROSION (1974 DEC)
4	15	LEACHING (1974 DEC)
5	47	GLASS (1974 DEC)
6	5	VITRIFICATION (1974 DEC)
7	139	S3-S6/OR
8	5	HIGH(W)LEVEL(W)WASTE?
9	103	RADIOACTIVE(W)WASTE?
10	11	NUCLEAR(W)WASTE?
11	3	(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

19

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

Date Time Description
18nov 01:43EST PR 11/5/1-25 (items 1-3)

Total items to be printed: 3

SDI032, UD 8912, SER. DD022

File(s) searched:

File 32: METADEX 66-89/DEC
(Copr. 1989 ASM International)

Sets selected:

Set	Items	Description
1	6	HIGH()LEVEL()WASTE? ? OR RADIOACTIVE()WASTE? OR NUCLEAR()WASTE?
2	1928	STEEL? ? OR ZIRCALOY? ? OR TITANIUM? ? OR COPPER
3	4	1*2
4	0	ANNA FRAKER, 223, B-254, X6009

Prints requested (* indicates user print cancellation) :

Date Time Description
18nov 20:38EST PR 3/5/1-25 (items 1-4)

Total items to be printed: 4

20

SDI293, UD 8912, SER. DD023

File(s) searched:

File 293:ENGINEERED MATERIALS ABS 86-89/DEC
(Copr. 1989 ASM INTERNATIONAL)

Sets selected:

Set	Items	Description
1	1	HIGH()LEVEL()WASTE? ? OR RADIOACTIVE()WASTE? OR NUCLEAR()WASTE?
2	286	STEEL? ? OR ZIRCALOY? ? OR TITANIUM? ? OR COPPER
3	0	S1*S2
4	0	ANNA FRAKER, 223, B-254, X6009

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

Date	Time	Description
22nov	01:45EST	PR 3/5/1-25 (no items to PRINT)

Total items to be printed: 0

21



November 13, 1989

To: Dr. Charles Interrante

From: P. B. Adams 

Re: Report of The Proceedings of the Fourth
International Symposium on Ceramics in Nuclear Waste Management
April 24-26, 1989. Indianapolis, IN.

1. Introduction

At your request and on behalf of the Nuclear Regulatory Commission, I attended the Fourth International Symposium on Ceramics in Nuclear Waste Management which was sponsored by the Nuclear Division of the American Ceramic Society in cooperation with the Divisions on Glass, on Cements and on Basic Science.

Following is an executive summary (section 2.0) which summarizes my reactions to the symposium plus my notes on individual papers (section 3.0). The written text of the various papers will be published by the Society.

2. Executive Summary

The conference highlighted the uncertainty in the ability at this time to predict the release rate from a nuclear waste glass that might be contained in a repository such as Yucca Flats. The inherent difficulties relate to the following:

- (1) The repository environment has not been fully defined. Of particular importance are the "out-of-bounds" scenarios.
- (2) The chemical durability of glass is not a specific physical property. Nor is there a single clearcut mechanism that will prevail under all circumstances.
- (3) Data acquisition usually results in substantial scatter, thus magnifying the statistical uncertainties of predicted release rates.

Specific impressions, comments and suggestions are as follows:

- (1) The role of iron in increasing the leach rate has not been quantified.
- (2) The role of radiation on the leachant and the glass has not been quantified.
- (3) "Out-of-bounds", or unusual, scenarios that might occur in the

- repository have not been identified. Thus their effect on leach rate have not been quantified.
- (4) There does not seem to be an active and complete involvement of the geochemical community in this activity. They should be fully participating in defining repository conditions and predicting glass response.
 - (5) The reaction layer that is formed can only be factored into the model if it can be proven to persist in the face of unusual scenarios.
 - (6) There should be a common framework for evaluating various competing leaching models.
 - (7) Leach rate data should clearly state the statistical certainty related to it.
 - (8) The "analog" approach is, in my opinion, suspect and can only be used as a qualitative support of other information.
 - (9) A disinterested agency, such as NIST, should develop and maintain standard reference glasses.

3.0 Notes and Comments on Papers Presented

Paper 1-SV-88 Macedo

This was a talk covering waste glass durability, particularly as it relates to the activity of ASTM C26.13, which is writing a recommended practice for prediction. The focus was on the Yucca Flats repository conditions since this is now a primary site option. There was nothing new in the mechanistic approach, but there are some central assumptions and approaches to the problem of long term prediction that are worth noting. Some of these triggered observations on my part.

The primary objective of the proposed test is to assure that a test can be conducted by qualified labs that will verify that a waste glass will meet the MCC-1 test criteria.

As I understand it, the ASTM test will be a "flow" test. The rationale for such a test lies in the premises that (a) this provides a "worst" case scenario since saturation effects cannot dominate and retard the reaction, (b) high S/V accelerates the process making analytical detection easier and (c) "out-of-bounds" mechanisms are most apt to be involved. Since reaction rates can tail off to near zero when one attempts to extrapolate to long times, the standard deviation can be 5 orders of magnitude greater than the nominal predicted value.

There was a discussion of mathematical approaches dependent on the theory that the initial rate drops off with time to approach some ultimate equilibrium value. The

(1-SV-88)

THE CHEMICAL DURABILITY OF NUCLEAR WASTE: GLASSES: ACCELERATED TESTING AND PREDICTION OF LONG TERM BEHAVIOR, P. B. Macedo*, Aa, Barkatt and I. L. Pegg, Vitreous State Lab. Catholic University, Washington, D.C. 20064

The licensing of both commercial and defense vitrification facilities requires defensible statements to be made concerning the long-term chemical durability of the glass waste form. The key elements of such a statement will be reviewed with particular regard to the consensus of the ASTM task group of C26.07/13 that has prepared a Recommended Practice on the subject. These include accelerated leach testing covering extended periods of time, mechanistic analysis to ensure that the extrapolation procedure is appropriate, validation by historical analogs, and confirmatory data extending up to repository closure. A number of short-comings in present accelerated test methods will be discussed and several modifications will be suggested. The principal mechanistic features of waste glass dissolution that have been identified will be summarized and the implication of each of these on the extrapolation of data to make defensible long-term predictions of release rates will be discussed.

author observed that the data usually fits this theory, but that at times there are deviations, e.g. (1) an abrupt change of slope (conc v. time) or (2) an increase in slope (The specifics of these experiments were not discussed).

The ASTM task group hopes to increase the confidence in prediction methods by ruling out the higher order terms using mechanistic analysis, validating results by the use of historical analogs and conducting repository in situ analyses.

The complex nature of the repository was highlighted by noting the wide range of variables such as ground water flow, glass composition, reaction rate barriers, trapped gas phases, precipitates and transport/removal processes.

There was some discussion of the "cliff" effect that has been noted re: the effect of composition on durability; i.e. the very abrupt change in durability as a result of a seemingly minor change in composition -- such as a factor of 10 with 1% SiO₂. The conclusion was that one must know where this durability cliff is and try to stay well within the composition plateau area.

Regarding the effect of pH, I got the impression that there was a belief that there was a marked break at about pH 9.6 for most glasses.

The author noted that he had observed that the rate of leach did not always increase with increasing SA/V, but that the opposite had been observed in some cases.

Regarding Yucca Flats, the conditions are 55-96 C, 0.5-50 lit/yr water flow rates and reducing for the first 300 years. Preliminary tests indicate that the laboratory tests are substantially more reactive than the actual site.

In conclusion, the author summarized his points as:

(1) A verified process model is needed. This depends on getting some good statistics. West Valley offers an opportunity to compile a sufficient body of data. So far, results suggest that the approach is correct.

(2) A verified product model is also needed. In particular, there is a need to be able to use composition to predict viscosity and durability with a high level of confidence.

(3) Must be able to predict glass performance in the repository with a high degree of certainty. Natural analogs are essential to this validation process.

Following are my thoughts re: some of the items above:

(1) The "out-of-bounds" reaction(s)/scenario(s) should be the primary focus. There is little doubt that a "normal", "average", "maximum" leach rate, can be predicted to some degree of certainty.

The question is what are the "unusual", "abnormal" conditions that can upset these predictions. In large degree, this is a question for the geologist and the geochemist. No amount of laboratory testing will fully answer the question. There is a need to know that assumptions are correct about the environment; the mechanism should then be relatively easy.

(2) The emphasis that focused on the necessity for good data is well founded. An uncertainty of 5 orders of magnitude increases the constraints on composition because it essentially means that predictions to be 100,000 times better than necessary for the real world. Although chemical durability data has historically

been difficult to reproduce with a high degree of precision, it may be that some effort directed toward improving precision would be more productive than trying to increase the statistical reliability by amassing huge quantities of data.

(3) It is essential to try to analyze the causes of the seeming deviations from the ideal mechanisms as alluded to in this talk.

These apparent anomalies are real jewels, because they provide an opportunity to gain a deeper understanding.

(4) I believe that further analysis will show that the so-called "cliff" should be viewed as a fairly broad composition band. My experience says that if you change the test, the position of the cliff will shift. i.e. it is highly environment dependent. I suggest this be explored before any specific conclusions are drawn.

(5) Similarly, the observation that there is a "boundary" at pH 9.6 may also be test dependent, as well as glass composition dependent.

(6) As I understand it, the "flow" test that has been described and discussed in this test is a bit of a misnomer. I.e., aliquots are taken periodically and replaced; it is not a true flow in the sense that the contact solvent is continually replaced. I suggest that another name be applied. There is a vast difference between the two conditions. It may be improper to suggest that the reaction rates observed where there is a fractional reduction in reactants will be the same as under true flowing conditions.

(7) Although most tests are done at or near real repository conditions, one must always keep in mind that there is no guarantee that the slope of the reaction rate with time curve will remain the same for different glasses. I.e., a

TAILORED CERAMIC CONSOLIDATION FORMS FOR ICPP HIGH ZR-CD-NA WASTE COMPOSITIONS, A. B. Harker* and J. F. Flintoff, Rockwell International Science Center, Thousand Oaks, CA 91360, (805) 373-4131

Experimental polyphase tailored ceramic forms designed for the consolidation of simulated ICPP HLW compositions at 70 to 80 wt % waste loading have been prepared and characterized. The microstructure, chemical composition and dissolution chemistry of the individual phases have been evaluated. Specific attention has been given to the immobilization of actinides and neutron poison Cd in the crystalline phases. The waste form is made up of calcium fluoride, zirconia, zircon, a Cd-containing zirconolite, a Ti-Ni-Cr-Cd alloy, and a designed glass phase. The uranium and actinide simulants are bound in crystalline phases and the Cs and Sr are dissolved in a borosilicate glass phase. The dissolution chemistry is phase specific in deionized water.

(3-SV-89)

A GLASS-CERAMIC COMPOSITION TO IMMOBILIZE ICPP HLW, R.S. Baker*, and B.A. Staples, Westinghouse Idaho Nuclear Co., Idaho Falls, ID 83403 (208) 526-3093

Candidate of glass-ceramic waste forms have been prepared by Hot Isostatic Pressing simulated calcined ICPP HLW and glass-ceramic forming additives including SiO₂, B₂O₃, Na₂O, and Li₂O. Titanium dioxide is added to enhance titanate phase formation to host cadmium and Ni powder is added as a reducing agent. Durable products with waste loadings up to 72 wt% and product densities up to 3.3 g/cm³ have been formed. These glass-ceramic waste forms have the potential to reduce final waste volumes by up to 60% compared to glass waste forms. Preliminary leach rates of the products determined using the MCC-1 leach test for 28 days are less than 1 gm²-day for the glass matrix elements of Si, B, Li, and Na and for the waste components of Cd, Cr, Ca, and Al. These leach rates are comparable to those measured with HLW glass products.

(4-SV-89)

IRRADIATION DAMAGE TO THE SIMULATED ICPP NUCLEAR WASTE, H. W. Chan*, Ceracon, Inc., Sacramento, CA 95826, 916-731-4707; D. G. Howitt, University of California, Davis, CA 95616, 916-752-1164

The overall irradiation response of the glass ceramic composite was studied by transmission electron microscopy. These composites were derived from the Idaho Chemical

relatively good glass at one temperature can turn out to be relatively bad at another temperature.

(8) There seemed to be a lot of reliance placed on the ability to use "analog" glasses to verify mechanistic approaches -- this is qualitative at best, depending on a very few special situations.

Paper no. 2-SV-89 Harker
 Paper no. 3-SV-89 Baker
 Paper no. 4-SV-89 Chan

These three papers discussed the properties of experimental glass ceramic materials that incorporated high loads, e.g. 73 weight %, of high level waste. Leach rates less than 1 gm/2 -day were said to be attainable. This is not surprising in view of the high concentrations of water-resistant oxides such as Zirconia, CaF₂, TiO₂ and SiO₂ and the low concentration of alkalis and other water soluble components. However, one questioner suggested that the durabilities were marginal -- this was not disputed.

Paper no. 6-SV-89 Ewing

The ultimate objective is to assess the effects of long term radiation damage on vitreous systems compared with crystalline systems. At this stage the results seem inconclusive; they are based on a single glass and a single ceramic type. There is no clear quantitative relationship that has been demonstrated between radiation and leach rate.

Processing Plant (ICPP) and are examined with emphasis on the microstructural changes introduced by the alpha, beta and gamma particles. These particles were simulated using lead ions, energetic electrons and Co⁶⁰ gamma-rays. In general, the crystalline phases were more resistant, but the amorphous phases went through significant changes after irradiation.

(6-SV-89)

RADIATION DAMAGE EFFECTS: COMPARISON OF SYNROC PHASES TO BOROSILICATE GLASS, R. C. Ewing, Dept. of Geology and Center for Micro-Engineered Ceramics, Un. of New. Mex., Albuquerque, NM 87131; W. Lutze, Hahn-Meitner Institut, 1000 Berlin 39, F. R. Germany

Alpha-decay damage effects in high-level nuclear waste forms is of primary importance in the evaluation of their long-term durability, as there are fundamental differences in the materials response of periodic vs. aperiodic solids. We summarize and contrast the changes in physical properties (e.g., density, fracture toughness, and elastic moduli), stored energy, and chemical durability with increasing alpha-decay dose. Specifically, we analyze the long-term radiation damage effects by describing annealing processes (alpha recoil track fading and removal of Frenkel defect pairs) in crystalline and glass waste forms and predict the final atomic structure of the waste forms as a function of waste loading and age.

(17-SV-89)

THE INFLUENCE OF GAMMA RADIATION ON THE LEACHING BEHAVIOR OF SIMULATED NUCLEAR WASTE GLASS IN J-13 SOLUTION, W. L. Ebert^a and J. K. Bates, Argonne National Laboratory, Argonne, IL

The results of modified MCC-1 leaching experiments performed to study the effects of penetrating gamma radiation on the reaction between simulated nuclear waste glass and J-13 water at 90°C are compared. Doped SRL 165, ATM-1c, and ATM-8 glasses were leached for up to 278 days under exposure rates of 2×10^5 , 1×10^4 , and 1×10^3 R/h; nonirradiated experiments were also performed. Irradiation was found to acidify the leachates at all exposures through radiolysis of the air in the vessel, although the high bicarbonate content of the J-13 water prevented the pH from dropping below about 6.4. Nonirradiated experiments attained leachate pH values near 9. The leachate Eh of all irradiated experiments decreased from the initial value of the J-13 water as evidenced by an increased NO₂⁻:NO₃⁻ ratio. The extent of glass reaction was not significantly affected by irradiation, as measured by the release of glass components, although the distribution of released transuranics between dissolved, suspended, and sorbed phases was different for the different exposures.

REDOX EFFECTS ON DURABILITY AND VISCOSITY OF NUCLEAR WASTE GLASSES.

X. Feng*, I. Pegg, E. Saad, S. Cucinell and Aa. Barkatt, VSL, Cath. Univ., Wash. DC, 20084, 202-635-5183

Iron oxide is one of the major components in West Valley nuclear waste glasses (about 12X). We report studies of the effect of the redox state of iron oxide on the viscosities and chemical durability of West Valley waste glasses that were prepared with Fe(II)/Fe ratios between 0.0 to 0.8 by melting in a controlled atmosphere of CO and CO₂. Durabilities were determined using modified MCC-3 tests and viscosities were measured between 950°C and 1150°C. It is found that the redox effects on durability are strongly dependent on glass composition; e.g. the leach rate differs by a factor of 12 from the most oxidized to most reduced glass at low alumina compositions, while this factor falls to below 2 for similar glass compositions but with higher alumina contents. The viscosities of these glasses decrease by about 30X over the range of redox states investigated.

(20-SV-89)

EFFECTS OF THE SA/V RATIO ON THE LONG-TERM CORROSION KINETICS OF R7T7 GLASS.

E. Vernaz,* T. Advocat, and J.L. Dussossoy, CEN Valrhô, BP 171, 30205 Bagnols-sur-Cèze, France.

Triplicate leach tests were conducted to measure the corrosion rate of R7T7 glass in saturation conditions. Monolithic and powdered glass specimens were leached at 90°C under static conditions in "Volvic" mineral water (simulating granitic water) for durations of up to one year with SA/V ratios of 500 m⁻¹, 2000 m⁻¹ and 8000 m⁻¹. The resulting silicon concentrations in solution were affected by the different pH obtained at each SA/V ratio. The concentrations thus cannot be directly related by the product (SA/V) × t. The small dispersion of experimental values allowed a final corrosion rate as low as 6 × 10⁻⁴ g·m⁻²·d⁻¹ to be estimated from the rise in the mobile element concentrations (B, Mo, Na). However, irrespective of the SA/V ratio the Si concentration increased slightly for all the test durations. The observed final rate cannot be considered as the "residual corrosion rate" in saturation conditions, inasmuch as the silicon concentration in solution does not remain constant.

(21-SV-89) ✓

DISSOLUTION MODEL FOR A GLASS HAVING AN ADHERENT INSOLUBLE SURFACE LAYER, K.B. Harvey*, and C.A. Boase, Atomic Energy of Canada Ltd., Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, Canada ROE 1LO

Previous glass dissolution models (Wallace and Wicks, Harvey and Boase) have not contained a mass balance equation to account for the surface-layer retention of major matrix components dissolved from the glass. We found it was possible to fit the model to the available experimental data only if a release-dependent or a time-dependent

Paper no. 17-SV-89 Ebert

This work was done with simulated nuclear waste glasses. There was some decrease in the durability of the less durable samples due to radiation but little effect on the better glasses. Radiation induced some slight acidification of the J-13 test water used.

Paper no. 19-SV-89 Feng

Reduction of iron caused a dramatic increase in leach rate for low durability (low alumina) glasses; for the more durable (higher alumina) glasses, there was a modest increase; intermediate compositions seemed to show an intermediate effect at low reduction levels which broke sharply to a dramatic effect at higher levels. The effect on viscosity was qualitatively similar but not as great. The significance of these results was that composition should be kept in the leach rate plateau region.

Paper no. 20-SV-89 Vernaz

The essence of this paper seemed to be that (1) the saturated Si concentration was dependent on pH rather than (SA/V) × t (as one would expect) and (2) the silica in solution does not reach saturation under the conditions of test (water at 90 C), since it is still

increasing at the end of the test (1 year).

Paper no. 21-SV-89 Harvey

The authors were able to fit experimental data to a kinetic model of glass dissolution by introducing a diffusion term to account for the transport rate of material through the layer formed on the surface of the glass.

Paper no. 23-SV-89 Bradley

Using direct observation techniques, the authors were able to verify the general model of the character of a reacted glass surface and to delineate it somewhat more specifically.

I.e. They describe a deposition layer, 1, on top of a reacted glass layer, 2. They further divide the reacted layer into 2B, a leached layer nearest the unreacted glass and showing very little depletion in silica, and 2A, a more hydrated leached layer that may evidence fracture. They divide the deposition layer into 1A, a fairly dense material, and 1B, the outermost part which is most porous. Layer 1 is the zone where most of the crystalline deposition and growth occurs.

Paper no. 24-SV-89 Trotignon

In the systems studied, the authors found that the less complex glasses simply showed a surface leaching and hydrolysis with some deposition of hydrolyzable elements, whereas the more complex glasses showed a heavy deposition of refractory oxides and hydroxides.

diffusion coefficient is assumed for transport through the layer. This paper presents a model containing such a mass balance equation to allow fitting using a constant value for the diffusion coefficient. The dissolution behavior of a layer-forming glass similar to DWRG (SRL Defense Waste Reference Glass) is described, using this model.

(23-SV-89)

AEM STUDY OF REACTED SURFACE LAYERS ON NUCLEAR WASTE GLASSES, T. A. Abrajano, Jr. and J. K. Bates Argonne National Laboratory, Argonne, IL 60439; J.P. Bradley, McCrone Associates, Inc., 850 Pasquinelli Dr., Westmont, IL 60559

A variety of techniques has been employed in the past to chemically and structurally characterize reacted surface layers on nuclear waste glasses. However, much of the existing speculations on the nature and origin of these reacted surface layers have been largely based on indirect observations (e.g., solution release patterns) or imprecise information on the reacted surface layers.

We report new results of analytical electron microscopic (AEM) analyses performed on a series of SRL glasses (SRL 131-based formulations) reacted using MCC-1 procedures. The AEM results (1) show the presence of variably hydrated and leached (B and alkalis) layer(s) immediately adjacent to the unreacted glass (transition zone), (2) indicate the occurrence of solid state transformation (crystallization) within this hydrated layer, and (3) show clear evidence of precipitation (from aqueous solution) of amorphous and crystalline phases on the solution side of the hydrated layer. The AEM results, together with results of other surface and solution analyses, are examined in relation to the rate controlling mechanisms of glass dissolution.

(24-SV-89)

NATURE OF LEACHED LAYERS FORMED ON BOROSILICATE GLASSES DURING AQUEOUS CORROSION, L. Trotignon, J.-C. Petit; J.-C. Dran; G. Della Mea. SESD/LECALT, CEN-FAR, BP.6, 92265 Fontenay aux Roses Cedex, France. CSNSM/CNRS, BP. 1, 91406 Orsay, France. Unita CISM-GNSM di Padova, 35131 Padova, Italy.

Borosilicate glasses with compositions of increasing complexity are submitted to aqueous corrosion at 65 and 90°C. Reacted surfaces are studied by means of electron microscopy (SEM, TEM), MeV ion beam techniques (RBS, RNRA) and infrared spectrometry. Two types of layers are identified. For the less complex and durable glasses, a thick hydrated silica compound where hydrolyzable elements tend to accumulate is developed (hydrosilicate). Inversely, for more complex and durable glasses, the outer part of the leached surface is formed by a silica-poor Fe/Zn/Zr oxo-hydroxide film, whereas the inner part exhibits only hydration.

Paper no. 27-SV-89 Tacca

After 2 years of burial, glasses show 4-6 um depth attack that is increasing at a decreasing rate with time. Buildup of surface layers is occurring.

Paper no. 28-SV-89 Brandys

Discussed the advantages and disadvantages of various analytical methods. Calculated an upper rate of 0.2 um/ year.

Paper no. 29-SV-89 Zoitos

This is a paper on plans and methods. No results yet.

Paper no. 30-SV-89 Sasoon

Calculate 0.1 um/ year upper limit.

Paper no 31-SV-89 Todding

This title and abstract not in preprint. "Concentration Profiles and Elemental Loss in Leached Layers after 2 Years in WIPP". Did SIMS profiles. Identified four layers: (1) An outermost precipitated layer, (2) An intermediate remnant of the original glass, (3) A gradient and (4) A Diffusion layer. Apparently all Al stays in glass. Leach rate is about 1 um/year. Leached layer about 5% void. Layer

(27-SV-89)

LEACHING OF SRP WASTE GLASS IN THE MIIT PROGRAM; SURFACE STUDIES, J. A. Tacca*, Clemson University, Clemson, SC; and G. G. Wicks, Savannah River Laboratory, Aiken, SC 29808, (803)725-3190

There are almost 2000 waste glass and package component samples buried in the salt site at WIPP. Among these samples are SRP waste glasses which have been buried for 6-mo., 1-yr. and 2-yrs., as part of a 5-yr. study. Analyses of these glasses, which are performing well thus far, will be presented.

(28-SV-89)

LEACHING OF SRL-Y NUCLEAR WASTE GLASS IN MIIT BY ANALYSIS OF BRINE SOLUTIONS, Marek Brandys, Meiling Gong*, Richard E. Sassoon Aaron Barkatt and Pedro B. Macedo, Vitreous State Laboratory, Catholic University of America, Washington, DC 20064

Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) studies made on the lithium - 6/lithium -7 isotope ratio allow identification of the source of lithium in the brine leachate of MIIT leach tests containing SRL-Y glass. Using these precise measurements of leach data from highly controlled tests an accurate determination of the upper limit of leaching from the nuclear waste glass is made.

(29-SV-89)

SURFACE LAYER FORMATION UNDER SIMULATED BURIAL CONDITIONS, B.K. Zoitos*, D.E. Clark, Department of Materials Science and Engineering, University of Florida, Gainesville, FL; A.R. Lodding, Chalmers University of Technology, Goteburg, Sweden

Interpretation of leaching results from in situ burial studies (Stripa, WIPP, Ballidon, etc.) relies heavily on leached layer thickness as an indicator of the extent of glass leaching. Studies currently underway will better establish the relationship between leaching and surface layer thickness. One objective of these studies is to determine the degree, if any, of congruent dissolution under simulated burial conditions. This is being studied through the leaching of glasses which have been implanted to a uniform depth with phosphorus. SIMS analysis will be performed after leaching to determine the position of the leached surface with respect to the implant. A second objective is to measure the rate of surface layer growth as a function of time, temperature, SA/V and solution residence time. All tests are being performed under repository relevant conditions using Stripa groundwater as leachant in the presence of Stripa granite.

(1) high in Si and Mg with considerable B. Layer (2) depleted in glass cations with Mg substituted.

Paper no. 32-SV-89 Ramsey

A216 steel contributed iron which induced as 4-fold increase in glass leach rate. 304 stainless had no effect. (The metal corrosion rate was not measured.)

Paper no. 33-SV-89 Grandstaff

The authors considered a variety of simulating systems ("analogs"), and a variety of geochemical fields. The former include hydrothermal experiments, active and fossil geothermal fields, simulation of composition chemistry and weathering. The later include, but are not limited to, Icelandic basalt, New Zealand granite and tuff, Idaho and Japan. They concluded that the experimental data agreed with the geochemical data and that experimental data was therefore valid for prediction. In view of the shotgun "correlations" which showed a factor of 100 or more deviation, it seems that such a correlation cannot be deemed quantitative based on this evidence.

Paper no. 41-SV-89 Feng

Using various physical constants, a model was postulated for the calculation of the viscosity from composition. It seemed to work for a wide variety of compositions when plotting on a log-log scale (

LEACHING OF NUCLEAR WASTE GLASSES DOPED WITH CHEMICAL TRACERS IN MIIT BY ANALYSIS OF BRINE SOLUTIONS, Richard E. Sassoon, Meiling Gong*, Marek Brandys, Mohammed Adel-Hadadi, Aaron Barkatt and Pedro B. Macedo, Vitreous State Laboratory, Catholic University of America, Washington, DC 20064

The versatile and powerful analytical tool of Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) may be used to detect very low concentrations of rare earth elements which possess few isotopic interferences in their mass spectra. Concentration data for brine leachates taken from leach tests containing nuclear waste glass samples doped with rare earth elements such as La, Ea, Yb, Ce, Nd and Pr will be presented which allow accurate determination of the upper limit of their appropriate leach rates.

-(31-SV-89)—Abstract Not Available.

4:20-4:40 p.m.—(32-SV-89)

LEACHING OF SRP WASTE GLASS IN BRINE; LABORATORY SUPPORT OF MIIT PROGRAM, W. G. Ramsey*, Clemson University, Clemson, SC; and G. G. Wicks, Savannah River Laboratory, Aiken, SC 29808, (803)725-3190

Simulated SRP waste glass and a standard were leached in WIPP brine and deionized water. The behavior of the system was assessed by combining solution analysis with surface studies and correlated with field test data. The glass performed well and its behavior was affected by the salt phases present.

(33-SV-89)

PREDICTION OF GROUNDWATER COMPOSITION IN HIGH-LEVEL NUCLEAR WASTE REPOSITORIES; LIMITS OF EXPERIMENTS-LIMITS OF ANALOGS, D.E. Grandstaff* and G.C. Ulmer, Temple University, Philadelphia PA 19122; G.H. Kacandes, Pennsylvania State University, University Park, PA

Groundwater composition is an important factor in predicting high-level nuclear waste repository performance. Data sources used to predict fluid properties include: natural geothermal fields, hydrothermal experiments, and equilibrium calculations. Predictions agree for some fluid composition parameters (fO₂, cation/cation ratios) but disagree for others (cation/proton ratios, FCO₂, pH). Data from analogs (9 areas) and experiments suggest that fluid composition parameters are fairly insensitive to host rock type and initial fluid composition. However, high-temperature fluids in analogs may have pH values lower than those in repositories due to addition of acidic gases, such as CO₂ and H₂S, in those magmatically-driven systems.

which tends to minimize deviations, at least to the eye).

Paper no. 43-SV-89 Kawamura

As with some other papers, there tends to be, in my opinion, a reliance on drawing conclusions from a single leach test. I.e., I note that several experimenters have observed that there are so-called "cliffs", or sharp changes in durability when plotted vs. composition; it is my belief that the location of many of these "cliffs" are also test-dependent. In other words, no one should not be lulled into thinking that chemical durability is a specific physical property, independent of other factors. Nor that it is possible to define an acceptable composition field on the basis of a single test.

Paper no. 47-SV-89 Piepel

Interpretation of the 95-95 criterion in the WAPS was discussed from a statistical point of view. First, it was noted that 95% of the leach test values must meet the true value, not the observed value, with 95 % confidence. Second, that it is not clear whether this is for each element, or for the total. Third, that this criterion applies equally to the MCC-1 and any alternative that the producer may elect. It was observed that in view of the possible uncertainties, i.e. glass inhomogeneity, leach test variations, model imprecisions and analytical reproducibility, it may require a lot of data to squeeze the true value out of the observed values. It is essential to remove as

(41-SV-89)

A STRUCTURAL THERMODYNAMIC MODEL FOR VISCOSITY OF GLASSES, X. Feng*, E. Saad, I. Pegg, and Aa. Barkatt, VSL, Cath. Univ., Wash. DC, 20064, 202-635-5183

This paper describes a model for the temperature and composition dependence of the viscosity of silicate glass melts, that is based on structural thermodynamic considerations. First, the model distinguishes among those components according to their structural roles in glasses. It is then postulated that the viscosity also depends in part on the strengths of the oxygen-metal interactions and that a measure of these may be obtained from the constituent oxide heats of formation. The viscosity is correlated with the known heats of formation modified with a few simple structural rules. A good correlation was obtained for the measured viscosities of nuclear waste glasses and also for a broader range of compositions from simple binary and ternary system to natural molten rocks.

(43-SV-89)

CHARACTERIZATION OF HIGH LEVEL WASTE GLASS, K. Kawamura*, T. Takahashi, M. Horie and N. Tsunoda, Power Reactor and Nuclear Fuel Development Corporation, Tokai-mura, Ibaraki-ken, 319-11, Japan

High level liquid wastes generated in the reprocessing process were simulated and vitrified in the laboratory. Sensitivity studies were carried out to assess the variations of the waste composition on the major glass properties: density, viscosity, electrical resistance, characteristic temperatures, thermal stability and chemical durability. Effect of the noble metals on viscosity and electrical resistance was elucidated.

(47-SV-89)

STATISTICAL ASPECTS OF COMPLIANCE WITH THE WAPS RADIONUCLIDE RELEASE SPECIFICATION, G.F. Piepel* and G.B. Mellinger, Materials Characterization Center, Pacific Northwest Laboratory, Richland, WA 99352

The paper discusses various statistical aspects of compliance with the Waste Acceptance Preliminary Specification (WAPS) radionuclide release specification, including: (1) how the 95/95 criterion in WAPS 1.3.2 should be interpreted, (2) the level of sampling and leach testing required, and (3) alternative approaches for demonstrating compliance.

many of these uncertainties as possible. One item needed in this regard is a reference glass (or glasses) of known composition. (Either NIST or ASTM or both should get on this ASAP if it has not been started). If these uncertainties cannot be controlled, then leach test values will have to be more conservative for certification.

Paper no. 48-SV-89 Westsik

Tables were presented defining the parameters required for sampling procedures that would presumably meet the WAPS requirements. I believe that these should receive careful review when the full paper is available. For instance, as an analytical glass chemist, I am not comfortable with one sample per batch of glass, although this depends on ones definition of "batch".

Paper no. 49-SV-89 Pulsipher

With respect to uncertainties in the analysis of the glass, data indicate that the glass itself is very homogeneous and thus a small contributor. Most of the total uncertainty, about 5%, comes from instrumental variations especially in the long term. Operator bias is yet to be evaluated.

Paper no. 50-SV-89 Walter

Startup is currently targeted for 1996.

(48-SV-89)

SAMPLING AND ANALYSIS STRATEGIES TO SUPPORT WASTE FORM QUALIFICATION, J.H. Westsik, Jr.*, B.A. Pulsipher, D.L. Eggett, and W.L. Kuhn, Pacific Northwest Laboratory, Richland, WA 99352

As part of the waste acceptance process, waste form producers will be required to demonstrate that the glass waste form will meet minimum specifications and that the process can be controlled to consistently produce an acceptable waste form and to provide documentation that the production waste form meets specifications. Key to the success of these endeavors is adequate sampling and chemical and radiochemical analyses of the waste streams from the waste tanks through the process to the final glass product. This paper suggests sampling and analysis strategies for meeting specific statistical objectives of detection of compositions outside specification limits, prediction of final glass product composition, and estimation of composition in process vessels for reporting and for guiding succeeding process steps.

(49-SV-89)

COMPOSITIONAL ANALYSES: WHERE IS THE UNCERTAINTY COMING FROM?, BA PULSIPHER* AND DL EGGETT, PACIFIC NORTHWEST LABORATORY RICHLAND, WA 99352 (509) 375-3989

The West Valley vitrification process is designed to solidify the high-level radioactive waste solids stored at West Valley, New York. As specified in the Waste Acceptance Preliminary Specification, an estimate of the chemical composition of the waste glass is required and an "estimate of precision and accuracy, and the basis for the estimate of the precision shall be reported in the Waste Compliance Plan."

Results from a statistically designed experiment to quantify: 1) short-term instrument variations, 2) long-term instrument variations, 3) short-term preparation variations, 4) long-term preparation variations, and 5) variations between replicate samples of the ground powder from a single glass sample are presented for ICP and AA analyses at West Valley. Besides determining the overall analytical precision, statistical analyses identified which major contributors to the uncertainty should be targeted for future improvements.

Paper no. 51-SV-89 Kurath

25 % of supernatant has been processed using zeolite to remove Cs and resulting in a pH 10-11 solution.

(50-SV-89)

 WASTE MANAGEMENT STRATEGY OF THE WEST VALLEY DEMONSTRATION PROJECT, E. Maestes, U.S. Department of Energy West Valley Project Office, West Valley, New York; H.F. Walter*, U.S. Department of Energy, Office of Remedial Action and Waste Technology, Washington, DC

Some Random Thoughts:

If not already begun, there should be a comprehensive program started to evaluate, compare and refine the various models that have been proposed. This should go beyond the composition scope involved in nuclear waste studies to include commercial glasses.

There should be an assessment of SA measurements as made by various techniques.

There needs to be a greater involvement than that which I am aware of, with respect to the geochemists. If I heard correctly during one conversation, there are app. 7000 geochemists in the world (or USA ?); only about 12 of these are involved with this activity.

During the course of one conversation, the view was expressed that there was too little consideration given to long term devitrification effects, and in fact that it was often summarily dismissed. The further comment was that the geochemists really don't know what the magnitude of such effects are. I certainly don't know. However, if doubt persists among reputable scientists, on this or other topics, it will not ease the ultimate process of certification.

High-level radioactive waste stored at West Valley (New York) is to be immobilized in a durable borosilicate glass for later emplacement in a federal repository. Technical choices concerning waste forms and solidification processes for both high-level and low-level wastes and the options ultimately selected will be discussed.

(51-SV-89)

CORRELATION OF LABORATORY TESTING AND ACTUAL OPERATIONS FOR THE WEST VALLEY SUPERNATANT TREATMENT SYSTEM, D. E. Kurath, L. A. Bray, W. A. Ross*, Pacific Northwest Laboratory, Richland, Washington, and D. K. Ploetz, West Valley Nuclear Services, West Valley, New York.

An ion exchange process which removes Cs-137 from the supernatant associated with neutralized PUREX high-level waste sludge at the West Valley Demonstration Project was developed at the Pacific Northwest Laboratory. Initial operation of the Supernatant Treatment System has now been achieved at West Valley and results have been in conformation with the Laboratory studies. The paper will address the development of the predictions of system operations and the initial system results.

Trip report - Anna C. Fraker, December 4, 1989

Meeting attended - Materials Research Society 1989 Fall Meeting, Nov. 27- Dec. 2, 1989, Boston, Massachusetts. Attended day and evening sessions of Symposium U, Scientific Basis for Nuclear Waste Management on November 28, 1989.

A copy of the abstracts from Symposium U, Scientific Basis for Nuclear Waste Management is attached. These abstracts present an overview of the subjects presented at the meeting and of the participants.

Daytime Sessions - The sessions during the day of Nov. 28, 1989 dealt with nuclear glass dissolution and durability. There are questions regarding the Product Consistency Test (PCT) developed at the Savannah River Site. This is a seven day test for use in routinely verifying waste glass durability. The Materials Characterization Center (MCC) conducted a round robin of a Product Consistency Test, that included eight laboratories. The test of the MCC round robin called for triplicate tests conducted over a period of three weeks. Another question is how does this test compare with the Materials Characterization Center's (MCC) MCC - 3, Agitated Leach Test for Powdered Glass? It would be useful to know how the different tests for glass leaching compare for a given form of glass such as powder.

There is an abstract of a paper presented in one of the sessions on another day that discussed the effects of the fluoride ion on passivity of Zircaloy-4. The conclusion was that fluoride in water increases the corrosion rate of Zircaloy by "modifying the passivation properties of the oxide film". This paper is entitled Fluoride Influence on Zircaloy-4 Corrosion in Water as a Function of pH, Temperature and Fluoride Content" by N. H. Uziemblo and H. D. Smith, Pacific Northwest Laboratory, Richland, Washington.

Evening Session - The evening session on Nov. 28, 1989 was a poster session. This session included a number of different topics. There were four posters relating to corrosion and to Zircaloy. Content of these is highlighted in the following paragraphs.

1. The National Institute of Standards and Technology (NIST) contributed a poster on "Corrosion Behavior of Zirconium Alloy Nuclear Fuel Cladding". The conclusions of these electrochemical studies which had been conducted in simulated J-13 water at 95° C were that the general corrosion rate of Zircaloy-2 and -4 were negligible and that a tendency for localized corrosion, in this case, crevice corrosion was indicated by hysteresis of the current vs. potential measurements shown in polarization curves. Results indicated that more work of this nature was needed to fully assess the corrosion behavior of the zirconium alloys.

2. John A. Beavers presented work of himself and Neil Thompson of Cortest Columbus, Inc., Columbus, Ohio on the topic "Potentiodynamic Polarization of Candidate Container Materials in Simulated Tuff Repository Environments". Cyclic potentiodynamic polarization curves are conducted on four candidate canister materials (CDA 102 copper, CDA 715 copper-nickel, 304L stainless steel and Incoloy 825) in 33 different environments. Other variables include pH, temperature, chemical species

in the ground water, and species produced by radiolysis. The various species that are present in the ground water were used in separate testing environments. Measured corrosion potentials for the metals in the various environments showed that in some cases, there were significant changes in the potential and that these materials should be studied further regarding their corrosion resistance in the specific environment. These tests are useful for determining corrosive effects of a given species on a given metal and for identifying other aspects of the corrosion behavior under specified conditions.

3. H. D. Smith, Pacific Northwest Laboratory, Richland, Washington, presented work on "An Interpretation of the High-Stress, Low-Temperature Cracking of Zircaloy-4 Spent Fuel Cladding". This work was designed to determine if Zircaloy spent fuel cladding will crack in 90°C water, and if cracking occurs, to determine how the time to failure varies with stress. C-Ring specimens were used, and the conclusions of this work were;

Cracking occurs in spent fuel cladding via delayed hydrogen cracking (dhc).

The presence of water augments dhc by providing additional hydrogen to the crack tip.

The observed time to failure stress relationship suggests low cracking occurrence under repository conditions because of the low stress levels expected; <10% of yield stress.

Material used in these studies was Zircaloy-4 from a Pressurized Water Reactor at a power level of 27 MWd/KgHM. There was a thick oxide of 12-20 um and a thin oxide of 3 - 6 um. Some alpha contamination had occurred during acid washing.

4. Ray B. Stoudt from the University of California, Lawrence Livermore National Laboratories, P. O. Box 808, L-201, Livermore, CA 94550 presented work entitled "Deformation and Thermodynamic Model for Hydride Precipitation Kinetics in Spent Fuel Cladding". A model was developed to show hydride platelet density. Hydrogen is contained in all spent fuel rods from nuclear reactors. As the temperature cools down toward ambient temperature, the hydrides will precipitate as zirconium hydride platelets. Hydrides with their basal poles in the radial direction will not affect cladding failure as much as hydrides with their basal poles oriented in the radial direction of the tube. "The development of deformation and thermodynamic models that depend on hydride density (including orientation) have provided expressions to calculate the probable strain field induced by hydrides and the functional dependence for probable hydride orientation on the state of nominal stress in the cladding." These models provide a basis for studying the effects of hydride precipitation, and it was indicated that a description of the expected failure rate due to zirconium hydrides is needed.

**SYMPOSIUM U:
SCIENTIFIC BASIS FOR NUCLEAR
WASTE MANAGEMENT XIII**



November 27-30, 1989

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SCIENTIFIC BASIS FOR CLEAR
WASTE MANAGEMENT XIII

November 27-30, 1989

SESSION U1: CEMENTITIOUS MATERIALS -
ASPECTS OF PERFORMANCE

Chairs: Paul Brown

Monday Morning, November 27

America North (W)

8:15 OPENING REMARKS

8:30 U1.1

NUCLEAR WASTE IMMOBILIZATION IN CEMENT-BASED MATERIALS: OVERVIEW OF FRENCH STUDIES, Pascal Bouniol, Eliane Revertegat, Jean Oliver, Philippe Gegout, Michel Jorda and Rosemarie Atabek, C.E.A, DRDD/SESD, CEN/FAR, Fontenay aux Roses, France.

9:00 U1.2

EFFECT OF CURING TEMPERATURE ON THE PROPERTIES OF CEMENTITIOUS WASTE FORMS, Ryan O. Lokken, John W. Shade and Paul F.C. Martin, Battelle-Pacific Northwest Laboratory, Richland, WA.

9:30 U1.3

BEHAVIOR OF CONCRETE AS A BARRIER MATERIAL FOR NUCLEAR WASTE DISPOSAL, R.J. James and Y.R. Rashid, ANATECH Research Corporation, La Jolla, CA.

9:45 U1.4

GROUTS AND CONCRETES FOR THE WASTE ISOLATION PILOT PROJECT (WIPP), Lillian D. Wakeley, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

10:00 BREAK

SESSION U2: CEMENTITIOUS MATERIALS -
ASPECTS OF DURABILITY

Chair: William Richmond

Monday Morning, November 27

America North (W)

10:30 *U2.1

ASSESSMENT OF THE PERFORMANCE OF CEMENT BASED COMPOSITE MATERIAL FOR RADIOACTIVE WASTE IMMOBILIZATION, M. Atkins, J. Cowie, L.P. Glasser, T. Jappy, A. Kindness and C. Pointer, University of Aberdeen, Department of Chemistry, Aberdeen, Scotland.

11:00 U2.2

DURABLE CONCRETE FOR A WASTE REPOSITORY-MEASUREMENT OF IONIC INGRESS, R.F. Feldman, J.J. Beaudoin, Institute for Research in Construction, National Research Council, Ottawa, Canada; and K.E. Philipose, Atomic Energy of Canada, Ltd., Waste Management Systems, Ontario, Canada.

*Invited Paper

11:30 U2.3

LOGNORMAL SIMULATION OF PORE EVOLUTION DURING CEMENT HARDENING, D. Shi, W. Ma and P.W. Brown, The Pennsylvania State University, Materials Research Laboratory, University Park, PA.

11:45 U2.4

MECHANISTIC MODEL FOR THE DURABILITY OF CONCRETE BARRIERS EXPOSED TO SULPHATE-BEARING GROUNDWATERS, Alan Atkinson and John A. Hearne, Harwell Laboratories, Materials Development Division, Oxon, United Kingdom.

SESSION U3: SORPTION AND
SPECIATION STUDIES

Chair: Greg Choppin

Monday Afternoon, November 27

America North (W)

1:30 U3.1

THE SOLUBILITY AND SORPTION OF URANIUM (VI) IN A CEMENTITIOUS REPOSITORY, M. Brownsword, A.B. Buchan, F.T. Ewart, R. McCrohon, G.J. Ormerod, J.L. Smith-Briggs and H.P. Thomason, Harwell Laboratory, Chemistry Division, Oxfordshire, United Kingdom.

1:45 U3.2

SPECIATION OF Pu(VI) IN NEAR-NEUTRAL TO BASIC SOLUTIONS VIA LASER PHOTOACOUSTIC SPECTROSCOPY, S. Okajima, J.V. Beitz, J.C. Sullivan and D.T. Reed, Argonne National Laboratory, Argonne, IL.

2:00 U3.3

MODELLING STUDIES OF SORPTION IN THE NEAR FIELD OF A CEMENTITIOUS REPOSITORY, A. Haworth, S.M. Sharland and C.J. Tweed, UKAEA, Harwell Laboratory, Theoretical Physics Division, Oxfordshire, United Kingdom.

2:30 U3.4

EVIDENCE OF LONG DISTANCE TRANSPORT OF NATURAL COLLOIDS IN A CRYSTALLINE ROCK GROUNDWATER, W.R. Alexander, R. Bruetsch, C. Degueldre, Paul Scherrer Institute, Villigen, Switzerland; and B. Hofmann, USGS, Denver, CO.

3:00 U3.5

ANALYTIC STUDIES OF COLLOID TRANSPORT, Y. Hwang, T.H. Pigford, P.L. Chambré, and W.W.-L. Lee, University of California, Berkeley, Department of Nuclear Engineering and Lawrence Berkeley Laboratory, Berkeley, CA.

3:15 BREAK

SESSION U4: CEMENTITIOUS MATERIALS -

ASPECTS OF LEACHING

Chair: William Bostick
Monday Afternoon, November 27
America North (W)

3:30 *U4.1
THE MICROSTRUCTURE OF ggbfs/OPC HARDENED CEMENT PASTES AND SOME EFFECTS OF ELEVATED TEMPERATURE LEACHING, I.G. Richardson, S.A. Rodger and G.W. Groves, University of Oxford, Department of Metallurgy and Science of Materials, Oxford, United Kingdom.

4:00 U4.2
THE EFFECTS OF TEMPERATURE ON THE LEACHING BEHAVIOR OF CEMENT WASTE FORMS, Mark Fuhrmann, Richard Pietrzak, John Heiser III, Eena-Mai Franz and Peter Colombo, Brookhaven National Laboratory, Radiological Sciences Division, Nuclear Waste Research Group, Upton, NY.

4:15 U4.3
THERMODYNAMIC MODELING OF CEMENTITIOUS WASTE FORM/GROUNDWATER INTERACTION AS A TOOL FOR LONG-TERM PERFORMANCE ASSESSMENT, Louise J. Criscenti and R. Jeff Serne, Battelle-Pacific Northwest Laboratory, Richland, WA.

4:30 U4.4
WASTE GROUT LEACH TESTS: PURSUIT OF MECHANISMS AND DATA FOR LONG-TERM PERFORMANCE ASSESSMENT, R. Jeff Serne, Battelle-Pacific Northwest Laboratory, Richland, WA.

SESSION U5: MODELING THE DISSOLUTION OF NUCLEAR WASTE FORMS

Chairs: Werne Lutze and Carol Jantzen
Tuesday Morning, November 28
America North (W)

8:30 *U5.1
THERMODYNAMICS OF GLASSES FOR NUCLEAR WASTE DISPOSAL, Alexandra Navrotsky, Princeton University, Department of Geological and Geophysical Sciences, Princeton, NJ.

9:00 U5.2
A KINETIC MODEL FOR BOROSILICATE GLASS DISSOLUTION BASED ON THE DISSOLUTION AFFINITY OF A SURFACE ALTERATION LAYER, William L. Bourcier, Dennis W. Peifer, Kevin G. Knauss, Kevin D. McKeegan and David K. Smith, Lawrence Livermore National Laboratory, Livermore, CA.

9:30 U5.3
PREDICTION OF RADIOACTIVE WASTE GLASS DURABILITY BY THE HYDRATION THERMODYNAMIC MODEL: APPLICATION TO SATURATED REPOSITORY ENVIRONMENTS, Carol M. Jantzen, Westinghouse Savannah River Company, Aiken, SC.

10:00 BREAK

10:30 U5.4
CHEMISTRY OF MASS CORROSION IN HIGH SALINE BRINES, B. Grambow, R. Müller, Hahn-Meitner-Institut Berlin, Berlin, Germany.

11:00 U5.5
THERMOKINETIC MODEL OF BOROSILICATE GLASS DISSOLUTION: CONTEXTUAL AFFINITY, T. Advocat, E. Vernaz, CEN-Valrhô, SDHA, Bagnols-sur-Cèze, France; J.L. Crovisier and B. Fritz, CNRS/CSGS, Strasbourg, France.

11:30 U5.6
COMPARISON OF THE LAYER STRUCTURE OF VAPOR PHASE AND LEACHED SRL GLASS BY USE OF AEM, B.M. Bixer, J.K. Bates, T.A. Abrajano Jr., Argonne National Laboratory, Argonne, IL; and J.P. Bradley, McCrone Environmental Services, Inc., Westmont, IL.

11:45 U5.7
DISSOLUTION MECHANISMS OF CaTiO_3 AND OTHER TITANATE PHASES IN THE SYNROC ASSEMBLAGE, S. Myhra, D.K. Pham, Griffith University, Division of Science and Technology, Nathan, Qld, Australia; R. St.C. Smart, South Australian Institute of Technology, School of Chemical Technology, Adelaide, Australia; and P.S. Turner, Griffith University, Division of Science and Technology, Nathan, Qld, Australia.

SESSION U6: WASTE GLASS PERFORMANCE STUDIES

Chairs: Ned Bibler and Claude Sombret
Tuesday Afternoon, November 28
America North (W)

1:30 U6.1
A COMPARISON OF THE BEHAVIOR OF VITRIFIED HLW IN REPOSITORIES IN SALT, CLAY AND GRANITE. PART II: RESULTS, W. Lutze, Hahn-Meitner-Institut, Berlin, West Germany; M. Kawanishi, Abico Research Laboratory, Abico, Japan; J.A.C. Marples, Harwell Laboratory, Oxon, United Kingdom; and P. Van Iseghem, SCK/CEN, Mol, Belgium.

2:00 U6.2
COMPARISON OF SURFACE LAYERS FORMED ON SYNTHETIC BASALTIC GLASS, FRENCH R7T7 AND HMI BOROSILICATE NUCLEAR WASTE FORM GLASSES - MATERIALS INTERFACE INTERACTIONS TESTS, Michael J. Jercinovic, Stacy Kaser, Rodney C. Ewing, University of New Mexico, Department of Geology, Albuquerque, NM; and Werner Lutze, Hahn Meitner Institut, Berlin, West Germany.

2:30 U6.3
THE INTERACTION BETWEEN NUCLEAR WASTE GLASSES AND CLAY-II, P. Van Iseghem, K. Berghman and W. Timmermans, SCK/CEN, Mol, Belgium.

3:00 BREAK

3:30 U6.4
R7-T7 NUCLEAR WASTE GLASS BEHAVIOR IN MOIST CLAY: ROLE OF THE CLAY MASS/GLASS SURFACE AREA RATIO, N. Godon and E. Vernaz, CEN-Valrhô, SDHA/SEMC, Bagnols-sur-Cèze, France.

4:00 U6.5
PRODUCT CONSISTENCY LEACH TESTS OF SAVANNAH RIVER SITE RADIOACTIVE WASTE GLASSES, Ned E. Bibler, Westinghouse Savannah River Company, Aiken, SC; and John K. Bates, Argonne National Laboratory, Argonne, IL.

4:30 U6.6
THE REACTION OF SYNTHETIC NUCLEAR WASTE GLASS IN STEAM AND HYDROTHERMAL SOLUTION, W.L. Ebert and J.K. Bates, Argonne National Laboratory, Argonne, IL.

SESSION U7: POSTER SESSION
Tuesday Evening, November 28
7:00 - 10:00 p.m.
America Ballroom (W)

U7.1 ESTIMATION OF LONGEVITY OF PORTLAND CEMENT GROUT USING CHEMICAL MODELING TECHNIQUES, Stephen R. Alcorn, Mark A. Gardiner, IT Corporation, Albuquerque, NM; and William E. Coons, RE/SPEC, Inc., Albuquerque, NM.

U7.2 MODELLING OF THE EVOLUTION OF POREWATER CHEMISTRY IN A CEMENTITIOUS REPOSITORY, A. Haworth, S.M. Sharland and C.J. Tweed, UKAEA, Harwell Laboratory, Theoretical Physics Division, Oxfordshire, United Kingdom.

U7.3 A THEORETICAL STUDY OF THE EFFECT OF THE LEACH INTERVAL ON A SEMIDYNAMIC LEACH TEST, Roger D. Spence, Oak Ridge National Laboratory, Oak Ridge, TN.

U7.4 INTERACTION BETWEEN BLENDED CEMENTS AND A SULPHATE BEARING GROUND WATER, Susan L. Duerden, Peter L. Walton, and Amal J. Majumdar, Building Research Station, Watford, United Kingdom.

U7.5 (ABSTRACT WITHDRAWN)

U7.6 IMMOBILIZATION IN CEMENT OF ION EXCHANGE RESINS, Patrick Le Bescop, Pascal Bouniol and Michel Jorda, CEN, DRDD/SESD, CEN-FAR, Fontenay aux Roses, France.

U7.7 ENCAPSULATION OF RADIOIODINE IN CEMENTITIOUS WASTE FORMS, Mark Atkins and Frederik P. Glasser, University of Aberdeen, Department of Chemistry, Aberdeen, Scotland.

U7.8 EFFECT OF γ -RADIATION ON THE MICROSTRUCTURE AND MICROCHEMISTRY OF ggbfs/OPC CEMENT BLENDS, I.G. Richardson and G.W. Groves, University of Oxford, Department of Metallurgy and Science of Materials, Oxford, United Kingdom; and C.R. Wilding, UKAEA Harwell Laboratory, Materials Development Division, Oxfordshire, United Kingdom.

U7.9 HYDROGEN GENERATION IN MORTARS IMMOBILIZING WASTE CHLORIDE SALTS, Michele A. Lewis and David W. Warren, Argonne National Laboratory, Argonne, IL.

U7.10 POROSITY AND ION DIFFUSIVITY OF LATEX-MODIFIED CEMENT, T. Nishi, O. Kuriyama, M. Matsuda, K. Chino, Hitachi Ltd., Energy Research Laboratory, Hitachi, Japan; and M. Kikuchi, Hitachi Ltd., Hitachi Works, Hitachi, Japan.

U7.11 A COMPARISON OF THE BEHAVIOUR OF VITRIFIED HLW IN REPOSITORIES IN SALT, CLAY AND GRANITE. PART I: EXPERIMENTAL, L.A. Mertens, W. Lutze, Hahn-Meitner-Institut, Berlin, West Germany; J.A.C. Marples, Harwell Laboratory, Oxon, United Kingdom; and P. Van Iseghem, SCK/CEN, Mol, Belgium; E. Vernaz, CEA Valrhô, Bagnols-sur-Cèze, France.

U7.12 IN-SITU TESTING OF NUCLEAR WASTE FORMS IN A CLAY LABORATORY - RESULTS AFTER TWO YEARS CORROSION, P. Van Iseghem, W. Timmermans and B. Neerdael, SCK/CEN, Mol, Belgium.

U7.13 DISSOLUTION KINETICS OF A SIMPLE ANALOGUE NUCLEAR WASTE GLASS AS A FUNCTION OF pH, TIME AND TEMPERATURE, Kevin G. Knauss, William L. Bourcier, Kevin D. McKeegan, Celia I. Merzbacher, Son N. Nguyen, Frederick J. Ryerson, David K. Smith and Homer C. Weed, Lawrence Livermore National Laboratory, Livermore, CA.

U7.14 HYDROTHERMAL LEACHING OF R7-T7 BOROSILICATE GLASS, J. Caurel and E. Vernaz, CEN-Valrhô, SDHA/SEMC, Bagnols-sur-Cèze, France; D. Beaufort, Université de Poitiers, Laboratoire de Pétrologie des Alterations Hydrothermales, Poitiers, France.

U7.15 EFFECTS OF SURFACE-AREA-TO-SOLUTION VOLUME RATIO ON THE CHEMICAL DURABILITY OF NUCLEAR WASTE GLASSES, X. Feng, I.L. Pegg, Aa. Barkatt, P.B. Macedo, Catholic University of America, Vitreous State Laboratory, Washington, DC.

U7.16 ALTERATION OF MICROSTRUCTURE AND LEACHING PROPERTIES OF W. VALLEY REFERENCE BY HEAT TREATMENT, A.C. Buechele, X. Feng, H. Gu, and I.L. Pegg, The Catholic University of America, Vitreous State Laboratory, Washington, DC.

U7.17 PARAMETRIC EFFECTS OF GLASS REACTION UNDER UNSATURATED CONDITIONS, J.K. Bates, T.J. Gerding and D.J. Wronkiewicz, Argonne National Laboratory, Argonne, IL.

U7.18 GROWTH RATES OF ALTERATION LAYERS AND ELEMENTAL MASS LOSSES DURING LEACHING OF BOROSILICATE NUCLEAR WASTE GLASS, Tsunetaka Banba and Takashi Murakami, Japan Atomic Energy Research Institute, Ibaraki, Japan.

U7.19 CHARACTERIZATION OF HIGHLY ACTIVE WASTE GLASSES PRODUCED IN A HOT VITRIFICATION PLANT, J.P. Glatz, E. Toscano, M. Coquerelle and J. Fuger, Institute for Transuranium Elements, Commission of the European Communities, Karlsruhe, West Germany.

U7.20 THE LONG-TERM CORROSION AND MODELING OF TWO SIMULATED BELGIAN REFERENCE HIGH-LEVEL WASTE GLASSES - PART II, J. Patyn, P. Van Iseghem, W. Timmermans, SCK/CEN, Mol, Belgium.

U7.21 SIMULTANEOUS EVAPORATION OF Cs AND Tc DURING VITRIFICATION - A THERMOCHEMICAL APPROACH, H. Migge, Hahn-Meitner-Institut, Berlin, West Germany.

U7.22 THE EFFECT OF TEMPERATURE ON THE REDOX CONSTRAINTS FOR THE PROCESSING OF HIGH-LEVEL NUCLEAR WASTE INTO A GLASS WASTE FORM, Henry D. Schreiber, Charlotte W. Schreiber, Margaret W. Riethmiller and J. Sloan Downey, Virginia Military Institute, Center for Glass Chemistry, Lexington, VA.

U7.23 CALCULATION OF THE VISCOSITY OF NUCLEAR WASTE GLASS SYSTEMS, Ritesh P. Shah, E.C. Behrman and D. Oksoy, Alfred University, New York State College of Ceramics, Alfred, NY.

U7.24 CHARACTERIZATION OF MECHANICAL STRENGTHS FOR SIMULATED SOLIDIFIED HIGH LEVEL WASTE FORMS, Hiroshi Igarashi, Takeshi Takahashi, Power Reactor and Nuclear Fuel Development Corporation, Ibaraki, Japan.

U7.25 DIFFUSION OF CESIUM IN SODIUM-BOROSILICATE GLASSES USED FOR IMMOBILISATION OF NUCLEAR WASTE, E.G.F. Sengers and E.J.J.G. Janssen, N.V. Kema, R&D Division, Chemical Research Department, Et Arnhem, The Netherlands.

U7.26 ENTHALPIES OF MIXING AND INCIPIENT IMMISCIBILITY IN GLASSES IN THE SYSTEM $K_2O-SiO_2-La_2O_3$, A.J.G. Ellison and A. Navrotsky, Princeton University, Department of Geological and Geophysical Sciences, Princeton, NJ.

U7.27 GRAIN BOUNDARY INVENTORY AND UC MATRIX DISSOLUTION STUDIES ON SPENT LF FUEL, W.J. Gray, D.M. Strachan, and M.J. Apted, Battelle-Pacific Northwest Laboratory, Richland, WA.

U7.28 IDENTIFICATION OF SECONDARY PHASES FORMED DURING UNSATURATED REACTION OF UC WITH EJ-13 WATER, J.K. Bates, B.S. Tani and E. Veleckis, Argonne National Laboratory, Argonne, IL.

U7.29 INVESTIGATIONS INTO THE ELECTROCHEMICAL LEACHING BEHAVIOUR OF UO_2 PELLETS IN VARIOUS SATURATED SALT SOLUTIONS, Cl. Keiling, P.-M. Heppner and G. Marx, Free University of Berlin, Institute for Inorganic and Analytical Chemistry, Radiochemistry Division, Berlin, West Germany.

U7.30 A DEFORMATION AND THERMODYNAMIC MODEL FOR HYDRIDE PRECIPITATION KINETICS IN SPENT FUEL CLADDING, R.B. Stout, University of California, Lawrence Livermore National Laboratory, Livermore, CA.

U7.31 FLUORIDE INFLUENCE ON ZIRCALOY-CORROSION IN WATER AS A FUNCTION OF pH, TEMPERATURE AND FLUORIDE CONTENT, N.J. Uziemblo and H.D. Smith, Battelle-Pacific Northwest Laboratory, Richland, WA.

U7.32 CORROSION BEHAVIOR OF ZIRCALOY IN AQUEOUS MEDIA, Anna C. Fraker and Jonice Harris, National Institute of Standards and Technology, Gaithersburg, MD.

U7.33 POTENTIODYNAMIC POLARIZATION STUDIES OF CANDIDATE CONTAINER MATERIALS IN SIMULATED TUFF REPOSITORY ENVIRONMENTS, John A. Beavers and Neil G. Thompson, Cortez Columbus, Inc., Columbus, OH.

U7.34 MIGRATION BEHAVIOR OF URANIUM SERIES NUCLIDES IN ALTERED QUARTZ-CHLORITE SCHIST, T. Ohnuki, T. Murakami, K. Sekino, N. Yanase, H. Isobe and Y. Kobayashi, Japan Atomic Energy Research Institute, Department of Environmental Safety Research Institute, Ibaraki, Japan.

U7.35 MIGRATION OF ANIONIC SPECIES OF RADIOACTIVE COBALT THROUGH SOIL, Toshihi Ohnuki, Japan Atomic Energy Research Institute, Department of Environmental Safety Research, Ibaraki, Japan; and David Robertson, Battelle-Pacific Northwest Laboratory, Chemical Science Department, Richland, WA.

U7.36 STUDY ON RELATION BETWEEN MIGRATION BEHAVIORS AND CHEMICAL FORMS OF COBALT, Shinzo Ueta, Naka Nuclear Development Center of Mitsubishi Metal Corporation, Ibaraki, Japan; and Naotake Katoh, Kogakuin University, Tokyo, Japan.

U7.37 GRIMSEL COLLOID EXERCISE, C. Degueldre, Paul Scherrer Institute, Villigen, Switzerland.

U7.38 AUTHIGENIC CLAY MINERALS IN THE RUSTLER FORMATION; WIPP SITE AREA, NEW MEXICO, Douglas G. Brookins, University of New Mexico, Department of Geology, Albuquerque, NM; Steven J. Lambert, Sandia National Laboratories, Albuquerque, NM; and David B. Ward, University of New Mexico, Albuquerque, NM.

U7.39 IN SITU OBSERVATION OF THE ALPHA/BETA-CRISTOBALITE TRANSITION USING HIGH VOLTAGE ELECTRON MICROSCOPY, Annemarie Meike, Lawrence Berkeley Laboratory, Materials and Chemical Sciences Division, Berkeley, CA; and William Glassley, Lawrence Livermore National Laboratory, Earth Sciences Division, Livermore, CA.

U7.40 ESTIMATION OF LONG-TERM DURABILITY OF BENTONITE FROM THE THERMAL HISTORY OF MURAKAMI DEPOSIT, JAPAN, G. Kamei, T. Arai, Y. Yusa, N. Sasaki, Power Reactor and Nuclear Fuel Development Company, Ibaraki, Japan; H. Takano, Dia Consultants Company, Tokyo, Japan.

U7.41 DIFFUSION OF SODIUM AND COPPER IN COMPACTED SODIUM BENTONITE AT ROOM TEMPERATURE, A. Muurinen, K. Uusheimo and M. Olin, Technical Research Centre of Finland, Reactor Laboratory, Espoo, Finland.

U7.42 THERMAL BEHAVIOUR OF BACKFILL MATERIAL FOR A NUCLEAR FUEL WASTE DISPOSAL VAULT, R.N. Yong and A.M.O. Mohamed, McGill University, Geotechnical Research Centre, Montreal, Canada; and S.C.H. Cheung, Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment, Pinawa, Canada.

U7.43 A COUPLED CHEMICAL-MASS TRANSPORT SUBMODEL FOR PREDICTING RADIONUCLIDE RELEASE FROM AN ENGINEERED BARRIER SYSTEM CONTAINING HIGH-LEVEL WASTE GLASS, B.P. McGrail, D.W. Engel, M.J. Apted, A.M. Liebetrau, Battelle-Pacific Northwest Laboratory, Richland, WA; and N. Sasaki, Power Reactor and Nuclear Fuel Development Corporation, Ibaraki-ken, Japan.

U7.44 (ABSTRACT WITHDRAWN)

SESSION U8 / SPENT FUEL PERFORMANCE

Chair: Lars Werme

Wednesday Morning, November 29
America North (W)

8:00 U8.1
ACTINIDES CHEMISTRY AND SPENT FUEL PERFORMANCE STUDIES, G. Choppin

8:30 U8.2
OXIDATION OF UO_2 FUEL BY RADICALS FORMED DURING RADIOLYSIS OF WATER, S. Sunder, D.W. Shoesmith, Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment, Geochemistry and Waste Immobilization Division, Pinawa, Canada; H. Christensen, Studsvik Energiteknik AB, Nyöping, Sweden; N.H. Miller and M.G. Bailey, Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment, Geochemistry and Waste Immobilization Division, Pinawa, Canada.

9:00 U8.3
CONSTRAINTS BY EXPERIMENTAL DATA FOR MODELING OF RADIONUCLIDE RELEASE FROM SPENT FUEL, B. Grambow, Hahn-Meitner-Institut Berlin, Berlin, West Germany; L.O. Werme, SKB, Stockholm, Sweden; R. Forsyth, Studsvik Energiteknik AB, Nyköping, Sweden; and J. Bruno, Royal Institut of Technology, Department of Inorganic Chemistry, Stockholm, Sweden.

9:30 U8.4
STATISTICAL MODEL FOR GRAIN BOUNDARY AND GRAIN VOLUME OXIDATION KINETICS IN UO_2 SPENT FUEL, R.B. Stout, H.F. Shaw, University of California, Lawrence Livermore National Laboratory, Livermore, CA; and R.E. Einziger, Battelle-Pacific Northwest Laboratory, Richland, WA.

9:45 U8.5
MEASUREMENT OF SOLUBLE NUCLIDE DISSOLUTION RATES FROM SPENT FUEL, Charles N. Wilson, Battelle-Pacific Northwest Laboratory, Richland, WA.

10:00 BREAK

SESSION U9: CONTAINER AND FUEL CLADDING STUDIES

Chair: Sham Sunder

Wednesday Morning, November 29
America North (W)

10:30 U9.1
THEORETICAL MODELING OF CREVICE AND PITTING CORROSION PROCESSES IN RELATION TO CORROSION OF RADIOACTIVE WASTE CONTAINERS, John C. Walton, Idaho National Engineering Laboratory, Idaho Falls, ID.

11:00 U9.2
CORROSION PRODUCT IDENTIFICATION AND RELATIVE RATES OF CORROSION OF CANDIDATE METALS IN AN IRRADIATED AIR-STEAM ENVIRONMENT, Donald T. Reed, V. Swayambunathan, Argonne National Laboratory, Argonne, IL; and Richard A. Van Konynenburg, Lawrence Livermore National Laboratory, Yucca Mountain Project, Livermore, CA..

11:15 U9.3
A STUDY ON FABRICATION TECHNOLOGY OF CERAMIC OVERPACK - A CONCEPTUAL DESIGN AND FABRIAC-TION OF A FULL SCALE CERAMIC OVERPACK, T. Teshima, Y. Karita, NGK Insulators, Ltd., Nagoya, Japan; H. Ishikawa and N. Sasaki, Power Reactor and Fuel Development Corpora-tion, Ibaraki, Japan.

11:30 U9.4
AN INTERPRETATION OF THE HIGH-STRESS, LOW-TEMPERATURE CRACKING OF ZIRCALOY-4 SPENT FUEL CLADDING, H.D. Smith, Battelle-Pacific Northwest Laboratory, Richland, WA.

11:45 U9.5
A CORROSION LOCALIZATION ASSESSMENT OF THE MILD STEEL USED FOR NUCLEAR WASTE PACKAGE, Masatsune Akashi, Ishikawajima-Harima Heavy Industries Company, Ltd., Research In-stitute, Tokyo, Japan.

SESSION U10/T4: JOINT SESSION
SIZING AND SCALING EFFECTS

Chairs: Jim Kaufman and Virginia Oversby
Wednesday Afternoon, November 29
America North (W)

1:30 *U10.1/T4.1
FRACTAL STRUCTURE AND DYNAMICS OF TWO FLUID FLOW IN POROUS MEDIA, Jens Feder, University of Oslo, Department of Physics, Oslo, Nor-way.

2:00 U10.2/T4.2
NUMERICAL AND ANALYTICAL MODELS OF TRANSPORT IN POROUS CEMENTITIOUS MATERIALS, Edward J. Garboczi and Dale P. Bentz, National In-stitute of Standards and Technology, Build-ing Materials Division, Gaithersburg, MD.

2:15 U10.3/T4.3
SIZING REQUIREMENTS FOR FLOW-THROUGH GEOCHE-MICAL TESTS: THEORETICAL CONSIDERATIONS, MODEL RESULTS, AND IMPLICATIONS FOR THE INTERPRETATION OF TEST DATA, J.D. Hoover and E.C. Thornton, Westinghouse Hanford Company, Richland, WA.

2:30 U10.4/T4.4
A LAGRANGIAN ACTIVE TRANSPORT SIMULATOR WITH MULTIPLE PATHS AND STATIONARY-STATES: CONCEPTS, IMPLEMENTATION AND VERIFICATION, R.B. Knapp, University of California, Law-rence Livermore National Laboratory, Earth Sciences Department, Livermore, CA.

2:45 BREAK

3:15 U10.5/T4.5
FRACTAL CHARACTERISTICS OF FRACTURE NETWORKS AND FLUID MOVEMENT IN ROCK, Christopher C. Barton, U.S. Geological Survey, Department MS 913, Denver, CO.

3:45 U10.6/T4.6
FLOW TO WELLS IN FRACTURED ROCK WITH FRACTAL STRUCTURE, Jim Polek, Kenzi Karasaki and Jane Long, Lawrence Berkeley Laboratory, Berkeley, CA; and John Barker, British Geological Survey, Oxfordshire, United Kingdom.

4:00 U10.7/T4.7
ANISOTROPIC SCALING OF INTERFACES IN POROUS MEDIA, Miguel A. Rubio, Haverford College, Department of Physics, Haverford, PA; and UNED, Madrid, Spain; Andrew Dougherty, Haverford College, Department of Physics, Haverford, PA; and Jerry P. Gollub, Haver-ford College, Department of Physics, Haver-ford, PA; and University of Pennsylvania, Philadelphia, PA.

4:15 U10.8/T4.8
SIZING AND SCALING REQUIREMENTS OF A LARGE-SCALE PHYSICAL MODEL FOR CODE VALIDATION, R. Khaleel, T. LeGore and J.D. Hoover, West-inghouse Hanford Company, Richland, WA.

4:30 U10.9/T4.9
PERFORMANCE OF CONCRETE BARRIERS IN RADIOAC-TIVE WASTE DISPOSAL IN THE UNSATURATED ZONE, John C. Walton and Mark D. Otis, ID National Engineering Laboratory, Idaho Falls, ID.

SESSION U11: NEAR-FIELD STUDIED AND
PERFORMANCE ASSESSMENT

Chair: Henry Shaw
Thursday Morning, November 30
America North (W)

8:30 U11.1
LEACHING/MIGRATION OF UO₂-FUEL IN COMPACTED BENTONITE, Y. Albinsson, G. Skarnemark, M. Skålberg, Chalmers University of Technology, Department of Nuclear Chemistry, Göteborg, Sweden; R. Forsyth, Studsvik AB, Nyköping, Sweden; B. Torstenfelt, ABB-Atom, Västerås, Sweden; L. Werme, Swedish Nuclear Fuel and Waste Management, Stockholm, Sweden.

9:00 U11.2
MODELLING THE IN SITU PERFORMANCE OF BENTONITE-SAND BUFFER, H.S. Radhakrishna, K.-C. Lau, Ontario Hydro Research Division, Toronto, Canada; B.H. Kjartanson and S.C.H. Cheung, Atomic Energy of Canada Ltd., Whiteshell Nuclear Research Establishment, Pinawa, Canada.

9:15 U11.3
THE EFFECT OF CRACKS ON DIFFUSIVE MASS TRANSPORT THROUGH A CLAY BARRIER, Nava C. Garisto and Frank Garisto, Atomic Energy of Canada Ltd., Whiteshell Nuclear Research Establishment, Pinawa, Canada.

9:30 U11.4
FINAL DISPOSAL OF CEMENTITIOUS WASTE FORMS IN THE SWEDISH REPOSITORY FOR REACTOR WASTE (SFR), Jan S. Carlsson, Swedish Nuclear Fuel and Waste Management Company, (SKB), Stockholm, Sweden.

9:45 U11.5
MASS TRANSFER IN WATER-SATURATED CONCRETES, Alan Atkinson, Peter A. Claisse, Nicola M. Everitt, Andrew W. Harris and Alan K. Nickerson, Harwell Laboratories, Materials Development Division, Oxon, United Kingdom.

10:00 BREAK

10:30 U11.6
COUPLED FLOW OF HEAT AND MASS IN BARRIER MATERIALS AND ITS SIGNIFICANCE, S.C.H. Cheung, Atomic Energy of Canada Ltd., Whiteshell Nuclear Research Establishment, Pinawa, Canada.

10:45 U11.7
EFFECTIVE DIFFUSIVITY OF CARBON DIOXIDE AND IODINE THROUGH "G TUNNEL TUFF", Tevfik Bardakci, Franklin G. King and Maung Sein, North Carolina A&T State University, Greensboro, NC.

11:00 U11.8
¹⁴C TRANSPORT IN A PARTIALLY SATURATED, FRACTURED, POROUS MEDIUM, W. B. Light, P.L. Chambré, W.W.-L. Lee and T.H. Pigford, University of California, Berkeley, Department of Nuclear Engineering and Lawrence Berkeley Laboratory, Berkeley, CA.

11:15 U11.9
THE APPLICATION OF A COUPLED CHEMICAL TRANSPORT MODEL IN A TRIAL ASSESSMENT OF DEEP DISPOSAL OF LOW AND INTERMEDIATE LEVEL RADIOACTIVE WASTE, Steve Liew, Vea Economides, Adrian Dawes and David Read, WS Atkins Engineering Sciences, Epsom, United Kingdom.

11:30 U11
ANALYSIS OF MASS TRANSPORT IN AN ENGINEERED BARRIERS SYSTEM FOR THE DISPOSAL OF USED NUCLEAR FUEL, Nava C. Garisto and Dennis M. LeNeveu, Atomic Energy of Canada Ltd., Whiteshell Nuclear Research Establishment, Pinawa, Canada.

11:45 U11.11
ATTEMPTED VERIFICATION OF MATRIX DIFFUSION IN GRANITE BY MEANS OF NATURAL DECAY SERIES DISEQUILIBRIA, W.R. Alexander, Paul Scherrer Institute, Villigen, Switzerland; I.G. McKinley, NAGRA, Baden, Switzerland; A.B. MacKenzie, R.D. Scott, SURRC, Glasgow, Scotland; and J. Meyer, Min.-pet. Institute, University of Berne, Berne, Switzerland.

U1.1

NUCLEAR WASTE IMMOBILIZATION IN CEMENT-BASED MATERIALS: OVERVIEW OF FRENCH STUDIES, Pascal Bouniol, Eliane Revertegate, Jean Oliver, Philippe Gegout, Michel Jorda, Rosemarie Atabek, C.E.A., DRDD/SESD, CEN/FAR, 92265 Fontenay aux Roses Cedex.

Cement-based materials are currently used in France for solidification of highly-salt-laden concentrates and ashes and for embedment of solid wastes. In the first case, the waste forms are considered to be "homogeneous" and are submitted to leach tests to evaluate radionuclide behavior. In the case of solid wastes, the whole package is regarded as a "heterogeneous waste form" and radionuclide confinement is ensured by an outer cover of pure mortar and measured using diffusion cells. In both cases the durability function is devolved to the concrete container and the waste package must abide by ANDRA specifications for Low Level Waste disposal.

An overview of the different problems to be solved is presented. Examples of cement-based matrices used to immobilize concentrates (containing F⁻, Cl⁻, SO₄²⁻, NO₃⁻, Na⁺ and trace species) and phosphate ashes are given in relation to cement chemistry. It was demonstrated that, in the same cases, phosphate may improve waste form behavior. Experimental studies, undertaken to assess concrete durability obviously indicated that pH is the starting parameter of chemical degradation reactions. Ion nature (such as Cl⁻, SO₄²⁻, HCO₃⁻/CO₃²⁻) and concentration are secondary factors which only act on kinetics.

It was found that slag and fly ash cement has a better cesium retention ability and stronger resistance to chloride and sulfate attack than portland cement.

U1.2

EFFECT OF CURING TEMPERATURE ON THE PROPERTIES OF CEMENTITIOUS WASTE FORMS^(a). Ryan D. Lokken, John W. Shade, and Paul F. C. Martin, Pacific Northwest Laboratory^(b) Richland, WA 99352.

Current plans at Hanford for disposing various low-level liquid wastes include solidification using cementitious materials. This process, known as grouting, involves mixing liquid wastes with a blend of cementitious materials and pumping the resultant slurry to lined, underground concrete vaults. The total volume of the vaults is approximately 1.4 million gallons. As the grout slurry begins to solidify and harden, the temperature increases due to the exothermic hydration reactions. Adiabatic temperature increases of greater than 70°C have been measured in the laboratory. With a starting waste temperature of 45°C, the temperature of the grout in the vaults may approach 115°C.

A study is currently underway to assess the effects of long-term, high-temperature curing on the properties of grouts produced with simulated double-shell slurry feed (DSSF) waste. The waste was a salt solution containing high concentrations of sodium nitrate, sodium aluminate, and sodium hydroxide. The solids blend consisted of 47 wt% class F fly ash, 47 wt% ground blast furnace slag, and 6 wt% type I/II portland cement. The solids were mixed with the liquid waste at a ratio of 1080 g/L. Samples of laboratory-produced grout samples, cured at 75, 85, 95, 120, and 150°C, and samples cured in a 4000-gallon monolith, were characterized by scanning electron microscopy, x-ray diffraction, and thermal analysis to determine the effects of curing temperature on leachability, microstructure, phase compositions, and strength. Results of these activities are discussed.

(a) Work supported by the U.S. Department of Energy under Contract DE-AC-76RLO 1830.

(b) Operated for the U.S. Department of Energy by Battelle Memorial Institute.

U1.3

BEHAVIOR OF CONCRETE AS A BARRIER MATERIAL FOR NUCLEAR WASTE DISPOSAL R. J. James and Y. R. Rashid, ANATECH Research Corp., P.O. Box 9165, La Jolla, CA 92038.

A current method for disposal of nuclear waste is the immobilization of the waste in cement-based grout and burial in reinforced concrete vaults. The concrete vault provides the containment barrier to prevent leaching into the

environment. Because of heat generation in the waste, the concrete is subjected to elevated temperatures for the extent of the vault life. Under these conditions of elevated temperatures and long hold times, the effects of creep and cracking in concrete play a significant role in determining the structural and barrier integrity of the containment structure. Significant amounts of compressive strain due to creep in thermally loaded, confined structures may lead to split cracking due to the Poisson effect. If thermal gradients are present, cracking due to local bending may occur. In addition, and more importantly, for temperatures above 150 °F, the elastic modulus of concrete degrades with time even at constant temperature due to thermally activated damage. Since the stress due to thermal loads is proportional to the modulus, this requires continual redistribution of load that may lead to additional cracking.

This paper examines cracking in concrete as a means for evaluating long term functional requirements under barrier applications for nuclear waste disposal. A material model for concrete at elevated temperatures, including cracking, thermal creep, and stiffness degradation, has been developed based on available experimental data. Application of this model to underground, reinforced concrete structures under thermal loads will demonstrate the importance of creep and stiffness degradation in the structural design for barrier protection under extended life at elevated temperatures. The importance of capturing the correct temperature distributions and the thermal history of the structure in the analysis will also be demonstrated.

U1.4

GROUTS AND CONCRETES FOR THE WASTE ISOLATION PILOT PROJECT (WIPP). Lillian D. Wakeley, U.S. Army Engineer Waterways Experiment Station, P.O. Box 631, Vicksburg, MS 39181-0631, USA

The Structures Laboratory of the U.S. Army Engineer Waterways Experiment Station has conducted research on cement-based composites for the Waste Isolation Pilot Project (WIPP) since 1977, in cooperation with Sandia National Laboratories. Field testing requirements guided initial development of grouts. Concurrent and later laboratory studies explored the chemical stability and probable durability of these mixtures. Beginning in 1985, a series of small-scale seal performance tests at the WIPP prompted development of an expansive salt-saturated concrete. Important lessons learned from this ongoing work include: (1) carefully tailored mixtures can tolerate phase changes involving Ca, Al, and SO₄, without loss of structural integrity; (2) handling and placement properties are probably more crucial to the mixtures than is exact chemistry; and (3) for the environment of a geologic repository, demonstrated chemical durability will be the best indicator of long-term performance.

U2.1

ASSESSMENT OF THE PERFORMANCE OF CEMENT BASED COMPOSITE MATERIAL FOR RADIOACTIVE WASTE IMMOBILIZATION. M. Atkins, J. Cowie, F.P. Glasser, T. Jappy, A. Kindness and C. Pointer, Dept. of Chemistry, University of Aberdeen, Neston Walk, Old Aberdeen, AB9 2UB, Scotland.

The problem of predicting the future performance of cement-based systems is complicated by a poor understanding of the behaviour of cement systems at long ages, as well as of the complex interactions which can occur between cement and waste components - active as well as inactive - and with cement blending agents including fly ash, glassy slags and natural pozzolans. The progress achieved in developing a predictive capability is reviewed. Considerable success has been achieved in modelling the chemically-related features of cement based systems in terms of pH, E_h, and of element partition between solid and aqueous phases. The behaviour of model radwaste elements - iodine and uranium - has been studied in depth and indicate that both sorption and precipitation occur. U(VI), in particular, forms solubility-limiting compounds e.g. B uranophane. But in general, presently-available data are inadequate to predict many

cement-waste stream interactions, even for the inorganic constituents; future progress in modelling is likely to rely heavily on additions to the data base.

The repository environment will also condition chemical exchanges in cement-based systems. Progress is being made in predicting the impact of ground water components - Cl^- , SO_4^{2-} , CO_2 - on the performance of cement systems.

U2.2

DURABLE CONCRETE FOR A WASTE REPOSITORY - MEASUREMENT OF IONIC INGRESS. R.F. Feldman and J.J. Beaudoin, Institute for Research in Construction, National Research Council, Ottawa, Canada; and K.E. Philipose, Waste Management Systems, Atomic Energy of Canada Limited, Chalk River, Ontario, Canada, K0J 1J0.

A waste repository, labelled Intrusion Resistant Underground Structure (IRUS), for the belowground disposal of low level radioactive waste, is planned at Chalk River Nuclear Laboratories. It relies greatly on the durability of concrete for the required 500 years service life. A research program based on laboratory testing to design a durable concrete and to predict its useful engineered service life is in progress.

It has been established that the degradation of the concrete will depend on the rate of ingress of corrosive agents - chlorides and sulphate ions and CO_2 . Twenty six formulations were developed to create various types and qualities of concrete, and to study their behaviour in different site environmental conditions. A total of 1000 concrete and 500 cement paste specimens with composition similar to the concrete binder are being exposed to 25 different combinations of the corrosive agents at 20°C and 45°C. Procedures to measure the ionic profiles and to determine the kinetics of diffusion of the ions in the various concretes have been developed. These incorporate modifications to SEM and EDXA techniques. Initial results from these measurements will be presented and discussed in terms of pore structure and permeability parameters of the concrete.

U2.3

LOGNORMAL SIMULATION OF PORE EVOLUTION DURING CEMENT HARDENING. D. Shi, W. Ma, and P. W. Brown, Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802.

Many properties of cement-based systems are determined by the pore size distribution. Our capability to predict such properties depends on our capability to predict pore size distributions, given some basic characteristics of the cement matrix, in terms of materials chemistry, preparation and processing.

Preliminary work has been done to simulate the pore evolution during hardening of cement paste, based on a five-parameter lognormal model of size distribution of pores in hardened cement pastes. For cement pastes of different ages but otherwise identical, the pore size distributions may be reduced to a single, self-similar distribution curve, in terms of a dimensionless size which is the pore diameter divided by the median pore diameter. The location parameter, μ , is indicative of the curing time, while the shape parameter, σ , may be related to other factors, such as water-to-cement ratio and curing temperature.

This model may enable us to quantify the relationships among the pore size distribution of cement paste, the curing time, the curing temperature, and the water-to-cement ratio. Therefore, prediction of the pore size distribution of cement pastes based on a given set of curing conditions (time, temperature, water-to-cement ratio) becomes possible. Furthermore, this model may help predict properties dependent on pore structure, such as permeability and strength of hardened cement pastes, by relating such properties to parameters characteristic of the pore size distribution, μ and σ , rather than to the entire distribution of sizes.

U2.4

MECHANISTIC MODEL FOR THE DURABILITY OF CONCRETE BARRIERS EXPOSED TO SULPHATE-BEARING GROUNDWATERS Alan Atkinson and John A. Hearne, Materials Development Division, Building 429, Harwell Laboratory, Oxon, OX11 0RA, UK

Concretes are favoured materials for the construction of radioactive waste repositories in disposal strategies adopted by many countries. Their durability as structural materials and as physical barriers to radionuclide migration can be limited by their reaction with sulphate-bearing groundwater. In such a situation the concrete degrades by sulphate penetrating the concrete where it reacts with the hydrated cement to form expansive reaction products that cause stress and eventual disruption.

Data obtained from old concretes and accelerated tests have enabled an empirical relationship to be derived to describe the rate of this degradation, but this relationship is not founded on the mechanism of degradation itself. In the work described here the individual contributions to the mechanism have been examined in appropriate experiments in which diffusion, reaction and expansion have been quantified. These results have been integrated into a simple overall model in which the criterion for degradation is the accumulation of a critical quantity of stored elastic energy in the reaction zone. The results of this mechanistic model are in good quantitative agreement with those of the empirical model and enable extrapolations to be made to different concretes, cements and sulphate-bearing groundwaters.

U3.1

THE SOLUBILITY AND SORPTION OF URANIUM(VI) IN A CEMENTITIOUS REPOSITORY. Brownsword, M., Buchan, A. B., Ewart, F. T., McCrohon, R., Ormerod, G. J., Smith-Briggs, J. L. and Thomason, H. P. Chemistry Division, Harwell Laboratory, Oxfordshire, OX11 0RA, UK.

In the context of UK radioactive waste disposal, uranium and its daughters have been shown to make an important contribution to the overall risk assessment. The aqueous chemistry of uranium in the near-field is complicated by the multiple valency states that may exist, under these particular conditions of pH and redox potential, and by the possible formation of solid alkali and alkaline earth uranates. The research programme in support of the repository safety assessment carries out studies of the aqueous chemistry of uranium that include the aqueous speciation, characterisation of the solid phases that are in equilibrium with the repository water, measurement of the solubility of these solids and determination of the sorption onto the major near field substrates.

The paper describes some recent results of these experimental measurements and includes a study of the composition of the sodium and calcium uranates formed, under the conditions applicable to the near-field of a cementitious repository and the determination of their solubilities. Measurements of the sorption of uranium(VI) onto a slag cement and onto specimens of the same slag cement, aged artificially using hydrothermal and leaching treatments are also described.

U3.2

SPECIATION OF Pu(VI) IN NEAR-NEUTRAL TO BASIC SOLUTIONS VIA LASER PHOTOACOUSTIC SPECTROSCOPY. S. Okajima, J. V. Beitz, J. C. Sullivan, and D. T. Reed, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439.

The high sensitivity technique of laser photoacoustic spectroscopy (LPAS) in combination with optical absorption spectroscopy was applied to the study of Pu(VI) speciation in systems important to their migration in the environment. Emphasis was on the hydroxo species formed although additional information on other groundwater-relevant ligands was obtained. Stability constants and speciation observed, based on the spectra obtained, are reported.

*This work was funded in part by developmental funds within Argonne National Laboratory and under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under contract number W-31-109-ENG-38.

U3.3

MODELLING STUDIES OF SORPTION IN THE NEAR FIELD OF A CEMENTITIOUS REPOSITORY A. Haworth, S.M. Sharland and C.J. Tweed, Theoretical Physics Division, Harwell Laboratory, UKAEA, Oxfordshire OX11 0RA, U.K.

Current plans for a low- and intermediate-level radioactive waste repository in the UK include a cement backfill. Sorption of radionuclides on to cement is an important process in limiting the aqueous concentrations in the near-field and is, therefore, likely to be of importance in constructing the safety case for a repository. Most experiments and modelling use a distribution coefficient approach. This quantifies sorption on to a material in terms of a simple linear isotherm, but does not take into account effects such as saturation of sites. The use of distribution coefficients for conditions other than those at which they were obtained may not be valid.

In this paper, we describe modelling studies of radionuclide transport through a cementitious backfill, based on a mechanistic interpretation of the processes. For this modelling we use the geochemical code PHREEQE and the coupled ionic transport/chemical equilibria code CHEQMATE. The predictions of the modelling will be compared with experimental data from various sorption experiments on cement.

U3.4

Evidence of long distance transport of natural colloids in a crystalline rock groundwater. W.R. Alexander, R. Bruetsch, C. Degueldre, Paul Scherrer Institute, 5232 Villigen, Switzerland and B. Hofmann, USGS, Denver CO 80225, USA.

The transport of radiocolloids (radionuclides in association with colloids) from the near field, through the geosphere, is recognised as a potential problem within current Swiss safety analysis models. Natural colloids could enhance doses to the biosphere by sorbing radionuclides released from a repository and then moving through fractured rock with minimal retardation, either by sorption on the rock or by filtration through the fracture infill.

NAGRA has therefore initiated a programme of research to study various aspects of colloid transport in both crystalline and sedimentary formations and, in this article, the results of a recent project are reported. An earlier study of the groundwater system of the Krunkebach uranium prospect, Black Forest, West Germany, produced evidence of long distance transport of natural particles (> 450 nm nominal pore size filters) in the crystalline groundwaters. Newly produced samples which includes colloidal material (filters with nominal pore sizes in the range of 15-1000 nm were utilised) have been subjected to semi-quantitative analyses and the results have confirmed the earlier work on larger particles.

Stable isotope data implies that the groundwater recharge area lies within a gneiss formation some 5 km away from the uranium prospect. Colloid samples were collected within the prospect (at a depth of 240 m) and the Mg, Ti, Y and Zr contents of these colloids were found to be characteristic of the near by gneiss rather than the granite body which hosts the prospect.

The implications of such natural colloid generation and long distance transport are examined with respect to Swiss concepts for a crystalline rock radwaste repository.

U3.5

ANALYTIC STUDIES OF COLLOID TRANSPORT.

Y. Hwang, T. H. Pigford, P. L. Chambré, and W. W.-L. Lee, Department of Nuclear Engineering and Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720.

There is evidence that radionuclides move as colloids at the Nevada Test Site. Because of their ubiquitous nature, fast movement, and low retardation, it is important to study colloid transport in association with the planned repository at Yucca Mountain. We present some analytic studies of colloid transport in fractured porous rock, considering filtration as well as interaction between colloids and dissolved radionuclides.

Colloids of radioactive material can be expected in ground water in a geologic repository. Radioactive species released from a waste solid can appear as colloids by chemical reaction of the dissolved species with container material, by reduction in solubility and precipitation from cooling a near-saturated solution, from a change in the redox potential, or by sorption of a radioactive solute onto colloids that are already present in the ground water. Here we include "pseudocolloids" as colloids.

Colloids can transport radionuclides through geologic media at rates that can differ considerably from the solute transport rates. Current approaches for predicting colloid transport focus on the transport of the colloid itself and may not be adequate for predicting the long-term behavior of geologic repositories. Colloids of a given species can be expected to establish some kind of interaction with the solute of that species. Some colloids are likely to exhibit solubility, similar to that of a consolidated solid. Others, such as pseudocolloids, may exhibit sorption equilibrium between the solute concentration and the concentration of that species sorbed on the colloid. In either case, the interaction between the solute and colloid can be important in predicting long-term transport. Moreover, hydrogeologic transport through a fracture is likely to be accompanied by diffusion of solute into and out of the rock matrix surrounding the fracture.

We develop and solve differential equations for the interactive transport of colloids and solute. We discuss the analytic solutions and illustrate the importance of the various processes in colloidal transport, as steps towards developing more comprehensive models of colloid transport of radioactive species.

U4.1

THE MICROSTRUCTURE OF ggbfs/OPC HARDENED CEMENT PASTES AND SOME EFFECTS OF ELEVATED TEMPERATURE LEACHING. I.G. Richardson, S.A. Rodger and G.W. Groves, Department of Metallurgy and Science of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, U.K.

Ground granulated blast-furnace slag (ggbfs)/Ordinary Portland cement (OPC) blends are possible materials for use in intermediate and low-level radioactive waste repositories. The microstructural development in neat OPC is reviewed. The effect of increasing the loading of ggbfs on the composition and microstructure of the hardened paste has been examined by a number of techniques, including transmission electron microscopy. The implications for performance are discussed. A ggbfs/OPC 9:1 blend which had been exposed, after normal hydration to aqueous leaching at 105°C was also examined. Marked changes in the microstructure and composition were observed.

U4.2

THE EFFECTS OF TEMPERATURE ON THE LEACHING BEHAVIOR OF CEMENT WASTE FORMS Mark Fuhrmann, Richard Pietrzak, John Heiser III, Eena-Mai Franz and Peter Colombo, Nuclear Waste Research Group, Brookhaven National Laboratory, Upton, NY, 11973.

The leaching mechanisms of simulated low-level radioactive waste forms are being determined as support for development of an accelerated leach test. Two approaches are being used: (1) comparisons of leaching data with results of a model that describes diffusion from a finite cylinder, and (2) observation of the leaching process at temperatures between 20°C and 65°C. To provide results that can be used for modeling, leaching at elevated temperatures must change neither the leaching mechanism nor the structural controls of leaching such as the porosity. Releases of cesium-137, strontium-85, calcium, sodium and potassium from plain portland cement, cement containing sodium sulfate and cement

containing incinerator ash have been determined under a variety of experimental conditions. To avoid experimental artifacts that could be misinterpreted as a release mechanism, minimal concentrations of ions in the leachate are necessary. Diffusion was observed to proceed without suppression when elemental concentrations in the leachate were less than 25 mg/L. Data from the leach tests were compared to model results for diffusion from the finite cylinder. While much of the data appears to be diffusion controlled, notable exceptions are cesium and sodium leached from cement/ash waste forms. For all samples activation energies ranging between 6 and 11 Kcal/mole have been calculated from the relationship of the effective diffusion coefficient to increasing temperature, close to the expected value of 5 Kcal/mole for diffusion. Solid phase analysis was performed to further examine the structural and mineralogical controls on leaching.

U4.3

THERMODYNAMIC MODELING OF CEMENTITIOUS WASTE FORM/GROUNDWATER INTERACTION AS A TOOL FOR LONG-TERM PERFORMANCE ASSESSMENT. Louise J. Criscenti and R. Jeff Serne, Pacific Northwest Laboratory, Richland, Washington 99352.

Experiments (i.e., static, modified ANS 16.1) have been conducted to study the leaching of elements from cementitious waste forms in groundwater. These experiments are completed in a short time period (150 days) and chemical equilibrium between the groundwater and waste form may not be achieved. Thermodynamic models can be used to determine if equilibrium between the waste form and groundwater has been established.

A conceptual model for the chemical interaction between a cementitious waste form and groundwater was developed and used with the MINTEQ computer code to predict the leachate compositions and solid phase assemblages that should be observed in several leaching experiments. The conceptual model includes (1) a modal analysis of the phases present in hydrated cement, (2) the chemical composition of the groundwater, and (3) a list of solid phases that may precipitate when the cement and groundwater react. To assist in developing the chemical model, MINTEQ calculations were performed on various leachate compositions from laboratory experiments to determine potential solubility controls. Once it can successfully predict the experimental results, the model can be used to investigate the long-term performance of a waste form.

The calculations indicate that the amount of carbonate present in the groundwater is a major factor influencing the stability of a waste form. Calculations using various partial pressures of CO₂ will be compared.

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U4.4

WASTE GROUT LEACH TESTS: PURSUIT OF MECHANISMS AND DATA FOR LONG-TERM PERFORMANCE ASSESSMENT. R. Jeff Serne, Pacific Northwest Laboratory, P.O. Box 999 K6-81, Richland, WA 99352.

At Hanford low-level liquid nuclear waste is being mixed with cementitious forming materials (grout) to form solid monoliths. Prior to grouting each liquid waste, a performance assessment must be performed to evaluate the long-term environmental impact. These predictions rely upon a diffusion controlled conceptual release model and short-term laboratory leach data on small grout samples. This paper describes size scale-up and inventory scale-up experiments that evaluate whether diffusion does in fact control the release of radionuclides (e.g., ¹²⁹I, ⁹⁹Tc) and regulated chemicals (e.g., NO₂, NO₃, Se, Cr and F).

Size-scale up leach tests on cylindrical grout specimens (3.2cm dia.x3.2cm L to 30.4cm dia.x30.4cm L) were performed

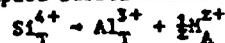
to evaluate whether leach rates follow the S/V dependency (geometric surface area to volume ratio) predicted by diffusion theory. After 200 days of leaching, species such as ⁹⁹Tc, NO₂, NO₃, Cr, Mo and Na show similar leach rates at all specimen sizes. However, the data suggest that simple diffusion theory (semi-infinite or finite source) is a less accurate predictor of observed leach rates than empirical relationships (see Cote and Constable 1987) that account for wash off, wash out and diffusion.

By changing the inventory of contaminants present in a waste form one can check whether diffusion or solubility processes appear to control leaching. Three sets of leach tests where ⁹⁹Tc, ¹²⁵I and Se were varied from (1X, 10X and 100X) were performed. Results to date suggest 1 leaching follows diffusion controlled release while Tc and Se are less well behaved (i.e., obey neither simple theory).

U5.1

THERMODYNAMICS OF GLASSES FOR NUCLEAR WASTE DISPOSAL. Alexandra Navrotsky, Department of Geological and Geophysical Sciences, Princeton University, Princeton, NJ 08544

Glasses containing nuclear waste typically have 5-10% or more of cations of high charge which perturb the aluminosilicate framework. Calorimetric studies of coupled substitutions



show the following trends. Greatest glass stabilization occurs when M is monovalent and large (e.g. Cs⁺), with thermodynamic stability decreasing with increasing z/r of M. For small alkaline earths (e.g. Mg²⁺) positive heats of mixing and a tendency toward clustering or unmixing develops. For cations of higher charge (e.g. La³⁺, Zr⁴⁺, Nb⁵⁺, Mo⁶⁺) this tendency is accentuated. Clustering on a microscopic scale implies that the local environment of these cations is independent of their concentration; the activity of the oxide component is virtually constant and relatively high and the system behaves more as a mechanical mixture than as a true solid solution. For consideration of the long-term stability, both kinetic and thermodynamic, of a waste-loaded glass, the relatively high thermodynamic activity of M-containing oxide implies a relative destabilization. However, because clustering may be pervasive, and only the volume fraction of the clusters changes with concentration of oxide, the reactivity of the waste form may be relatively insensitive to the degree of loading as long as a glass can be made.

U5.2

A KINETIC MODEL FOR BOROSILICATE GLASS DISSOLUTION BASED ON THE DISSOLUTION AFFINITY OF A SURFACE ALTERATION LAYER William L. Bourcier, Dennis W. Peifer, Kevin G. Knauss, Kevin D. McKeegan, and David K. Smith, Lawrence Livermore National Laboratory, Livermore, CA 94550

A kinetic model incorporated in the EQ3/6 geochemical modeling code is used to predict borosilicate waste glass dissolution rates. The dissolution rate is assumed to be controlled by the dissolution affinity of an alkali and boron-depleted altered surface layer on the glass. Model results predict the non-linear glass dissolution rate where the relatively rapid initial rate slows and approaches a linear release with time.

The model has been used to predict the results of static closed-system dissolution tests of a uranium-doped SRL-165 glass. The tests were performed in gold-bag and Teflon-lined stainless steel vessels from 100 to 250°C for up to 4 months in a dilute (0.003 molal) NaHCO₃ solution. The gold bag tests were used for solution sampling; the tests in Teflon run in parallel were used for solids characterization. Solids were analyzed using SEM, SIMS, x-ray diffraction, and nuclear reaction profiling methods.

Comparison of model and experimental results show that the release

rates of elements not strongly concentrated in surface layers or secondary phases (e.g. Li, B, Na) can be successfully predicted by the model. The release rates of elements that are concentrated in surface layers and secondary phases are more difficult to predict and accurate prediction is possible only if observed secondary phases are used to constrain species concentrations.

Work performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory.

U5.3

PREDICTION OF RADIOACTIVE WASTE GLASS DURABILITY BY THE HYDRATION THERMODYNAMIC MODEL: APPLICATION TO SATURATED REPOSITORY ENVIRONMENTS. Carol M. Jantzen, Westinghouse Savannah River Company, Savannah River Site, Aiken, SC 29808.

The effects of groundwater chemistry on glass durability were examined using the hydration thermodynamic model. The relative durabilities of SiO₂, tektites, basalts, waste glasses, medieval window glasses, and a frit glass were determined in tuffaceous J-13 groundwater, basaltic GR-4 groundwater, WIPP-B brine, and Permian-A brine using the MCC-1 test. For silicate groundwaters, the free energy of hydration, calculated from the glass composition and the final experimental pH, was linearly related to the logarithm of the measured silica concentration. The linear equation was identical to that observed previously for these glasses during MCC-1 testing in deionized water. The superposition of the line from the silicate groundwater and deionized water experiments occurs because the pH values for all the glasses tested in groundwater remained constant. Constant pH values decreased the calculated ΔG_{hyd} values while in turn, lower Si releases were measured. The slope defined by the groundwater and deionized water data is the theoretical slope, in $(1/2.303RT)$, for glass dissolution controlled by the dissolution of amorphous silica. For brines, the influence of the ion activity product (IAP) on the solubility of silica and other species was determined. Using the hydration thermodynamic model, nuclear waste glass durability in saturated repository environments can be predicted from the glass composition and the groundwater pH.

U5.4

CHEMISTRY OF GLASS CORROSION IN HIGH SALINE BRINES. B. Grambow, R. Müller, Hahn-Meitner-Institut Berlin, Glienicker Str. 100, D-1000 Berlin 39, FRG

This paper describes a geochemical model and a comparison to experimental data for glass corrosion in concentrated salt brines. Modeling was performed with the computer code EQ3/6. The brine chemistry was described with the Pitzer formalism [Pitzer 1973] for osmotic and activity coefficients.

The reaction path was calculated of a nuclear waste glass as a function of brine chemistry and of the formation of major alteration products. In agreement with the experimental data it was calculated that in MgCl₂ dominated brines a major alteration product are Mg rich clay minerals and due to the consumption of Mg by these products the pH decreases with the proceeding reaction. A constant pH and composition of alteration products is achieved, when the alkali release from the glass balances the Mg consumption. In the NaCl dominated brine MgCl₂ becomes exhausted by clay minerals. As long as there is still Mg left in solution the pH decreases. After exhaustion of Mg the pH rises with the alkali release from the glass and analcime is formed.

U5.5

THERMOKINETIC MODEL OF BOROSILICATE GLASS DISSOLUTION: CONTEXTUAL AFFINITY. I. Advocat & E. Vernaz, CEN-Valrhé, SDHA, BP 171, 30205 Bagnols-sur-Cèze Cedex, France; J.L. Crovisier & B. Fritz, CNRS/CSGS, 1 rue Blessig, 67000 Strasbourg, France.

Short and long term geochemical interactions of R7-T7 nuclear glass with water at 100°C were simulated with the DISSOL thermo-kinetic computer code. Both the dissolved glass quantity and the resulting water composition, saturation states and mineral quantities produced were calculated as a function of time.

The rate equation used in the simulation was first proposed by Aagard and Helgeson: $dc/dt = S/V \times k^* \times (a_{\text{H}_2\text{O}})^n \times (1-Q/K)$. The predicted mineral phases were iron hydroxides, 2:1 clay mineral represented by an ideal solid solution model, manganese and zinc hydroxides, laumontite, strontianite, metastable amorphous silica, calcite and low albite. The calculated evolution of the glass/water system showed good agreement with short term experimental results (up to 1 year).

The best agreement with the one-year data was obtained with a reaction affinity calculated from silica activity (Grambow's hypothesis) rather than taking into account the activity of all the glass components as proposed by Jantzen and Plodinec.

Under near-equilibrium conditions, the reaction rate was proportional to the (Q/K) chemical affinity of the overall reaction. Under these conditions, chemical affinity was dependent on the stability or metastability of the reaction products. The dissolution rates observed experimentally at different SA/V ratios are therefore not intrinsically constant, but depend on the conditions under which reaction products form and on their physicochemical properties.

U5.6

COMPARISON OF THE LAYER STRUCTURE OF VAPOR PHASE AND LEACHED SRL GLASS BY USE OF AEM.* B. M. Biber, J. K. Bates, T. A. Abrajano, Jr., Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439; and J. P. Bradley, McCrone Environmental Services, Inc., 850 Pasquinnelli Drive, Westmont, IL 60559.

The initial corrosion of nuclear waste glass in an underground repository may be expected to occur through interaction with water vapor prior to liquid water contact. The current U.S. underground repository site selected for characterization is located in the unsaturated zone where proper waste package design and emplacement will limit, if not exclude, groundwater contact with the waste glass even after breach of the waste form container. Analytical electron microscopy has been used to examine the detailed structure of 131 glass that has been reacted in water vapor under relative humidities ranging from 60 to 100%, temperatures between 75° and 200°C, and time periods up to two years. An intercomparison of the reaction progress and alteration products identified under the different reaction conditions provides insight as to the mechanisms controlling glass reaction. The results from the vapor phase reacted glasses are then compared to those from glass of similar composition that has been reacted under standard MCC-1 type conditions for time periods up to four years. 131 glass was chosen for study because it has been identified as a representative composition for the least durable DWPf glass to be produced for storage.

*Work supported by the U.S. Department of Energy, Office of Civilian Radioactive Waste Management, Yucca Mountain Project Office, under Contract Numbers W-31-109-Eng-38 and AX0848606.

DISSOLUTION MECHANISMS OF CaTiO_3 AND OTHER TITANATE PHASES IN THE SYNROC ASSEMBLAGE

S. Myhra, D.K. Pham, R.St.C. Smart* and P.S. Turner, Division of Science and Technology, Griffith University, Nathan, Qld, Australia (* Now at: School of Chemical Technology, South Australian Institute of Technology, Adelaide, S.A. Australia).

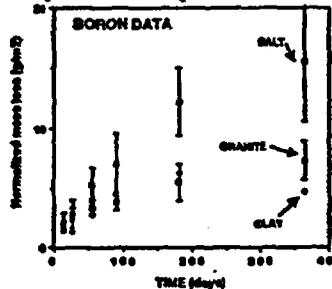
Perovskite, hollandite and zirconolite are the major phases of the Synroc C titanate assemblage. The chemical durability in an aqueous environment of the separate minerals and the total assemblage is one of the most relevant performance criteria for the Synroc concept. Methodologies, incorporating complementary approaches with solution, surface and electron-optical analyses, have been developed for assessing performance in the epithermal and hydrothermal regimes. A detailed study of CaTiO_3 has been completed identifying the mechanisms which are operative as well as the kinetic and thermodynamic factors which affect the evolution of the system. It has been found that thermodynamic stability for CaTiO_3 can easily be engineered into the waste repository for $T < 90^\circ\text{C}$, while the same is probably more difficult to achieve at higher hydrothermal temperatures. A similar study, using a comparable methodology, is underway for hollandite. Preliminary results will be reported for the chemical durability of this phase.

U6.1

A COMPARISON OF THE BEHAVIOUR OF VITRIFIED HLW IN REPOSITORIES IN SALT, CLAY AND GRANITE. Part II: RESULTS. M. Lutze, Hahn-Meitner-Institut, Glienicke Strasse 100, 1000 Berlin 39, FRG., M. Kawanishi, Abico Research Laboratory, Abico, Chiba-pre, 270-11, Japan, J. A. C. Marples, Harwell Laboratory, Oxon OX11 0RA, UK., and P. van Iseghem, SCK/CEN, Boeretang 200, 2400 Mol, Belgium.

A 'Round Robin' test of the European Commission's "Repository Systems Simulation Leach Test" has been undertaken. This involved testing an inactive simulant of the French high-level waste glass SON68 (R7T7) containers which also held water, backfill, and either salt, clay or granite geological material. Ten laboratories undertook the granite option, six salt and three clay. The test procedure was closely specified and is given in detail in a companion paper.

Experiments with glass powder in contact with aqueous solutions were run for periods of time up to one year at 90°C and the solutions were analyzed for Si, B, Li and Mo (compulsory) and other corroded glass constituents (optional). The analytical results are discussed in terms of accuracy and precision and are used to evaluate and compare the performance of the glass (fig.1) under



conditions representing those which might occur after disposal in future repository environments. The paper discusses the underlying corrosion mechanisms and the different degrees of corrosion in salt vs. clay and granite.

Fig. 1: Corrosion of HLW glass SON68 in salt, granite and clay, respectively.

U6.2

COMPARISON OF SURFACE LAYERS FORMED ON SYNTHETIC BASALTIC GLASS, FRENCH R7T7 AND HMI BOROSILICATE NUCLEAR WASTE FORM GLASSES - MATERIALS INTERFACE INTERACTIONS TESTS. Michael J. Jercinovic, Stacy Kaser, and Rodney C. Ewing, Dept. of Geology, Univ. of New Mexico, Albuquerque, NM 87131; Werner Lutze, Hahn Meitner Institut, Berlin GmbH, Glienicke Straße, 1000 Berlin 39, F.R. Germany.

Surface precipitates have formed on basaltic and borosilicate nuclear waste form glasses during the 6 month, 1 year, and 2 year *in situ* Materials Interface Interactions Tests (MIIT) conducted at the WIPP site using WIPP Brine A as a leachant at 90°C . The surface layers were characterized by scanning electron microscopy, x-ray diffraction, electron microprobe analysis, and analytical electron microscopy.

The surface layers formed on synthetic basaltic glass are primarily Mg-chloride and halite with a minor silicate component. HMI borosilicate glass exposed to the same experiments have surface layers dominated by amorphous Mg-silicate with 6 month layers being overgrown by minor Mg-chloride, which is not seen after 1 year. Sub-micron sized anhydrite crystals have formed within the Mg-silicate layer. Minor dissolution pitting of the glass is seen in 1 and 2 year samples of the basaltic and HMI glasses, but is not as pervasive as is reported for basaltic glass altered naturally at low temperature in seawater. Natural alteration of basaltic glass results in the formation of clay-like Fe-Al silicate gel (palagonite) surface layers. Dissolution pitting of the French R7T7 glass during the MIIT experiments is more advanced than seen in either the synthetic basaltic glass or the HMI borosilicate glass. The R7T7 glass has surface layers of Mg-silicate, similar in composition to the surface layers formed on the HMI borosilicate glass.

The differences in surface layer compositions between synthetic basaltic glass compared to borosilicate waste form glasses in the *in situ* MIIT experiments may indicate a difference in corrosion behaviour between the two glass types when exposed to the repository environment. In addition, the differences between natural environments and those of waste repositories may limit the usefulness of natural analogues toward verification of models developed for use in the prediction of the long term corrosion of nuclear waste form glasses.

U6.3

THE INTERACTION BETWEEN NUCLEAR WASTE GLASSES AND CLAY-II. P. Van Iseghem, K. Berghman and W. Timmermans, SCK/CEN, Boeretang 200, B-2400 Mol, Belgium.

Results are summarized of an experimental programme which started as a continuation of an earlier programme (ref. 1), to evaluate the compatibility of the high level waste glasses of interest to Belgium (the Cogema R7T7 glass SON 68 and the Pamela glasses SM 513 and SM 527) with the clay repository host. The corrosion tests are performed in clay/claywater mixtures, in controlled Eh conditions, and consider inactive glasses, glasses tracers with Pu/Cs/Sr/Tc/..., and the presence of a γ irradiation field.

Some of the main indications after two year test duration are :

- Glass dissolution (B, Li, ...) occurs in a Si/Al/Fe equilibrated solution.
- Pu, Cs, Sr leach in similar way from the different glasses ; distribution coefficients, Kd, for Pu are glass dependent ; the Pu inventory leached in a mobile form (about 4×10^4 MW cut-off) is extremely small.
- The γ irradiation induces considerable hydrogen production, which decreases with higher clay concentration ; glass corrosion slightly decreases in a γ irradiation field.

The paper will discuss the results in terms of leaching mechanisms and source term determination.

U6.4

R7-T7 NUCLEAR WASTE GLASS BEHAVIOR IN MOIST CLAY: ROLE OF THE CLAY MASS/GLASS SURFACE AREA RATIO. N. Godon and E. Vernaz, CEN-Valrhô, SDHA, BP 171, 30205 Bagnols-sur-Cèze Cedex, France.

R7-T7 glass alteration in moist clay media was investigated with various clays. In contact with smectite 4a, selected in France as a potential engineered barrier material, the glass was significantly corroded: after 6 months the glass corrosion rate was practically the same as the initial alteration rate in double-distilled water. Substantially lower alteration was observed in contact with a "bentonite" (montmorillonite) activated by sodium carbonate.

Smectite 4a consumes silicon released by glass corrosion. This action retards the rise to high silicon concentrations in solution that diminish the glass corrosion rate. The duration of this phenomenon is proportional to the ratio between the clay mass (C) and the glass surface area (SA). Comparing the results of studies at variable C/SA ratios indicates that low glass corrosion rates are obtained more slowly at higher C/SA ratios.

Tests with ²³⁹Pu-doped R7-T7 glass have also shown that the radionuclide retention factor in the alteration film at the glass surface is only 6, compared with a factor of nearly 50 in double-distilled water under static conditions.

In order to determine the influence of clay activation by sodium (saturation of exchange sites by Na⁺) on glass alteration, tests were conducted with moist activated smectite 4a and unactivated bentonite.

This work highlights the importance of selecting the clay for possible use as an engineered barrier material. The interpretations advanced can provide guidelines for this selection.

U6.5

PRODUCT CONSISTENCY LEACH TESTS OF SAVANNAH RIVER SITE RADIOACTIVE WASTE GLASSES.

Ned E. Bibler, Westinghouse Savannah River Co., Aiken, SC, 29808; and John K. Bates, Argonne National Laboratory, Argonne, IL, 60439.

The Product Consistency Test (PCT) was developed at the Savannah River Site (SRS) to routinely verify the durability of nuclear waste glasses that will be produced in the Defense Waste Processing Facility. The PCT is a 7 day, crushed glass leach test in deionized water at 90°C. Final leachates are filtered and acidified prior to analysis. To demonstrate the reproducibility of the PCT when performed remotely, SRS and Argonne National Laboratory have performed the PCT on samples of two radioactive glasses. The tests were also performed in order to compare the releases of the radionuclides with the major nonradioactive glass components and to determine if an effect of radiation was present.

Results from the two laboratories for the releases of B, Li, Na, and Si, agreed within 10%. For the radionuclides Cs-137, Sb-125, Eu-154, and Sr-90, and alpha activity, the agreement was not as good (up to 2X difference) possibly due to different counting techniques at the two facilities. At both facilities, the normalized releases were in the same order, e.g. Li-B-Na>Si>Cs-137>Sb-125>Eu-154>Sr-90. The normalized releases for the nonradioactive elements and the final pH values in these tests agreed with those for nonradioactive glasses with similar composition indicating no significant effect of radiation.

U6.6

THE REACTION OF SYNTHETIC NUCLEAR WASTE GLASS IN STEAM AND HYDROTHERMAL SOLUTION. W. L. Ebert and J. K. Bates, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439.

Glass monoliths of the WVCM 50, WVCM 44, SRL 165, and SRL 202 compositions were reacted in steam and hydrothermally (static leaching) at temperatures between 90° and 200°C. The glass reaction resulted in the formation of leached surface layers in both environments. Secondary precipitates were formed on all glass types in the steam environment only. The assemblage of phases formed was unique to each glass type, but several precipitates were common to all glasses, including analcime and several calcium silicate phases. Reaction in steam is thought to occur in a thin layer of sorbed water which becomes

saturated with respect to the observed phases after only a few days of reaction. These phases establish lower equilibrium solution concentrations of several glass components which allow the glass reaction to proceed at a higher rate than in the hydrothermal environment. The reaction is accelerated in the sense that secondary phases form after a shorter reaction time in the steam environment than in the hydrothermal environment because of large differences in the glass surface area/leachant volume ratio. A knowledge of the secondary phases which form is crucial to the modeling effort of the repository program.

*Work supported by the U.S. Department of Energy, Office of Civilian Radioactive Waste Management, Yucca Mountain Project Office, under Contract Number W-31-109-Eng-38.

U7.1

ESTIMATION OF LONGEVITY OF PORTLAND CEMENT GROUT USING CHEMICAL MODELING TECHNIQUES. Stephen R. Alcorn and Mark A. Gardiner, IT Corporation, 5301 Central Avenue, NE, Albuquerque, NM 87108; and William E. Coons, RE/SPEC, Inc. 3815 Eubank Boulevard, NE, Albuquerque, NM 87111.

Portland cement-based grout is a favored candidate material for nuclear waste repository seals due to its low permeability, ability to be injected into narrow fractures, ability to self-heal, and apparent persistence. The long-term performance of this material is uncertain, since many phases which comprise cement are metastable. It may be assumed that cement-based grout will degrade with time and increase in permeability. Therefore, it is important to be able to estimate the duration of acceptable performance.

To address this issue, a two-part approach was taken: (1) characterize the chemical degradation that would occur from the interaction of grout with natural groundwater, and (2) assess the consequences with a permeability development model. To establish bounds, three scenarios were analyzed: (1) closed system (very slow flow/dissolution/precipitation), (2) dynamic (slow flow/dissolution/limited precipitation), and (3) open system (fast flow/dissolution). To assess the consequences of the chemical interactions, an empirical relationship between porosity and permeability was developed. Changes in grout performance with time were predicted by assuming a sequence of hydraulic heads that varied in response to changing repository conditions. Preliminary results indicate that cement grout may maintain acceptable performance for thousands to millions of years, providing its initial hydraulic conductivity is around 10⁻¹² m/sec, the grout mix is engineered to minimize the more soluble phases (e.g., ettringite), and it is placed at a site with elevated TDS groundwater where the local hydraulic gradient is low or repository repressurization times are short.

U7.2

MODELLING OF THE EVOLUTION OF POREWATER CHEMISTRY IN A CEMENTITIOUS REPOSITORY. A. Haworth, S.M. Sharland and C.J. Tweed, Theoretical Physics Division, Harwell Laboratory, UKAEA, Oxfordshire OX11 0RA, U.K.

The current UK concept for disposal of low- or intermediate-level nuclear waste comprises an underground repository with a largely cementitious backfill. The aqueous phase within the cement provides a high pH environment in which the solubilities of many nuclides are low and the rate of general corrosion of metal canisters is slow. Variation in porewater chemistry in the repository is likely to have implications for the release rates of nuclides. Several experimental studies on the effect of the interaction of seawater with cement are being carried out at Harwell as part of the Nirex Safety Assessment Research Programme. In particular, changes in the solution composition of the contact water are being investigated. Last year, a preliminary model of cement degradation was

developed using the coupled transport/chemical equilibrium code CHEQMATE. This model has been further developed for use in modelling the experimental studies to aid interpretation of results. In particular, mineral changes at the surface of the cement are investigated. Such changes may be important for both solution conditions in cracks within the backfill and adsorption of nuclides on to the surfaces.

U7.3

A THEORETICAL STUDY OF THE EFFECT OF THE LEACH INTERVAL ON A SEMIDYNAMIC LEACH TEST. Roger D. Spence, Oak Ridge National Laboratory, P. O. Box 2003, Oak Ridge, TN 37831-7273

A diffusion model is used to explore limitations of a standard leach procedure, specifically, the effect of the leach intervals for the ANSI/ANS-16.1 procedure. The suppression of the leach rate by allowing the concentration to build up, as in such semidynamic procedures, is well known and can be predicted by the diffusion model. The originators of this procedure were also aware of this effect, but leaching must proceed for a finite time in order to achieve detectable concentrations of a species. In fact, the model can be used to give the correlation between detection limit, starting sample concentration, measurable effective diffusion coefficient, and leach interval.

The ANSI/ANS-16.1 procedure specifies a leachant volume and a set of leach intervals spanning a total of 90 d. Using the initial and boundary conditions presented by this leach procedure, the second order partial differential equation representing Fick's second law is solved numerically using finite differences. This allows the prediction of the cumulative amount leached, taking into account the suppression of the driving force as the concentration increases during each interval. This prediction can be compared to the predicted amount leached without this suppression, that is the true dynamic case, for the same effective diffusion coefficient. The effective diffusion coefficients at which the difference between these two predicted values becomes significant was studied. The effect of varying the leach interval for a given effective diffusion coefficient is also explored. With these predictive tools, the limited resources of an experimental program can be concentrated on those situations that cannot be predicted by the model, such as nondiffusion mechanisms.

U7.4

INTERACTION BETWEEN BLENDED CEMENTS AND A SULPHATE BEARING GROUND WATER. Susan L. Duerden, Peter L. Walton, and Amal J. Majumdar. Building Research Station, Watford, UK.

Blended cement mixes containing pulverized fuel ash (pfa) and ground granulated blastfurnace slag (ggbs) with ordinary Portland cement (OPC) have been reacted with a sulphate bearing ground water for 9 months at 50° and 80°C and atmospheric pressure. The blends were 9:1 and 75:25 pfa or ggbs:OPC and are of interest to the radioactive waste disposal schemes currently under consideration in the UK.

Two types of specimens were used in the reaction, 150mm diameter and 50mm long cylinders, and 75µm powders prepared from the mixes after 7 days' hydration. The reaction products were examined by x-ray diffraction, differential scanning calorimetry and scanning electron microscopy.

After 28 days hydration in water some of the cylinders showed evidence of cracking when stored in air at 90% R.H. Heat evolution and volume change effects in these cylinders have been studied. During reaction of these cylinders with ground water the cracks act as loci for crystallization of ettringite and gypsum. For uncracked cylinders there is minimal interaction between cements and ground water after 9 months, but an outer layer of calcite and/or vaterite, approx. 3mm thick, was present in all reacted cylinders.

With powder specimens reactions proceed much faster. In the case of the 75:25 ggbs/OPC sample at 50°C the reaction products include the sulphate minerals ettringite, monosulphate and gypsum, and calcite. Hydrotalcite that forms during the first 7 days of initial curing persists in the presence of ground water, but calcium hydroxide disappears after 3 days. There is some indication that α-quartz begins to form after about 4 months.

U7.5 ABSTRACT WITHDRAWN

U7.6

IMMOBILIZATION IN CEMENT OF ION EXCHANGE RESINS. Patrick LE BESCOPE; Pascal BOUNIOL; and Michel JORDA, C.E.A., DRDD/SESD, CEN-FAR, 92265 Fontenay aux Roses Cedex, FRANCE

Recent studies were carried out in FRANCE to improve ion exchange resin solidification in cement-based matrices. Work was conducted on different types of waste - cation, anion and mixed-bed resins - under regenerated and loaded states. Industrial applications could be found considering ion exchange resins from the water purification systems of COGEMA Reprocessing Plant (regenerated resins) and of PWR cooling circuits (loaded resins).

The main objective is to reach a waste incorporation rate of at least 50% (in volume). Imposed acceptability criteria for subsurface disposal required that waste forms must be monolithic solids with a) no free standing water, b) no significant dimensional variations and no loss of mechanical integrity both after curing and during immersion testing, c) leach rates compatible with ANDRA specifications. Hydraulic cement formulations were developed taking into account waste chemistry, more precisely the presence of ions which inhibit setting. Two types of cement based material were investigated: Portland cement with additives and blended cement (named C.L.C) containing silica fume and smectite. Properties of cement-ion exchange resin waste forms (mechanical properties, shrinkage or swelling) as well as chemical interaction of the waste and the cement matrix were examined.

The previous results mainly concerned "homogeneous waste forms" in which ion exchange resins were intimately mixed with the hydraulic binder. A new concept, allowing a higher incorporation rate, was promoted, considering the whole package as an "heterogeneous waste form". In this last case, radionuclide confinement was ensured by an outer cover of pure mortar.

U7.7

ENCAPSULATION OF RADIOIODINE IN CEMENTITIOUS WASTE FORMS. Mark Atkins and Frederik P. Glasser, Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen, AB9 2UE Scotland.

Risk assessment models applied to radioactive waste repository design disclose that iodine is one of the nuclides causing most concern. Computer calculations for these scenario studies assume that iodine, in the form of I⁻, is poorly sorbed on most geological materials. Thus it is important that iodine be retained at source, i.e. within the vault, for as long as is practicable.

In the UK context, cements are likely to form a major part of the waste package for low and medium active wastes, and of engineered vault structures. These cements are likely to be blends of one form or another, including Portland cement blended with blast furnace slag, or fly ash. These materials are chemically reactive with OPC during the first 10²-10³ years. It is important, therefore, to assess the effect of Portland cement and blending agent on iodine speciation and on iodine uptake by the constituent solid phases. Data are presented on uptake of I⁻ and IO₃⁻ on specific phases: Ca(OH)₂, calcium aluminosulphate hydrates, hydrotalcite and calcium silicate hydrogel (C-S-H). Precipitation of iodide as AgI, prior to cementation, is also considered.

Radiolytic effects on I are also described; the production of gaseous radioiodine (I_2) is potentially a serious problem.

U7.8

EFFECT OF γ -RADIATION ON THE MICROSTRUCTURE AND MICROCHEMISTRY OF ggbfs/OPC CEMENT BLENDS. I.G. Richardson and G.W. Groves, Department of Metallurgy and Science of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, U.K.; and C.R. Wilding, Materials Development Division, UKAEA Harwell Laboratory, Oxfordshire OX11 0RA, U.K.

Ground granulated blast-furnace slag (ggbfs)/OPC blends are among the materials being considered as possible encapsulating matrices for low and intermediate level radioactive wastes. It is therefore desirable to identify any microstructural modifications which may result in these systems from exposure to ionizing radiations.

In order to investigate this, ggbfs/OPC blends were γ -irradiated to $>80\text{MGy}$ at 50°C over a period of 2 years. These were examined by electron optical, X-ray and thermal analysis techniques and the results compared with controls subjected to a similar hydration regime. The morphological and compositional similarities and differences revealed between the irradiated and control samples are presented and discussed.

U7.9

HYDROGEN GENERATION IN MORTARS IMMOBILIZING WASTE CHLORIDE SALTS.* Michele A. Lewis and David W. Warren, Argonne National Laboratory, 9700 So. Cass Avenue, Argonne, IL 60439.

A mortar formulation capable of immobilizing chloride salts containing fission product cesium and strontium has been developed. This formulation, which consists of cement, fly ash, slag, water, and 3 to 10 wt% LiCl-KCl salt, is strong and leach-resistant, and under irradiation only hydrogen gas is generated. The $G(\text{H}_2)$ value depended on temperature and chloride salt concentration and varied from 0.02 to 0.2. Higher salt concentrations led to higher hydrogen yields at 25°C but lower yields at 75 and 120°C . Steady state pressures were not attained. Mechanistic studies showed that reduced sulfur species in the slag primarily controlled the radiolysis mechanism in slag-containing mortars. Since hydrogen pressures were comparatively high (250 psig for a total dose of 500 Mrad) and since the feasibility of using venting to reduce hydrogen buildup was uncertain, several different methods to reduce hydrogen yields were investigated. These included the addition of small quantities of materials which function as electron scavengers, as oxidizers, or as precipitating agents for sulfides, the use of different containment materials, the partial dehydration of the waste form and the use of a hydrogen getter.

*Work supported by the U.S. Department of Energy, Nuclear Energy Research & Development Program, under Contract W-31-109-Eng-38.

U7.10

POROSITY AND ION DIFFUSIVITY OF LATEX-MODIFIED CEMENT. T. Nishi, O. Kuriyama, M. Matsuda, K. Chino, Energy Research Lab., Hitachi Ltd.; and M. Kikuchi, Hitachi Works, Hitachi Ltd., Hitachi, JAPAN.

Latex-modified Portland cement was studied as a solidification agent for radioactive wastes. In order to predict the leaching rate of radionuclides from the cementitious waste forms using the mixing parameters such as water or latex content, the influence of these parameters was quantitatively estimated by porosity and ion diffusivity of hardened cement paste.

Total porosity of hardened cement paste decreased with water content and it was reduced by latex addition. Also the diffusion coefficient of ions decreased exponentially

with total porosity. Two experimental equations, by which total porosity was related to water and latex content and the diffusion coefficient of ions was related to total porosity, were derived from these results. The calculated results had good agreement with the measured ones.

U7.11

A COMPARISON OF THE BEHAVIOUR OF VITRIFIED HLW IN REPOSITORIES IN SALT, CLAY AND GRANITE. Part I: EXPERIMENTAL. L. A. Mertens, W. Lutze, Mahn-Meitner-Institut, Glienicke Strasse 100, 1000 Berlin 39, FRG., J. A. C. Marples, Harwell Laboratory, Oxon OX11 0RA, UK., and P. van Iseghem, SCK/CEN, Boeretang 200, 2400 Mol, Belgium, E. Vernaz, CEA Valrho, Marcoule BP 171, 30200 Bagnols sur Ceze, France.

Based on a universal "European Commission's Repository Systems Simulation Leach Test", a limited number of conditions were selected to be applied in a 'Round Robin' test in which 15 laboratories from 11 countries participated. Ten laboratories undertook the granite option, six salt and three clay. This contribution and a companion paper summarize the acquired information. The HLW borosilicate glass SON68 (R7T7), to be returned to and eventually disposed of in various geological repositories by Cogema's reprocessing customers, was tested in a standardized leach container developed and provided by CEA, Marcoule. The glass (2g of powder, 125-250 μm , and a coupon, 25x25x3mm, for each experiment) was prepared and delivered by CEA; together with crushed granite, sand, smectite and groundwater for the granite option. SCK-Mol provided the clay, smectite, sand and the recipe for claywater, HMI-Berlin the recipe for the rock salt composition. All materials were used in proportions and positions in the leach container as prescribed. The analytical method was the only variable to be chosen by the participants. After termination of the experiments (duration 14-36d, temperature 90°C), the concentrations of the glass constituents Si, B, Mo, Li, in solution had to be determined. Results for other elements (e.g., Zn, Sr, Na) and of surface analyses have been reported. The data base was used to evaluate the test procedure, the usage and versatility of the apparatus, and to identify analytical problems.

U7.12

IN-SITU TESTING OF NUCLEAR WASTE FORMS IN A CLAY LABORATORY - RESULTS AFTER TWO YEARS CORROSION. P. Van Iseghem, W. Timmermans and B. Neerdael, SCK/CEN, Boeretang 200, B-2400 Mol, Belgium.

Beginning of 1986, four tubes were introduced into the clay host formation from the underground Mol laboratory, at 220 m below surface level. About sixty-four waste form samples (40 x 15 x 5 mm) loaded on each tube, were brought directly in contact with the clay. One of the rigs is being held at ambient temperature for 5 years, two are heated at 90°C for respectively 2 and 5 years, and one is heated at 170°C for 5 years (ref. 1). These experiments are part of a large in-situ research programme, to demonstrate the suitability of the "Boom" clay layer at the Mol site as a waste repository host formation.

The paper discusses the results obtained from the first tube (two years at 90°C) which was retrieved by overcoring in August 1988. The main results are:

- The in-situ test was successful in terms of tube performance, operation (including retrieval), configuration (settling of the clay) and reliability of the results.
- The mass loss data and surface layer observations for the various glasses of interest (various CEC reference glasses) reveal a close similarity with parallel laboratory tests; the thickness of glass dissolved within two years varies between 40 and 325 μm .
- Glass composition effectively influences glass dissolution; the presence of canister and overpack corrosion products seems to enhance glass dissolution.

U7.13

DISSOLUTION KINETICS OF A SIMPLE ANALOGUE NUCLEAR WASTE GLASS AS A FUNCTION OF pH, TIME AND TEMPERATURE. Kevin G. Knauss, William L. Bourcier, Kevin D. McKeegan, Celia I. Merzbacher, Son N. Nguyen, Frederick J. Ryerson, David K. Smith and Homer C. Weed, Lawrence Livermore National Laboratory, Livermore, CA 94550

We have measured the dissolution rate of a simple five-component borosilicate glass (Na_2O , CaO , Al_2O_3 , B_2O_3 , SiO_2) using a flow-through system. The experiments were designed to measure the dissolution rate constant over the interval pH 1 through pH 13 at 3 temperatures (25, 50 and 70°C). Dilute buffers were used to fix pH as the glass dissolved. Solution and surface solid analyses provided information that are used to develop a kinetic model for glass dissolution.

Under all conditions we eventually observed linear dissolution kinetics. Above pH 8 or pH 9 dissolution was congruent and the gel layer was very thin. In strongly acidic solutions (pH 1 to pH 3) all components but Si were released in their stoichiometric proportions and a thick, Si-rich gel was formed. In mildly acidic to neutral solutions the gel was thinner and was both Si- and Al-rich, while the other components were released to solution in stoichiometric proportions. By varying the flow rate we demonstrated a lack of transport control of the dissolution rate.

The dissolution rates were found to be lowest at near-neutral pH and to increase at both low and high pH. A rate equation based on transition-state theory (TST) was used to calculate dissolution rate constants and reaction order with respect to pH over two pH intervals at each temperature. At 25°C between pH 1 and pH 7 the log rate constant for glass dissolution ($\text{g glass/m}^2\text{-d}$) was -0.77 and the order with respect to pH was -0.48 . Between pH 7 and pH 13 the log rate constant for glass dissolution was -8.1 and the order with respect to pH was $+0.51$. The measured simple glass dissolution rate constants compare very well with constants estimated by fitting the same TST equation to experimental results obtained for SRL-165 glass and to dissolution rate estimates made for synthetic basaltic glasses.

U7.14

HYDROTHERMAL LEACHING OF R7-T7 BOROSILICATE GLASS.

J. Caurel and E. Vernaz, CEN-Valrhô, SDHA/SEMC, BP 171, 30205 Bagnols-sur-Cèze Cedex, FRANCE; D. Beaufort, Laboratoire de Pétrologie des Alterations Hydrothermales, Université de Poitiers, 40 avenue du Recteur Pineau, 86022 Poitiers Cedex.

The results of hydrothermal leach tests are intended to be used to predict long-term low-temperature glass dissolution. It is often assumed that experimental data can be extrapolated to other conditions using Arrhenius-type rate laws.

Hydrothermal leaching mechanisms and their temperature dependence in R7-T7 glass were investigated in static experiments lasting from 7 days to 1 year at 150°C and 250°C, and in 7-day experiments at temperatures from 100°C to 300°C. Leachates, surface layers, and crystalline products were analyzed by ICP, SEM, EMP, XRD, and cathodoluminescence. Activation energies of 24 to 33 $\text{kJ}\cdot\text{mol}^{-1}$ were obtained for the 7-day tests, and 70 $\text{kJ}\cdot\text{mol}^{-1}$ from established kinetics for boron at 150°C and 250°C for up to 6-months (the discrepancy is discussed below).

The formation of metastable alteration products and large cracks through the bulk glass result in a different chemical and physical system at 250°C than at lower temperatures. Arrhenius calculations between 250°C and 100°C obviously do not allow for this. The assumption of extrapolability will be discussed in light of these changes in the chemical and physical (SA/V) system rather than simple activation energy considerations alone.

U7.15

Effects of Surface-Area-to-Solution Volume Ratio on the Chemical Durability of Nuclear Waste Glasses. I. L. Pegg, Aa. Barkatt, P. B. Macedo. Catholic University of America, Vitreous State Laboratory, Washington DC 22064.

The ratio of glass surface area to solution volume is an important parameter that affects both dissolution and precipitation processes. The effect

of this ratio on chemical durability has been investigated in a number of studies. These studies reported that the leach rates decrease as the SA/V ratios increase for such nuclear waste glasses as PNL-7668, DWRG, and SRL-131. Most of these studies also found that glass leaching data for a range of times and SA/V can be represented by a single curve when plotted versus the product of SA/V and time. In this paper we report some of our findings concerning the SA/V effects on the durability of such nuclear waste glasses as WV205, WVCM47 and WVCM50 which suggest a rather more complicated behavior. We find that the leach rates of waste glasses do not always decrease as the SA/V increases. In fact, the effect is highly composition and SA/V dependent: in the same SA/V range, the leach rate of one glass may increase while that of another decreases with increasing SA/V. Similarly, for the same glass the leach rate may increase within one SA/V range but decrease within another. A consequence of these results is that the effect of (SA/V)t scaling is also composition and SA/V ratio dependent, and therefore the concentration data do not generally collapse into a single curve when plotted against (SA/V)t.

U7.16

ALTERATION OF MICROSTRUCTURE AND LEACHING PROPERTIES OF WEST VALLEY REFERENCE BY HEAT TREATMENT. A. C. Buechele, X. Feng, H. Gu, and I. L. Pegg, Vitreous State Laboratory, The Catholic University of America, Washington, D.C. 20064

Samples of West Valley reference glass WVCM-59 were subjected to isothermal heat treatment according to a systematic schedule of time-temperature combinations to simulate conditions which might be encountered during cooling after the glass is poured into canisters. Phases differentiating during heat treatment were observed, analyzed, and quantified using an SEM equipped with WDS, EDS and image processing and analyzing capabilities. A hitherto unobserved phosphorus-rich phase of indefinite morphology developed after 3 hours at 700°C and continued to grow in extent as time elapsed. Small amounts of rare metal (e.g. Rh, Ru, Pd) crystalline phases were always present in the as-melted glass and frequently served as nucleation sites during heat treatment. Iron-group spinels containing Fe, Ni, Cr, and Mn in variable proportions were the most common phases observed, appearing in quantities up to 3 vol% in heat treated glass. The formation of a thoria-ceria phase occurred at temperatures of 900°C and below but required a progressively longer time as the temperature was lowered. Acmites formed at temperatures of 700°C and below. MCC-3 tests were done to assess the durability of samples substantially altered in microstructure.

U7.17

PARAMETRIC EFFECTS OF GLASS REACTION UNDER UNSATURATED CONDITIONS. J. K. Bates, T. J. Gerding, and D. J. Wronkiewicz, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439.

Eventual liquid water contact of high-level waste glass stored under the unsaturated conditions anticipated at the Yucca Mountain site will be by slow intrusion of water into a breached container/canister assembly. The water flow patterns under these unsaturated conditions will vary, and the Unsaturated Test method has been developed by the YMP to study glass reaction. The results from seven different sets of tests done to investigate the effect of systematically varying parameters such as glass composition, composition and degree of sensitization of 304L stainless steel, water

input volume, and the interval water contact are discussed. Glass reaction has been monitored over a period of five years, and the parametric effects can result in up to a ten-fold variance in the degree of glass reaction.

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U7.18

GROWTH RATES OF ALTERATION LAYERS AND ELEMENTAL MASS LOSSES DURING LEACHING OF BOROSILICATE NUCLEAR WASTE GLASS. Isunetaka Banha and Takashi Murakami, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-11, Japan.

MCC-1 static leaching experiments were carried out on a simulated waste glass in deionized water for up to 364 days at 90°C in order to examine the relationship between alteration layer thickness and elemental mass losses.

The thickness of the alteration layers increased linearly at a rate of 0.63 $\mu\text{m}/\text{day}$ for up to 91 days. After 91 days, however, the thickness was kept constant (about 60 μm) independent of time. The observed growth rate was in good agreement with the calculated one obtained by assuming that all boron in the leachates was due to the complete depletion of boron in the alteration layers. This means that shrinkage of the alteration layers is not significant, and suggests that the alteration layers retain their framework even after the depletion of part of the glass network formers and the recrystallization reported previously. The agreement of the leach rates also implies that the apparent release of elements from the glass almost ceases and the reaction between the alteration layers and the leachate plays a major role in the corrosion after 91-day leaching.

Two differently prepared layers, ethanol replacement of leachate and conventional air-drying before resin impregnation, revealed that the air-dried layers were thinner by about 5 percent because of shrinkage of the layers during air-drying.

U7.19

CHARACTERIZATION OF HIGHLY ACTIVE WASTE GLASSES PRODUCED IN A HOT VITRIFICATION PLANT, J.P. Glatz, E. Toscano and M. Coquerelle, and J. Fuger, Institute for Transuranium Elements, Commission of the European Communities, Karlsruhe, West Germany.

In the hot vitrification pilot plant operated by ENEA at JRC-Ispra were produced several high-level waste glass forms (up to 287 Ci/kg), containing 15 to 33 wt% fission products. These glasses were characterized in the hot cell laboratory at JRC-Karlsruhe.

The work comprised:

- mass and fission product distribution in the crucibles by gamma-scanning and radiography,
- microstructural and phase composition analysis by optical, SEM + EDAX and quantitative microscopy,
- leaching behaviour by the SOXHLET-method. The tests were performed on all glasses in water for 72 h. The analysis of the leachates was performed by ICP-MS and OES, and compared with the qualitative analysis by EDAX of the gel-layers found on the specimens after the dissolution tests.

Depending on glass and waste composition and loading, the products showed partial devitrification process or a two-glass system. In the partially devitrified glass, several precipitate morphologies were identified and analyzed. The precipitates, in the form of crystalline inclusions, were enriched in the main waste elements (metals, rare earths and actinides). In the two-glass system, the minor phase showed

a strong Al enrichment, with Cr and Ni as additional elements. Analysis of the leachates showed a good qualitative agreement with those performed on the gel-layers.

U7.20

THE LONG-TERM CORROSION AND MODELLING OF TWO SIMULATED BELGIAN REFERENCE HIGH-LEVEL WASTE GLASSES - PART II
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- ABSTRACT -

As part of a larger study to establish the performance of high level waste glass in repository conditions, long term phenomena related to the glass corrosion are being investigated, and modelling of the long term glass corrosion has been attempted. In a previous paper (ref 1) it was shown how for precursor glasses for two kinds of high level waste of importance for Belgium, modelling using the PHREEQE and GLASSOL codes could relatively well fit to the experimental data. The key role of Al_2O_3 on the long term behaviour was demonstrated. The experimental conditions were 90°C, $\text{SA.V}^1 = 10$ or 100m^{-1} , with distilled water as corrosion medium.

Recently, additional corrosion experiments in distilled water, but using powdered glass ($\text{SA.V}^1 = 7000\text{m}^{-1}$) at 90 or 120°C, provided a further confirmation about the final corrosion rate, but revealed also an additional corrosion accelerating (crystallisation?) phenomenon in case of the high Al_2O_3 glass.

Modelling efforts at present managed to fit the calculated values with the experimental data (but not the final acceleration) for the different SA.V^1 conditions.

The paper will discuss the experimental data, and the modelling approach, focusing the role of surface area to volume ratio (SA.V^1), temperature and the Al_2O_3 content of the glass

U7.21

SIMULTANEOUS EVAPORATION OF Cs AND Tc DURING VITRIFICATION - A THERMOCHEMICAL APPROACH
H. Migge, Hahn-Meitner-Institut, Glienicke Strasse 100, 1000 Berlin 39, FRG

In vitrification of nuclear waste technetium tends to be lost substantially by evaporation. For the case that Cs is not present this behaviour was satisfactorily described by thermochemistry in the simple Tc-O system considering the predominance areas of the different oxides and the partial pressures of Tc_2O_7 above them. If Cs is present there are contradictory observations from the condensation products whether or not Tc evaporates simultaneously with Cs by forming gaseous CsTcO_4 . This compound - in contrast to solid CsTcO_4 - has not yet been identified experimentally. Its existence may be concluded, however, from the existence of the gaseous alkali-perrhenates. From comparison with these perrhenates the standard formation enthalpy and the entropies of condensed as well as of gaseous CsTcO_4 are estimated, and solid CsTcO_4 is assumed to melt above 1200K. Free energies of these compounds and tentative isothermal predominance area diagrams of the Cs-Tc-O system up to 1200K were calculated including isobars of the gases CsO , Cs_2O , TcO , Tc_2O_7 , and CsTcO_4 and their dependence on the condensed phase present. The pressure of gaseous CsTcO_4 above solid CsTcO_4 is very high even at lower temperatures ($\log p(\text{Pa}) = 3$ at 500K and $\log p(\text{Pa}) = 8.3$ at 1200K). From comparison with voltammetric and thermochemical results for borosilicate glass containing Tc it is concluded that condensed CsTcO_4 does exist in glass which contains Cs as well. Therefore, the appearance of condensates of CsTcO_4 during vitrification has to be expected. The pressure of CsTcO_4 decreases only slowly, if the oxygen or caesium potentials are reduced and condensed CsTcO_4 becomes unstable and condensed Tc, TcO_2 or Tc_2O_7 resp. are formed.

U7.22

THE EFFECT OF TEMPERATURE ON THE REDOX CONSTRAINTS FOR THE PROCESSING OF HIGH-LEVEL NUCLEAR WASTE INTO A GLASS WASTE FORM. Henry D. Schreiber, Charlotte W. Schreiber, Margaret W. Riethmiller, and J. Sloan Downey; Center for Glass Chemistry, Virginia Military Institute, Lexington, VA, 24450.

Efficient processing of high-level nuclear waste into a borosilicate glass matrix requires the consideration of the melt's redox properties. If the conditions that accompany the dissolution of the waste into the glass melt are too oxidizing, foaming problems may arise; conversely, if the conditions during processing are too reducing, sulfide and metal phases might precipitate from the melt and result in short circuiting between the electrodes.

Savannah River Laboratory glass frit #131 (SRL-131), the reference system for this study, is an alkali borosilicate glass whose redox chemistry has been extensively characterized at 1150°C. The oxidation-reduction equilibria of selected multivalent elements in this reference composition were investigated as a function of the imposed oxygen fugacity for several temperatures from 950°C to 1350°C.

The redox chemistry of the system defines an acceptable operating range in SRL-131 with respect to the imposed oxygen fugacity of about 10^{-5} to 10^{-12} atm at 950°C, of about 10^{-2} to 10^{-9} atm at 1150°C, and of about 10^0 to 10^{-7} atm at 1350°C in order to alleviate potential foaming problems at the upper limit and potential precipitation of metals and sulfides at the lower extreme. For the processing of the glass waste form, the previously prescribed range of 0.1 to 0.5 for $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$ in the resulting glass should be acceptable at all temperatures from 950°C to 1350°C.

U7.23

CALCULATION OF THE VISCOSITY OF NUCLEAR WASTE GLASS SYSTEMS. Ritesh P. Shah, E.C. Behrman, and D. Oksoy, New York State College of Ceramics, Alfred University, Alfred, NY 14802

Viscosity of one of the most important processing parameters and one of the most difficult to calculate theoretically, particularly for multicomponent systems like nuclear waste glasses. Here, we propose a semi-empirical approach based on the Fulcher equation, involving identification of key component variables, for which coefficients are then determined by regression analysis. Results are presented for a variety of glass systems, and compared both to experimental data and to statistical mechanical perturbation theory calculations.

U7.24

CHARACTERIZATION OF MECHANICAL STRENGTHS FOR SIMULATED SOLIDIFIED HIGH LEVEL WASTE FORMS. Hiroschi Igarashi, Takeshi Takahashi, Power Reactor & Nuclear Fuel Development Corp. (PNC), 4-33, Muramatsu, Tokai-mura, Ibaraki, 319-11, JAPAN

Various types of waste form have been developed and characterized in PNC to immobilize high level liquid waste generated from reprocessing nuclear spent fuel. Mechanical strength tests were made on simulated solidified high level waste forms which were borosilicate glass and diopside-glass-ceramic form. Commercial glasses were also tested for comparison with the waste forms.

Measured strengths were three-point bending strength, uniaxial compressive strength, impact strength by falling weight method, and vickers hardness. Fracture toughness and fracture surface energy were also measured by both of notch-beam and indentation technique. The strengths measured were evaluated with statistical errors.

The effect of change in composition was studied on the glass form. The change in waste content from 20 to 40 wt% did not influence the strength. No significant effect of the change of iron content in waste was observed. The difference in glass additives composition did not result in the change of strengths. The mechanical strengths measured of the glass forms were comparable with those of commercial glasses.

Clearer difference in the fracture toughness and fracture surface energy was observed between glass and glass-ceramic waste form. The fracture toughness of glass form by indentation test was about $0.7 \text{ MN}/\text{m}^{3/2}$ which was comparable with commercial glass. And fracture toughness of the glass-ceramic form was 30% higher than that of glass form.

U7.25

DIFFUSION OF CESIUM IN SODIUM-BOROSILICATE GLASSES USED FOR IMMOBILISATION OF NUCLEAR WASTE. E.G.F. Sengers and F.J.J.G. Janssen, N.V. KEMA, R&D Division, Chemical Research Department, P.O. Box 9035, 6800 ET Arnhem, The Netherlands.

Sodium-borosilicate glasses used for the immobilisation of nuclear waste were studied in experiments using concentration couples in order to determine the diffusion coefficient of Cs. The couples were made by pouring successively sodium-borosilicate glass and sodium-borosilicate glass containing 2 mol% cesiumoxide in alumina crucibles. Diffusion experiments were performed by heating the crucibles at various temperatures for five hundred hours. A scanning electron microscope, in combination with an energy dispersive spectrometer was used to determine concentration profiles.

In the temperature range 850 - 975 K diffusion coefficients between 10^{-16} and $10^{-15} \text{ m}^2/\text{s}$ were found. The activation energy for the cesium diffusion in that temperature range appears to be about 425 kJ/mol.

Diffusion coefficients for cesium diffusion have also been measured in glasses containing cesium and different amounts of other fission products, such as Sr and Zr, and impurities, such as Ca and Fe, and in simulated nuclear waste glasses. It can be concluded that the diffusion of cesium does not depend critically on the addition of other fission-product elements or other impurities.

U7.26

ENTHALPIES OF MIXING AND INCIPIENT IMMISCIBILITY IN GLASSES IN THE SYSTEM $\text{K}_2\text{O}-\text{SiO}_2-\text{La}_2\text{O}_3$. A.J.G. Ellison and A. Navrotsky, Department of Geological and Geophysical Sciences, Princeton University, Princeton, NJ 08544

Enthalpies of mixing of quenched glasses along three joins have been determined using high-temperature solution calorimetry in molten $2\text{PbO}-\text{B}_2\text{O}_3$ at 977 K. In $\text{K}_2\text{O}-5\text{SiO}_2-n\text{La}_2\text{O}_3$ and $\text{SiO}_2-n(\text{K}_2\text{O}-\text{La}_2\text{O}_3)$ ($0 \leq n \leq 1$) glasses, the concentration of network-modifying cations and the ratio of non-bridging oxygen to silicon atoms (NBO/Si) increases with n. Along the join $(1-x)\text{K}_2\text{O}-5\text{SiO}_2-(x/3)\text{La}_2\text{O}_3$ ($0 \leq x \leq 0.75$), La is substituted for K in glasses with fixed NBO/Si. Despite differences in NBO/Si and the valences of K and La, enthalpies of mixing show no deviations from ideal mixing greater than -1 kJ/mole of the ternary system. $\text{K}_2\text{O}-5\text{SiO}_2-\text{La}_2\text{O}_3$ undergoes glass-glass phase separation at 1200 K, but the enthalpy of solutions of the clear glass and the phase-separated glass are identical within error.

These data indicate that phase-ordering (a cursor to liquid immiscibility) is present even at low La_2O_3 concentrations - increasing La_2O_3 adjusts the size and/or distribution of phase-ordered regions. Vibrational spectra of glasses in this system support this interpretation, and indicate that K and La do not share the same NBO; hence, phase-ordering is driven by the presence of La in the glass.

U7.27

GRAIN BOUNDARY INVENTORY AND UO_2 MATRIX DISSOLUTION STUDIES ON SPENT LWR FUEL. W. J. Gray, D. M. Strachan, L. E. Thomas, R. E. Einziger, and M. J. Apted. Pacific Northwest Laboratory, P. O. Box 999, Richland, WA 99352.

An experimental method is being developed for measuring the grain boundary inventory of radionuclides and for determining whether radionuclides within the UO_2 matrix of spent LWR fuel will dissolve congruently with the UO_2 . The method involves limited oxidation of spent fuel in air at low temperatures (150°C to 200°C). At these temperatures, spent LWR fuel oxidizes preferentially along the grain boundaries making the fuel fragments friable. This technique has been used successfully to prepare individual grains of irradiated UO_2 . Following oxidation, the spent fuel particles are mounted and thinned to permit examination by transmission electron microscopy (TEM). This analysis can show the presence of higher oxides, such as U_3O_8 , and provide assurance that the limited oxidation affected only the grain boundary material plus a few hundred nanometers of the UO_2 grain periphery.

Once the spent fuel has been dissociated into individual grains, the grain-boundary inventories of radionuclides can be measured. This is accomplished through a series of dissolution tests in which the solvent (e.g., dilute HCl) is changed and analyzed frequently. This technique gives an upper limit to the grain boundary inventory because it is not possible to prevent a small amount of the UO_2 grain periphery from oxidizing and subsequently dissolving. After the oxidized portions of the grains are completely removed, fluid-flow dissolution tests are used to determine whether the remaining UO_2 matrix material dissolves congruently. Water is pumped through a column containing spent fuel grains while the concentration of radionuclides in the column effluent is monitored. At high flow rates, the forward reaction rates of the various radionuclides can be measured and the degree of congruency determined.

U7.28

IDENTIFICATION OF SECONDARY PHASES FORMED DURING UNSATURATED REACTION OF UO_2 WITH EJ-13 WATER. J. K. Bates, B. S. Tani, and E. Veleckis, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439.

The reaction of spent fuel under the unsaturated conditions anticipated to exist at the Yucca Mountain repository site will likely include contact between the fuel and small volumes of water under oxidizing conditions. To evaluate procedures that may be required to perform such testing, a set of parametric experiments has been conducted over a four-year period. One aspect of these experiments has been to identify the secondary phases that form during the reaction process. More than five distinct phases have been identified, including uranophane, boltwoodite, sklodowskite, and becquerelite. The methods used to identify the phases together with a temporal and spatial description as to how these phases formed with respect to the water flow pattern and cation depletion are discussed.

*Work supported by the U.S. Department of Energy, Office of Civilian Radioactive Waste Management, Yucca Mountain Project Office, under Contract Number W-31-109-Eng-38.

U7.29

INVESTIGATIONS INTO THE ELECTROCHEMICAL LEACHING BEHAVIOUR OF UO_2 PELLETS IN VARIOUS SATURATED SALT SOLUTIONS

Ch. Keilung, P.-M. Heppner, Marx; Free University of Berlin; Institute for Inorganic and Analytical Chemistry; Radiochem. Div.; Fabeckstr. 34-36; D-1000 Berlin - Dahlem (33); FRG

Within the frame of investigations into the safety aspects for direct waste disposal excluding spent fuel reprocessing experiments are made for characterizing the leaching behaviour of UO_2 pellets in various saturated salt solutions. The solutions taken into consideration are saturated NaCl solutions and also Q and R brines. The redox potentials for the various systems are realized electrochemically. Quite a number of electrode forms have been tested with respect to their applicability for performing measurements in solutions of significant high ionic strength. Using a newly developed UO_2 electrode the rest potentials of UO_2 electrodes have been determined in various systems. The corrosion rates could be potentiostatically obtained under a variety of different experimental conditions.

U7.30

A DEFORMATION AND THERMODYNAMIC MODEL FOR HYDRIDE PRECIPITATION KINETICS IN SPENT FUEL CLADDING
R. B. Stout, University of California-LLNL
P.O.Box 808, L-201, Livermore, CA 94550

ABSTRACT* Hydrogen is contained in the Zircaloy cladding of spent fuel rods from nuclear reactors. All the spent fuel rods placed in a nuclear waste repository will have a temperature history that decreases toward ambient; and as a result, most all of the hydrogen in the Zircaloy will eventually precipitate as zirconium hydride platelets. A model for the density of hydride platelets is a necessary sub-part for predicting Zircaloy cladding failure rate in a nuclear waste repository. A model is developed to describe statistically the hydride platelet density, and the density function includes the orientation as a physical attribute. The model applies concepts from statistical mechanics to derive probable deformation and thermodynamic functionals for cladding material response that depend explicitly on the hydride platelet density function. From this model, hydride precipitation kinetics depend on a thermodynamic potential for hydride density change and the inner product of a stress tensor and a tensor measure for the incremental volume change due to hydride platelets. The development of a material response model for Zircaloy cladding exposed to the expected conditions in a nuclear waste repository is supported by the U.S. DOE Yucca Mountain Project.

* Work performed under the auspices of the U.S. Department of Energy, Office of Civilian Radioactive Waste Management, Yucca Mountain Project Office, by the Lawrence Livermore National Laboratory under contract W-7405-ENG-48.

U7.31

"Fluoride Influence on Zircaloy-4 Corrosion in Water, as a Function of pH, Temperature and Fluoride Content."^(a)
N. H. Uziemblo and H. D. Smith, Pacific Northwest Laboratory,^(b) Richland Washington

The corrosion rate of Zircaloy-4 was determined in fluoride-doped water (100, 500, 1000ppm) using a pH stat system. The results were strong functions of pH, fluoride ion concentration and temperature. The calculated amount of corrosion using homogeneous corrosion rates correlated well with the observed weight loss exhibited by those same specimens. The weight loss indicates that the normal passivating film usually formed on Zircaloy in water is not present. This result is consistent with 1) observed increase in corrosion rate, 2) extensive pitting observed with scanning electron microscopy, 3) detected fluoride and

oxyfluoride compounds of zirconium on the surface observed via photo-electron spectroscopy, and 4) Zircaloy components in solution in the fluoride-doped water. Anodized Zircaloy specimens are observed to be attacked at a similar rate to the non-anodized material. Furthermore, specimens exhibit a temporary elevation of corrosion rate when they are cycled from high corrosion rate to low corrosion rate conditions. It can be concluded that fluoride in the water influences the corrosion rate of Zircaloy by modifying the passivation properties of the oxide film.

(a) The Yucca Mountain Project of the U.S. DOE is investigating the suitability of a site in the unsaturated zone at Yucca Mountain, Nevada, for a high-level waste repository.

(b) Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

U7.32

CORROSION BEHAVIOR OF ZIRCALOY* IN AQUEOUS MEDIA
Anna C. Fraker and Jonice S. Harris, National Institute of Standards and Technology, Gaithersburg, MD 20899.

Zircaloy-2 (Zr-2) and Zircaloy-4 (Zr-4) are used as nuclear fuel cladding. Both alloys are more than ninety eight percent zirconium (Zr) and are highly corrosion resistant to various media. The thickness of nuclear fuel cladding is less than 1 mm, and it is important to establish whether the cladding will remain intact for the required time periods of nuclear waste storage. Electrochemical measurements using polarization techniques have been made on these alloys in aqueous media with a pH of 8.3 and varying ionic concentrations (1X and 10X) at temperatures of 22°C and 95°C.

Results of open circuit electrode potential measurements indicate that the Zircaloys passivate after immersion in the test media used. Anodic polarization measurements in concentrated media at 95°C show a passive region extending over a range of -400 millivolts to +850 millivolts where breakdown occurred. All potentials were measured versus a saturated calomel electrode (SCE). Cyclic polarization curves show the same passive region and breakdown potential and in addition, show hysteresis in the return portion of the curve. The hysteresis indicates possible susceptibility to localized corrosion, and selected experimental parameters were varied to investigate the reason for the hysteresis. Measured corrosion rates were low, but some white corrosion product was observed in one area after a thirty day exposure at 95°C.

Data will be presented and discussed in terms of corrosion rates, passivity, breakdown potential and susceptibility to localized corrosion under the conditions studied.

*Zircaloy is a registered trademark of the Westinghouse Electric Corp., Specialty Metals Division, Pittsburgh, PA

U7.33

POTENTIODYNAMIC POLARIZATION STUDIES OF CANDIDATE CONTAINER MATERIALS IN SIMULATED TUFF REPOSITORY ENVIRONMENTS. John A. Beavers and Neil G. Thompson, Cortest Columbus, Inc., Columbus, Ohio.

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. In one task of the program, a cyclic potentiodynamic polarization (CPF) technique is being used to evaluate the corrosion behavior of the candidate container materials, which include copper-base alloys and Fe-Cr-Ni alloys. In order to evaluate the expected range of environmental variables (groundwater composition and temperature), a statistical

experimental design approach is being used. Complete matrices of CPF tests, which consist of 33 environments, have been completed on four candidate container materials; CDA 102 Copper, CDA 715 Copper-Nickel, Type 304L Stainless Steels and Incoloy Alloy 825. The test matrix was a Resolution IV experimental design for 15 environmental variables, including temperature and pH, species present in the groundwater, and those generated by radiolysis. In these environments, all four alloys tested exhibited a wide range of behavior including passive behavior, pitting, crevice corrosion and active corrosion. The CPF behavior of the Fe-Cr-Ni alloys was found to conform with a conventional interpretation of CPF curves while this was not the case for the copper-base alloys.

U7.34

MIGRATION BEHAVIOR OF URANIUM SERIES NUCLIDES IN ALTERED QUARTZ-CHLORITE SCHIST. T. Ohnuki, T. Murakami, K. Sekine, N. Yanase, H. Isobe and Y. Kobayashi, Department of Environmental Safety Research, Japan Atomic Energy Research Institute, Tokai, Ibaraki, 319-11, Japan

Migration behavior of uranium series nuclides in the altered quartz-chlorite schist has been studied utilizing data on the concentration distribution of uranium and thorium series nuclides at Koongarra in Australia. The distribution of $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ activity ratios in the schist reveals that the migration behavior of uranium series nuclides differs between depths. The variation of $^{230}\text{Th}/^{234}\text{U}$ activity ratios against distance along the surface, intermediate and deep layers shows different trend in different layers. The X-ray diffraction patterns of the three rock samples collected at different layers show; quartz is found in all layers; chlorite is present only in the deep layer; kaolinite-smectite and goethite which are converted from chlorite, in the intermediate layer, and kaolinite-smectite, goethite and hematite which are converted from chlorite in the surface layer. Relationships between $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ activity ratios along the surface, intermediate and deep layers reveal that the retardation factors of ^{234}U are greater by a factor of 1.1 and 1.9 than those of ^{238}U in the surface and intermediate layers, respectively. These suggest that different uranium adsorption between depths is probably due to different mineral assemblages.

U7.35

MIGRATION OF ANIONIC SPECIES OF RADIOACTIVE COBALT THROUGH SOIL. Yoshihiko Ohnuki, Department of Environmental Safety Research, Japan Atomic Energy Research Institute, Shirakata, Tokai, Ibaraki, Japan and David E. Robertson, Chemical Science Department, Pacific Northwest Laboratories, Richland, WA.

The migration of an anionic species of ^{60}Co through soil has been examined utilizing data on the migration of radionuclides leached from an aqueous waste disposal site. Correlation coefficients between the concentrations of the anionic species of ^{60}Co and those of particulate, cationic and non-ionic species of ^{60}Co reveal that the anionic species of ^{60}Co was not interconverted with other species during migration. The cross-correlations between the concentrations of the anionic species of ^{60}Co gives a calculated retardation factor of the anionic species of ^{60}Co of approximately 19 being 1200 times lower than the laboratory measurements. The average concentration distribution of the anionic species

of ^{60}Co suggests that the migration of the anionic species of ^{60}Co consists of two migration fractions which was characterized by different migration mechanism.

U7.36

SHINZO UETA * AND NAOTAKE KATOH **

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Sorption is one of the most important mechanisms for the migration of radionuclide which released from the nuclear wastes.

The sorption behaviors strongly depend on the chemical species of radionuclides. Therefore it is necessary to study on the migration from the point of view of chemical forms.

We carried out the column experiments, where Co was used as the tracer elements. The tracer solutions were prepared to treat three different chemical forms of Co^{2+} , $\text{Co}(\text{OH})_2$, and Co-EDTA . In the sand column which simulated the natural barrier, Co^{2+} and $\text{Co}(\text{OH})_2$ could be well retained and Co-EDTA showed no retardation.

On the contrary, Co-EDTA could be retained in the column filled with artificial absorbent, for example activated carbon and silica-alumina, then the distribution coefficients were about 60 ml/g in each case. In these experiments, the breakthrough curves of Co^{2+} , $\text{Co}(\text{OH})_2$, and Co-EDTA showed good agreements with the calculations which based on the ion exchange, filtration, and absorption model, respectively.

U7.37

GRIMSEL COLLOID EXERCISE. C. DEGUELDRE, Paul Scherrer Institute, CH-5232 Villigen, Switzerland

The Grimsel Colloid Exercise is an intercomparison exercise which consisted of an in situ sampling phase followed by a colloid characterization step. The goal of this benchmark, which involved 12 laboratories, is to evaluate both sampling and characterization techniques with emphasis on the colloid specific size distribution. The sampling took place at the Grimsel Test Site (NAGRA facility) and colloids were sampled from the water flowing in the granitic fracture. The production of colloid samples was carried out in duplicate by cross flow filtration (CEA, PSI) and by tangential flow filtration (AECL, UKAEA) while unfiltered water was also collected. CEA and PSI produced colloid samples on membranes changing both the pore size (3 - 450 nm) and the volume of water collected (20 - 150 ml). The colloid concentrates were yielded by tangential filtration with a cut-off of 1.5 (AECL) and 2.1 (UKAEA) nm respectively, the former concentrates being produced after a 1 μm prefiltration. While shipping and storage may affect the colloid samples, as well as the composition of both unfiltered/filtered water and concentrate samples, major element composition of the fluid samples was comparable for the chemical analysis groups. However, CO_2 contamination from the air decreases the pH from 9.6 to about 8 while increasing the total inorganic carbon. The exercise differentiates the colloid samples produced on site from those obtained after transfer of the fluid samples in the laboratory. The colloid concentration estimated by transmission electron microscopy and by gravimetry is around 10^{14} pt.L^{-1} for diameters larger than 10 nm. For colloids larger than 50 nm the concentration measured by scanning electron microscopy is about 10^{10} pt.L^{-1} . For colloids/particles larger than 450 nm, the concentration measured by gravimetry, scanning electron microscopy and single particle counting is about $2 \cdot 10^7$ pt.L^{-1} . On a weight basis, the total colloid and particle concentration measured by gravimetry, laser photoacoustic spectroscopy, chemical analysis of fluid samples, scanning electron microscopy, single particle counting and static light scattering is 200 ± 100 ppb. They consist of silica, illite/muscovite, biotite, calcium silicate, and organic material. These particles are negatively charged in the in situ conditions and the average cumulative specific size distribution is given by: $\log[\text{coll}] = 15.82(\pm 0.36) - 3.17(\pm 0.16)\log\phi$ with ϕ the colloid diameter ranging from 10 to 10,000 nm and $[\text{coll}]$ given in pt.L^{-1} . On the basis of an average site density of 3 nm^{-2} the calculated cation exchange capacity is of the order of nM and below the detection limit of the classical CEC tests. These results are discussed on the basis of the detection limit, lateral resolution and counting conditions of the techniques (precision) as well as the sample preparation (accuracy). The main recommendations are the need of in situ sampling, track of artefact production (e.g. ion retention, aggregation ...) and the minimization of potential contamination during sample preparation. Details on this study are published in a PSI/NAGRA/CEC report.

U7.38

AUTHIGENIC CLAY MINERALS IN THE RUSTLER FORMATION, WIPP SITE AREA, NEW MEXICO. Douglas G. Brookins, University New Mexico, Albuquerque, NM 87131; Steven J. Lambert, Sandia National Laboratories, Albuquerque, NM 87185; and David B. Ward, University of New Mexico, Albuquerque, NM 87131.

Transuranic waste is planned for disposal in the Late Permian evaporites of the Delaware Basin, southeastern New

Mexico, at the WIPP site. The disposal horizon is located in the bedded halite of the Salado Formation, which is overlain by the impure halite-anhydrite (gypsum)-siltstone-mudstone of the Rustler Formation. The Rustler Formation also contains two dolomite members, the Magenta and Culebra, which transmit water. The Culebra Member is suspected to have actively interacted with waters at time(s) from the Late Permian to the present, and it is important to assess the reactivity of these waters in conjunction with WIPP Site stability.

We have investigated the Rb-Sr systematics of clay minerals from the Culebra Member and elsewhere in the Rustler Formation. By separating the less than 0.5 micron size material we are able to deal with presumed true authigenic clay minerals. The authigenic fraction is especially sensitive to chemical and isotopic exchange with waters, and exposure to large amount of water will reset the clay minerals to such a time. Our data yield a $250 \pm \text{Ma}$ Rb-Sr isochron, which is consistent with the Late Permian age of the Rustler Formation. This age is significant in that it demonstrates that these clay minerals have preserved their isotopic and chemical integrity since the Late Permian and have not been subjected to any pronounced interaction with waters since. This information lends further support to the suitability of the WIPP Site for transuranic waste disposal.

U7.39

IN SITU OBSERVATION OF THE ALPHA/BETA-CRISTOBALITE TRANSITION USING HIGH VOLTAGE ELECTRON MICROSCOPY. Annemarie Meike, Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720; and William Glassley, Earth Sciences Division, Lawrence Livermore National Laboratory, Livermore, CA 94550.

To predict the behavior of the near-field environment of high-level radioactive waste containers, single phase dissolution and precipitation kinetics data are required. In the course of obtaining such data on cristobalite at LLNL, it was noted that synthetic cristobalite dissolved at rates slightly higher than natural cristobalite. Detailed characterization of the starting materials, using the 1.5 Mev High Voltage Electron Microscope (HVEM) at LBL, revealed that both samples contained beta-cristobalite and amorphous silica, in addition to alpha-cristobalite. To understand the mechanism responsible for the apparent metastable persistence of beta-cristobalite and amorphous silica, in-situ experiments were conducted on synthetic alpha-cristobalite using an environmental cell in which it was possible to introduce either dry CO_2 or a $\text{CO}_2 + \text{H}_2\text{O}$ vapor during heating and cooling sequences. Direct observation of electron diffraction patterns during the experiments suggests that the presence of water vapor affects the alpha-beta transition temperature, and may be responsible in part for the development of a stability field for amorphous silica at the transition. Preliminary results suggest that the temperature interval over which amorphous silica may persist could be several tens of degrees. The amorphous phase was not observed during the dry heating experiments. Because a high temperature, water-saturated vapor phase is expected to persist in the near-field environment for several hundred years, the chemical and mechanical properties of the proposed repository tuff may be modified by the development of amorphous silica from cristobalite. Further work is continuing in order to more precisely characterize the properties of this structural transition and its implications for near-field behavior.

Performed under contract W-7405-ENG-48 for Department of Energy Office of Civilian Radioactive Waste Management, Yucca Mountain Project.

U7.40

ESTIMATION OF LONG-TERM DURABILITY OF BENTONITE FROM THE THERMAL HISTORY OF MURAKAMI DEPOSIT, JAPAN. G. Kamei, T. Arai, Y. Yusa, N. Sasaki, Power Reactor & Nuclear Fuel Development Co., Tokai-mura, Ibaraki, Japan, H. Takano, Dia Consultants Company, Ikebukuro, Toshima-ku, Tokyo, Japan.

The illitization of smectite in natural environment affords information on the long-term durability of bentonite which is a candidate for buffer materials. Murakami bentonite deposit, central Japan, where the bentonite and rhyolitic intrusive are distributed, was surveyed and lateral varia-

tion of smectite to illite in the aureole of the rhyolite was studied.

Geochronology: The radiometric ages of some minerals from the intrusive rock and the clay deposit were measured. Comparison of the mineral ages (obtained by K-Ar, Rb-Sr, and fission track methods) with closure temperature estimates for the various isotopic systems has allowed the thermal history of the area. The age of the intrusion was 7.1 ± 0.5 Ma (at 350°C), and the cooling rate of the intrusive rock was estimated to be $30\text{--}60^\circ\text{C/Ma}$.

Durability of bentonite: The reported values of the fission track age of zircon in the bentonite around Murakami mine are mostly within the range from 16 to 18 Ma. The age of zircon in the bentonite obtained at Murakami mine is, however 7.3 ± 0.4 Ma, which is very close to that of the intrusion. The latter value must be explained as the result of annealing for fission tracks in zircon. Hurford (1986) reported that minimum temperature of the annealing is taken to be 190°C for a $10\text{--}100^\circ\text{C/Ma}$ cooling rate. The annealing and the estimated cooling rate concludes that illitization was not scarcely occurred in $1.6\text{--}2.6$ Ma under the temperature range from 190°C to 100°C .

The waterchemistry related with the illitization was also discussed from the isotope-geochemical point of view.

U7.41

DIFFUSION OF SODIUM AND COPPER IN COMPACTED SODIUM BENTONITE AT ROOM TEMPERATURE A. Muurinen, K. Uusheimo and M. Olin, Technical Research Centre of Finland, Reactor Laboratory, Otakaari 3A, SF-02150 ESPOO, Finland

Compacted sodium bentonite has been considered as possible buffer material for final disposal of spent fuel in many countries. For safety analysis the migration mechanisms of substances in bentonite and the corresponding parameters must be known. In this research the diffusion mechanisms of sodium and copper in bentonite were studied experimentally at room temperature.

Diffusion of sodium seems to follow similar mechanisms as has been observed for cesium and strontium in several previous studies. The phenomena could be explained by some kind of diffusion of sorbed ions or surface diffusion. The measured apparent diffusivities of sodium varied from $5 \cdot 10^{-11}$ to $3 \cdot 10^{-10}$ m^2/s and the effective diffusivities from $8 \cdot 10^{-11}$ to $1.6 \cdot 10^{-9}$ m^2/s depending on the density of bentonite and the salt concentration of water solution.

Low solubility of copper caused precipitation thus interfering the diffusion experiments. However, the part of copper which did diffuse into bentonite seemed to follow the same type of mechanism as sodium. The measured apparent diffusivities of copper varied from $5 \cdot 10^{-12}$ to $5 \cdot 10^{-11}$ m^2/s .

U7.42

THERMAL BEHAVIOUR OF BACKFILL MATERIAL FOR A NUCLEAR FUEL WASTE DISPOSAL VAULT, R.N. Yong and A.M.O Mohamed, Geotechnical Research Centre, McGill University, 8167 Sherbrooke Street V., Montreal, Quebec H3A 2K6, and S.C.H. Cheung, Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, Canada ROE 1L0.

One of the performance requirements of the backfill material in a nuclear fuel-waste disposal vault is to effectively conduct heat generated by the decay of the waste into the surrounding rock. This paper presents the experimental results of the thermal behaviour of the reference Canadian backfill material subjected to various temperature gradients. The results show that the time for the backfill material to establish thermal equilibrium under a tempera-

ture gradient is much shorter than that required for moisture equilibrium. The migration of moisture in the backfill has little effect on the heat transfer process.

U7.43

A COUPLED CHEMICAL-MASS TRANSPORT SUBMODEL FOR PREDICTING RADIONUCLIDE RELEASE FROM AN ENGINEERED BARRIER SYSTEM CONTAINING HIGH-LEVEL WASTE GLASS. B. P. McGrail, D. W. Engel, M. J. Apted, A. M. Liebetau, Battelle, Pacific Northwest Laboratories, P. O. Box 999, Richland, WA 99352, and N. Sasaki, Power Reactor and Nuclear Fuel Development Corporation, Tokai-mura, Ibaraki-ken, Japan.

Battelle, Pacific Northwest Laboratories is assisting the Power Reactor and Nuclear Fuel Development Corporation of Japan (PNC) in developing models to predict the performance of an engineered barrier system (EBS) in a deep geologic repository for the permanent disposal of high-level nuclear waste. Mass transport models developed at the University of California-Berkeley and implemented in the Analytical Repository Source-Term (AREST) computer code for spent reactor fuel were modified to accommodate the borosilicate glass waste forms being considered by PNC. An analytical solution to the mass balance equations was derived that demonstrates the importance of understanding the kinetics of glass/water interactions to accurately predict diffusive mass transfer rates into the host rock. Preliminary results with the modified AREST code show that, unlike spent fuel, a distribution of containment failures over time does not significantly reduce the peak release of U-238 and Cs-135 from the glass relative to a limiting case in which all containers are assumed to fail simultaneously.

U7.44 ABSTRACT WITHDRAWN

U8.1 ABSTRACT NOT AVAILABLE

U8.2

OXIDATION OF UO_2 FUEL BY RADICALS FORMED DURING RADIOLYSIS OF WATER. S. Sunder, D.V. Shoesmith, E. Christensen, N.H. Miller and M.G. Bailey, Geochemistry and Waste Immobilization Division, Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, Canada ROE 1L0; Studsvik, S-611 82 Nykoping, Sweden.

Our studies have shown that the radical species, formed during radiolysis of water, are much more effective in causing UO_2 oxidation than the molecular oxidants formed during radiolysis of water or present in water from atmospheric sources. The effects of specific radicals on UO_2 oxidation were determined by controlling the solution chemistry, during radiolysis, to maximize the yield of a particular radical. The rate of oxidation of UO_2 during radiolysis was monitored by recording the corrosion potential of the UO_2 electrode as a function of time. Under steady-state conditions, the corrosion rate can be obtained from the corrosion potential by doing an electrochemical Tafel analysis. Our studies suggest that the oxidation of UO_2 in irradiated de-oxygenated solutions, consists of two stages. The first stage consists of the growth of a surface film of composition close to UO_2 , and similar in thickness to that obtained in unirradiated oxygenated solutions over longer exposure periods. For small doses, the rate of growth of this film appears to be proportional to the square root of the dose rate. The second stage consists of oxidative dissolution of this film (as UO_2^{2+}). This step mainly occurs at a higher dose. In irradiated oxygenated solutions, where O_2 radicals can reach concentrations of 10^{-6} $\text{mol}\cdot\text{L}^{-1}$, further surface oxidation to UO_2 and other higher uranium oxides occurs. Our electrochemical results indicate the corrosion rates of UO_2 in irradiated solutions are substantially higher in the presence of dissolved oxygen than in its absence.

U8.3

CONSTRAINTS BY EXPERIMENTAL DATA FOR MODELING OF RADIONUCLIDE RELEASE FROM SPENT FUEL.

B. Grambow*, L.O. Werme**, R. Forsyth***, J. Bruno****, Hahn-Meitner-Institut Berlin, FRG; **SKB, Stockholm, Sweden; *** Studsvik, Nyköping, Sweden; **** Royal Institut of Technology, Stockholm, Sweden

In order to find constraints for the contributions to fission product release from spent UO₂ fuel we compared a large body of data of various fuel types from research projects in Canada, USA and Sweden. There is evidence that the release data of ⁹⁰Sr can be used to describe the degradation (oxidation/ dissolution) of the matrix. A compilation of ⁹⁰Sr release data under oxidic conditions from the Swedish, the Canadian and the US spent fuel corrosion program shows surprising quantitative similarities. After 1000 days typical fractional release rates of soluble radionuclides are 10⁻⁷/d. The rate of fuel alteration under oxidic conditions is either controlled by (1) the growth rate of secondary alteration products, (2) the solubility controlled dissolution rate of the matrix or (3) the rate of formation of oxidants by radiolysis. The various explanations and their quantitative contribution are discussed in the paper.

U8.4

STATISTICAL MODEL FOR GRAIN BOUNDARY AND GRAIN VOLUME OXIDATION KINETICS IN UO₂ SPENT FUEL¹

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The Yucca Mountain Project of the USDOE is investigating the suitability of a site in the unsaturated zone at Yucca Mtn., NV for a high-level nuclear waste repository. Most of the waste will consist of UO₂ 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 UO₂ 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 UO₂ 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.

¹Work performed under the auspices of the U.S. Department of Energy, Office of Civilian Radioactive Waste Management, Yucca Mountain Project Office, by the Lawrence Livermore National Laboratory under contract W-7405-ENG-48.

U8.5

MEASUREMENT OF SOLUBLE NUCLIDE DISSOLUTION RATES FROM SPENT FUEL. Charles N. Wilson, Pacific Northwest Laboratory, P. O. Box 999, Richland, WA 99352.

Laboratory tests are being initiated to gain a better understanding of potential soluble nuclide dissolution rates from spent fuel under proposed Yucca Mountain repository conditions. The release of actinide nuclides, which account for most of the long-term radioactivity in spent fuel, should be limited by solubility to levels sufficiently low to meet Nuclear Regulatory Commission controlled release limits. The release potential for soluble nuclides such as ⁹⁹Tc, ¹³⁵Cs, ¹²⁶Sn, ¹⁴C and ¹²⁹I, which account for about 1 - 2 % of the activity in spent fuel at 1000-years, is less certain. Factors potentially affecting soluble nuclide dissolution rates include degradation of the fuel structure by oxidation in the repository air atmosphere, temperature, and fuel characteristics such as fractional fission gas release.

Semi-static tests (total water changed each test cycle and periodic sample volumes replenished during test cycles) with low temperature oxidized fuel and "high gas release" fuel are being initiated. Semi-static tests are relatively simple and simulate potential dissolution scenarios in the repository, but do not measure the fuel matrix dissolution rate or indicate the degree to which soluble nuclides are preferentially dissolved from limited concentrations at grain boundaries. Flow-through tests are being developed to determine the degree to which soluble nuclides are preferentially released relative to fuel matrix dissolution rates. A challenging aspect of the flow-through test development is the measurement of soluble nuclides at concentrations that are much lower than in the semi-static tests. The rationale for conducting these types of tests, results from semi-static scoping tests with oxidized spent fuel, analytical requirements and results from preliminary flow-through tests are discussed.

U9.1

THEORETICAL MODELING OF CREVICE AND PITTING CORROSION PROCESSES IN RELATION TO CORROSION OF RADIOACTIVE WASTE CONTAINERS, John C. Walton, Idaho National Engineering Laboratory, P.O. Box 1625, Idaho Falls, Idaho 83415

A mathematical and numerical model for evaluation of crevice and pitting corrosion in radioactive waste containers is presented. The model considers mass transport, mass transfer at the metal/solution interface, and chemical speciation in the corrosion cavity. The model is compared against experimental data obtained in artificial crevices. Excellent agreement is found between modeled and experimental values. The importance of full consideration of complex ion formation in the aqueous solution is emphasized and illustrated.

U9.2

CORROSION PRODUCT IDENTIFICATION AND RELATIVE RATES OF CORROSION OF CANDIDATE METALS IN AN IRRADIATED AIR-STEAM ENVIRONMENT.* Donald T. Reed, V. Swayambunathan, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439; and Richard A. Van Konynenburg, Lawrence Livermore National Laboratory, Yucca Mountain Project, P. O. Box 5514, Livermore, CA 94551.

Yucca Mountain Project (YMP) is investigating the feasibility of constructing a high-level nuclear waste repository in the unsaturated zone of the Yucca Mountain located in Southwestern Nevada. The high-level nuclear waste container will initially be subjected to an air-steam environment with a gamma dose rate that may be in excess of 0.01 Mrad/h. To provide input to the YMP material selection process, a literature review was performed to identify the nature of the corrosion products formed on copper-based materials. In addition, short-term experiments were performed to identify the corrosion products formed as a function of irradiation conditions. These data are also reported.

*Work supported by the U.S. Department of Energy, Office of Civilian Radioactive Waste Management, Yucca Mountain Project Office, under Contract Number W-31-109-Eng-38.

U9.3

A STUDY ON FABRICATION TECHNOLOGY OF CERAMIC OVERPACK - A CONCEPTUAL DESIGN AND FABRICATION OF A FULL SCALE CERAMIC OVERPACK. T. Teshima, Y. Karita, NGK Insulators, Ltd., Suda-cho, Mizuho-ku, Nagoya, Japan; H. Ishikawa, and N. Sasaki, Power Reactor and Fuel Development Corp., Tokai-mura, Ibaraki, Japan.

Ceramic materials are being considered as candidate materials for overpacks because of their high durability. This paper describes the conceptual design and fabrication of a full-scale ceramic overpack.

The external pressure loading, equivalent to the initial rock pressures at the depth of 1000 m, was estimated to be in the range of 280-560 kg/cm². Materials investigated were porcelain for insulators, one of traditional ceramic, and Al₂O₃ with high purity of 99.7%, one of specialized ceramic. The selected design consisted of a cylindrical shell with hemispherical heads at each end. The design thickness of overpack is the sum of the structural thickness and corrosion allowance. The thickness required to resist the lithostatic pressure, estimated by the semi-empirical design equations for buckling of shells and finite element stress analyses is 119 mm for porcelain and 40 mm for Al₂O₃. The calculated corrosion thickness for 1000 years (based on preliminary corrosion test results) is 20 mm for porcelain and <1 mm for Al₂O₃, and leads to a design thickness of 150 mm for porcelain and 50 mm for Al₂O₃.

A full-scale overpack of porcelain, of dimensions 800 mm outer diameter x 2200 mm length x 150 mm wall thickness, was fabricated under the ordinary level of fabrication technology.

U9.4

*AN INTERPRETATION OF THE HIGH-STRESS, LOW-TEMPERATURE CRACKING OF ZIRCALOY-4 SPENT FUEL CLADDING. (a) H. D. Smith, Pacific Northwest Laboratory (b), Richland, Washington 99352.

Zircaloy spent fuel cladding is expected to inhibit the access of the repository environment to spent fuel and the subsequent release of radionuclides to the environment after failure of the waste package container. Experiments were conducted on Zircaloy-4 spent fuel cladding C-rings to ascertain their susceptibility to cracking under tuff repository conditions. (These spent fuel rods will be stored in a pressurized state.) This was accomplished by stressing the C-rings with a dead-weight load while they were exposed to 90°C well J-13 water. The stress levels ranged from 80 to 96% of the observed yield stress as determined from proportional limit testing of sibling Zircaloy-4 C-rings. The C-rings broke in 26 to 245 days, depending on the stress level. Fracture characteristics observed by optical microscopy and scanning electron microscopy show the development of transgranular fractures at the beginning of cracking of the C-rings. Rapid deformation produces only ductile failure. This indicates that stress corrosion cracking or delayed hydrogen cracking are the probable mechanisms initiating failure. Two experiments run in laboratory air took longer to fail but still failed. In all cases, the fracture surface and apparent initial crack growth rates were consistent with delayed hydrogen cracking as the cause of the C-ring failure.

(a)The Yucca Mountain Project of the U.S. DOE is investigating the suitability of a site in the unsaturated zone at Yucca Mountain, Nevada, for a high-level waste repository.
(b)Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

U9.5

A CORROSION LOCALIZATION ASSESSMENT OF THE MILD STEEL USED FOR NUCLEAR WASTE PACKAGE. Masatsune Akashi, Research Institute, Ishikawajima-Harima Heavy Industries Co., Ltd., Tokyo, JAPAN

This paper describes a study of the corrosion behavior of high-level nuclear waste packages made of mild steels in the geological disposal. It has aimed at establishing the model estimates the corrosion allowance required to achieve a 1000-year life.

Series of galvanostatic tests, which can be modeled on the corrosion behavior governed by the diffusion of dissolved oxygen in the neutral environment. The maximum penetration depth and the depth distribution were measured for each specimen by a sophisticated ultrasonic inspection technique.

The Gumbel distribution model was applied to the analysis of each data set of maximum penetration depths. For the purpose of the prediction of corrosion allowance required, the distribution parameters were estimated due to the linear unbiased estimator method which allowed for extrapolation in space. The relations among the average penetration depth, the maximum penetration depth and the corrosion allowance required were discussed.

U10.1/T4.1

FRACTAL STRUCTURE AND DYNAMICS OF TWO FLUID FLOW IN POROUS MEDIA. Jens Feder, Department of Physics, University of Oslo, Box 1048 Blindern, 0316 Oslo 3, Norway.

The flow of fluids in porous media leads to displacement fronts that are fractal in many situations. We discuss results obtained in experiments on two-dimensional models. The dispersion of tracers, the invasion percolation at low displacement rates and the viscous fingering at high displacement rates are discussed. Symmetry breaking by gravity effects due to density differences leads to crossover phenomena that can be described by scaling functions. New results on the displacement in three-dimensional models are presented.

Fractal displacement processes exhibit dynamic scaling behavior characterized by new exponents, which we discuss in the context of invasion percolation.

U10.2/T4.2

NUMERICAL AND ANALYTICAL MODELS OF TRANSPORT IN POROUS CEMENTITIOUS MATERIALS. Edward J. Garboczi and Dale P. Bentz, National Institute of Standards and Technology, Building Materials Division, 226/B348, Gaithersburg, MD 20899.

Fluid flow under applied pressure gradients and ionic diffusion under applied concentration gradients in the pore space of a cementitious material are the key transport mechanisms that take place in these materials. Recent theoretical developments in the research labs of the oil exploration industry give new insight into how these processes can be successfully modelled at a fundamental level for cementitious materials. This talk will describe new computational methods for computing effective diffusion constants in models of porous materials, and analytical percolation-theory-based equations for predicting effective permeabilities. Digitized image modeling techniques developed at NIST will also be described.

U10.3/T4.3

SIZING REQUIREMENTS FOR FLOW-THROUGH GEOCHEMICAL TESTS THEORETICAL CONSIDERATIONS. J. D. Hoover and E. C. Thornton, Westinghouse Hanford Company, P.O. Box 1970, Richland, WA 99352

A methodology for evaluating test apparatus size requirements has been applied to the sizing of flow-through tests used in the evaluation of coupled processes in open hydrothermal systems. The results of the sizing evaluation provide limits on the apparatus dimensions and test conditions required to yield results representative of the processes of interest. It is indicated from these evaluations that this information is critical in the design of flow-through tests and in the interpretation of test results. Size considerations, therefore, impact the use of flow-through test results in simulating the processes expected to occur in the near-field environment of a nuclear waste repository.

The main objective of this size evaluation is determination of the column dimensions and test conditions necessary to produce reactions pertinent to the processes of interest. The basis of the evaluation is treatment of the time required for reactions or processes of interest to occur, as the required column residence time for the fluid. Reaction paths and reaction times for model systems were determined using geochemical models involving reaction rate equations based on transition state theory. The range of appropriate column dimensions may then be obtained using expressions relating residence time to apparatus dimensions and flow conditions.

A finite range of appropriate column dimensions and test conditions exist for a given residence time requirement. However, determination of appropriate residence time depends on the purpose of the test and processes of interest. Factors such as test duration, sampling requirements, and engineering limitations must also impact the size and/or scale requirements and these criteria can be used in the choice of the most practical combination of column dimensions and test conditions. It is indicated from the results of this study that size evaluations provide a technical basis for the design and construction of flow-through tests, and also for the interpretation of test results.

U10.4/T4.4

A LAGRANGIAN REACTIVE TRANSPORT SIMULATOR WITH MULTIPLE PATHS AND STATIONARY-STATES: CONCEPTS, IMPLEMENTATION AND VERIFICATION. E. B. Knapp, L206, Earth Sciences Department, Lawrence Livermore National Laboratory, University of California, Livermore, California 94550

A geochemical software package which models static, single-path kinetic water-rock interactions, EQ3/6 [Wolery, T. J., Lawrence Livermore National Laboratory, UCRL-52658, 1979], has been modified to incorporate multiple-paths and stationary states under high Peclet number transport conditions in a Lagrangian reference frame [Lichtner, 1988]. These modifications permit calculation of reactive transport with reasonable computational requirements. Results from the new code, mpeq6, have been compared with analytical results for the simple HCl - SiO₂ system; excellent agreements were achieved. Results from mpeq6 have also been compared with published results [Lichtner, P., *Geochim. Cosmochim. Acta*, 52, 143-165, 1988] for a portion of the Al₂O₃ - HCl - K₂O - SiO₂ system. The results are in good qualitative and, in some cases, good quantitative agreement. However, the values of some variables differ substantially; these differences can be attributed to use of a different set of Al and Si aqueous species.

U10.5/T4.5

FRACTAL CHARACTERISTICS OF FRACTURE NETWORKS AND FLUID MOVEMENT IN ROCK. Christopher C. Barton, Box 25046, MS 913, Federal Center, Denver, CO 80225

Society's need to recover fluid resources (water, oil, and gas) from the Earth and to inject toxic waste materials in a reliable manner requires quantitative models to describe and predict the movement of fluids in rock. Existing models based on pore-space flow are inappropriate for study of the more rapid process of fluid flow through fracture networks. This type of flow is not a simple function of the fracture characteristics at any particular scale, but rather the integration of contributions at all scales.

The mathematical constructs of fractal geometry are uniquely suited to quantify and model relationships within complex systems that are statistically equivalent (that is, self-similar) at all scales. My results show that natural fracture networks in rock follow a fractal scaling law over six orders of magnitude. Detailed

measurements of two-dimensional samples of three-dimensional fracture networks (at diverse scales in rocks of dissimilar age, lithology, and tectonic setting) show similar fractal dimensions in the range 1.6-1.8.

The small range in fractal dimension implies that a single physical process of rock fracturing operates over a wide range of scales, from microscopic cracks to large, regional fault systems. Independent field evidence has previously demonstrated that rock fracturing is an iterative process in which preexisting fractures influence the formation of subsequent fractures (such behavior is characteristic of fractal processes). The fractal behavior implies that fracture-network development is governed by a nonlinear equation. Fortunately, the ability of fractal mathematics to accurately quantify and model the system is not dependent on specific knowledge of this equation, as the equation has not yet been identified.

Knowledge that rock fracture networks are fractal allows use of data from a one-dimensional drill-hole sample to predict the two- and three-dimensional attributes of the fracture system. The spacing of fractures in drill holes is a fractal Cantor distribution, and the range of fractal dimension is 0.6-0.8, which is an integer dimension less than that of fracture-trace patterns exposed on two-dimensional, planar sections. The pattern of rock-matrix flow can exhibit fractal fingering, and matrix permeability is patchy in a manner analogous to fractal percolation clusters.

U10.6/T4.6

FLOW TO WELLS IN FRACTURED ROCK WITH FRACTAL STRUCTURE. Jim Polek, Kenzi Karasaki and Jane Long, Lawrence Berkeley Laboratory, Berkeley, CA; and John Barker, British Geological Survey, Wallingford, Oxfordshire, U.K.

Traditionally, models of fluid transport in rocks have been based on an integral (Euclidean) flow dimension. However, this assumption is not necessary and may not always be appropriate, especially for rocks with poorly connected fractures. Barker (1988) has formulated and solved the equation of flow to a well in a rock system characterized by an arbitrary flow dimension.

Using Sierpinski's carpet and a random percolating network, we generated two types of fractured rock systems with fractal properties. We then simulated hydraulic well tests in these systems. Both the fractal dimensions and the "radial" fractal dimensions of the systems were calculated using Orbach's (1986) method. The latter was calculated by accounting for only the radial component of the conductor. Of the two, we found that the radial fractal dimension better describes the physical processes occurring during a well test. The results from the well tests were in agreement with Barker's solution and a relationship between the slope of the pressure response curve and the radial fractal dimension was found. This relationship is significant because it could lead to a value for the fractal dimension of rock from field well test data. This field fractal dimension could then be used to estimate the rock's flow geometry and flow characteristics.

U10.7/T4.7

ANISOTROPIC SCALING OF INTERFACES IN POROUS MEDIA. Miguel A. Rubio, Haverford College, Haverford, PA, and UNED, Madrid, Spain; Andrew Dougherty, Haverford College, Haverford, PA; and Jerry P. Gollub, Haverford College, Haverford, PA, and University of Pennsylvania, Philadelphia, PA.

Two-fluid immiscible displacement may produce self-similar fractal interfaces, often described by invasion percolation or DLA models, for certain ranges of the relative viscosities and wetting properties of the fluids. These self-similar structures have the same scaling behavior in all directions.

Here we show that when the displacing fluid is more viscous and more efficient in wetting the medium, the interfaces are self-affine fractals, i.e., they show different scaling in different directions. We present experimental results on the interfaces obtained when water displaces air in a thin layer of glass beads. We have characterized the interfaces by computing their roughness (r.m.s. value of the interfacial width) as a function of length scale. The roughness shows power-law behavior with exponent $\beta = 0.73 \pm 0.03$, independent of the control parameter (capillary number, Ca). This exponent is related to the box dimension

2- β , and the divider or compass dimension $1/\beta$. This behavior means that the interfaces are self-affine fractals with a box dimension of 1.27.

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U10.8/T4.8

SIZING AND SCALING REQUIREMENTS OF A LARGE-SCALE PHYSICAL MODEL FOR CODE VALIDATION. R. Khaleel, T. LeGore, and J. D. Hoover, Westinghouse Hanford Co., Richland, WA.

Post-closure performance assessment and the associated application of mathematical models play a critical role in assessing the long-term behavior of the engineered and natural barriers of a geologic repository. Although verification and benchmarking constitute an important part of determining model acceptability, it does not establish that the model is a reasonable approximation to physical reality. This is accomplished in the validation step in which model calculations are compared with data from controlled experiments.

Although in-situ field experiments provide useful data, information needed for model validation cannot be obtained from field observations alone because of the inherent uncertainties associated with the natural system. However, physical models, when properly scaled, constructed, and instrumented can provide the necessary information for validation of mathematical models and computer codes, and can overcome many of the uncertainties associated with large-scale in-situ testing. The relationships between measurement, size, scaling, and discretization (block size) used in a numerical model must be incorporated in the conceptualization of a physical model. Sizing and scaling requirements of a large-scale physical model for hydrological testing are discussed. The justification for the minimum size of a physical model for hydrological testing can be based on the nature of heterogeneities introduced into the model. Results of numerical simulations used to determine the preliminary size requirements of a porous medium model are presented.

U10.9/T4.9

PERFORMANCE OF CONCRETE BARRIERS IN RADIOACTIVE WASTE DISPOSAL IN THE UNSATURATED ZONE. John C. Walton and Mark D. Otis, Idaho National Engineering Laboratory, P.O. Box 1625, Idaho Falls, Idaho 83415

Concrete barriers are an important component of many designs for disposal of radioactive waste in the unsaturated zone. In order to evaluate the effectiveness of the concrete barriers performance assessment models representing the material degradation and behavior must be developed. Models for evaluation of fluid flow and mass transport through concrete barriers located in the unsaturated zone are presented. Implications of the use of impermeable membranes in barrier design are discussed. The effectiveness of the concrete is shown to be dependent upon effective design. Concrete of highest quality may not always be desirable for use in waste disposal vaults.

U11.1

LEACHING/MIGRATION OF UO₂-FUEL IN COMPACTED BENTONITE. Y. Albinsson, G. Skarnemark, M. Skälberg, Department of Nuclear Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden; R. Forsyth, Studsvik AB, S-611 82 Nyköping, Sweden; B. Torstenfelt, ABB-Atom, S-721 63 Västerås, Sweden; L. Werme, Swedish Nuclear Fuel and Waste Management, Box 5864, S-102 48 Stockholm, Sweden.

In the Swedish concept for final disposal of high-level radioactive waste, bentonite clay (BC) has

been proposed as a suitable backfill material. It is therefore important to investigate the influence of BC on the corrosion of spent UO₂-fuel and on the release behaviour of fission products (FP's) and actinides (An's). In this investigation the leaching/migration of FP and An's from spent fuel pellets into highly compacted BC is measured.

The release and migration of the FP's Cs, Eu and Tc and the An's U, Pu, Am and Cm is measured after different contact times (0.3, 0.5 and 1.1 a). Experiments aiming at longer contact times are in progress. In some cases small amounts (0.5-1%) of Cu, Fe or vivianite have been added to the BC.

The results indicate a high mobility of Cs. The An's have a very low mobility. After 1.1 year, Pu has diffused less than 0.5 mm away from the fuel. Am and Cm appear to be somewhat more mobile. The behaviour of Eu is similar to that of An(III). Tc has a high mobility in BC, except in the case of iron addition.

U11.2

MODELLING THE IN SITU PERFORMANCE OF BENTONITE-SAND BUFFER. H.S. Radhakrishna, K.-C. Lau, Ontario Hydro Research Division, Location KR252, 800 Kipling Avenue, Toronto, Ontario, Canada M8Z 5S4, B.H. Kjartanson and S.C.H. Cheung, Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, Canada ROE 1L0.

In the Canadian nuclear fuel waste management concept, a number of engineered barriers, such as the waste containers and the bentonite-sand buffer, are used to inhibit the transport of radionuclides. The buffer material is also required to effectively conduct the heat from the waste containers to the surrounding rock. This paper examines the principal processes occurring in the buffer before water saturation takes place, and the impacts of such processes on buffer performance. Particular emphasis is placed on the modelling of heat and moisture transfer. Numerical simulations show that the temperature distribution can be reasonably predicted by the Philip-DeVries model, while the moisture distribution is found to be sensitive to the transport coefficients, and also depends on the hydraulic boundary conditions.

U11.3

THE EFFECT OF CRACKS ON DIFFUSIVE MASS TRANSPORT THROUGH A CLAY BARRIER. Nava C. Caristo and Frank Caristo, Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, Canada ROE 1L0

Clay-based barriers are often proposed as engineered sealing systems for underground disposal vaults of used nuclear fuel. Thus, in the Canadian conceptual vault design, each used-fuel container is emplaced in a vertical borehole in rock and surrounded by a compacted buffer material, made up of a mixture of sodium bentonite and sand. There is some evidence, however, that the buffer may be susceptible to fracturing due to, for example, cementation or moisture depletion.

In this paper we estimate numerically the consequences of fracturing on radionuclide diffusion through a finite buffer layer. The cases studied represent hypothetical crack widths and density of cracks in a reference system based on the Canadian conceptual vault design.

The results indicate that for swept away boundary conditions at the buffer/rock interface, the total flux through the cracked buffer system is, as expected, greater than through the corresponding uncracked buffer. However, the effect of the cracks, which depends on the crack's width and the inter-crack spacing, is relatively small.

Moreover, for the case in which the rock at the buffer/rock interface is intact and thus, the mass transport of material

from the buffer into the rock is small, the effects of cracks on the total release flux is negligible.

U11.4

FINAL DISPOSAL OF CEMENTITIOUS WASTE FORMS IN THE SWEDISH REPOSITORY FOR REACTOR WASTE (SFR). Jan S Carlsson, Swedish Nuclear Fuel and Waste Management Co (SKB), P O Box 5864, S-102 48 Stockholm, SWEDEN.

Disposal of LLW/ILW from the operation of Nuclear Power Plants in Sweden takes place in an underground repository (SFR) close to the Nuclear Power Plant in Forsmark. The waste is mainly spent ion exchange resins solidified in cement or bitumen. Approximately 90% of the radionuclide inventory will be allocated to a concrete silo surrounded by bentonite, at the time of sealing. This paper focus on requirements on ion exchange resins immobilized in cement for final disposal in the SFR silo.

Apart from general requirements on the design (dimensions, weight etc) and management (marking, documentation etc) the requirements could be divided into groups with respect to:

- radiological, chemical and mechanical properties

To ensure a diffusion scenario for transport of radionuclides from the silo the surrounding clay (bentonite) barrier has to be intact.

Gas production inside the silo, or swelling of waste packages, could crack the silo walls.

All requirements on a waste package and how they are fulfilled are described in a Waste Type Description.

U11.5

MASS TRANSFER IN WATER-SATURATED CONCRETES
Alan Atkinson, Peter A Claisse, Nicola M Everitt, Andrew W Harris, and Alan K Nickerson, Materials Development Division, Building 429, Harwell Laboratory, Oxon, OX11 0RA, UK

Cements and concretes are often considered as barriers helping to contain radionuclides in waste repositories. The performance of cementitious material as a mainly physical barrier to the escape of dissolved radionuclides depends on the mass transfer characteristics of the chosen material(s). In particular the diffusion and sorption behaviour of individual radionuclides and the water permeability are important. These parameters also influence the way in which the chemistry of the concrete is imposed on the rest of the repository and, in addition, the transport of gas through concretes controls the way in which gases escape from the repository. These parameters have been measured for a variety of cementitious materials covering different types of structural concrete and cementitious backfills; all possible repository construction materials. Diffusion measurements have been made using aqueous iodide, strontium and caesium ions and tritiated water as diffusing species. The results show that diffusion of tritiated water is much more rapid from that of other species whilst the transport of strontium and caesium is hindered by sorption; particularly in materials containing blast furnace slag. The transport of gas through these materials has been found to be very sensitive to the degree of water saturation and is extremely low in fully saturated structural concretes. Cementitious backfills have, nevertheless, been identified that have appreciable gas transport even when almost saturated.

The consequences of the results for the performance of cementitious barriers are discussed.

U11.6

COUPLED FLOW OF HEAT AND MASS IN BARRIER MATERIALS AND ITS SIGNIFICANCE, S.C.H. Cheung, Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, Canada ROE 1L0.

In a nuclear fuel waste disposal vault, simultaneous non-congruent flow of heat, fluid and solutes due to differences of temperature, hydraulic potential and solute concentration will occur in the water-saturated clay-sealing material. The coupled processes have been assessed by a method that uses irreversible thermodynamic processes. The theoretical results show that the coupling effects depend on the relative magnitude of the gradient of the temperature, solute concentration and hydraulic potential as well as the permeabilities of the sealing materials and of the rock. For the Canadian disposal concept, the results indicate that mass transport in the saturated buffer and backfill should be controlled mainly by molecular diffusion.

U11.7

EFFECTIVE DIFFUSIVITY OF CARBON DIOXIDE AND IODINE THROUGH "G TUNNEL TUFF". Tefvik Bardakci, Franklin G. King, and Maung Sein, North Carolina A&T State University, Greensboro, NC, 27411.

The Topopah Spring Member of the Paintbrush Tuff in Yucca Mountain, Nevada is a prime candidate for the site of the first national high level radioactive waste repository. One of the questions to be answered in characterizing the site is the extent of diffusion of radioactive gases, such as carbon dioxide and iodine, to the accessible environment. The objectives of this study were to measure the effect of temperature and water content on the effective diffusivity of carbon dioxide and the effect of temperature on the effective diffusivity of iodine through Topopah Spring Tuff and to characterize the pore structure of Topopah Spring Tuff. Since Topopah Spring Tuff samples were not made available, experiments were conducted with tuff samples from a nearby location called Rainier Mesa Ash flow from "G" tunnel.

Information obtained on the diffusion of gases through tuff provides data to determine whether the Nuclear Regulatory Commission and Environmental Protection Agency regulations can be met. There is presently no available data for the diffusion of carbon dioxide and iodine, which are released from the nuclear waste, through tuff.

The effective diffusivity of carbon dioxide and iodine through "G" tunnel tuff were determined using a steady-state method (counter diffusion) and an unsteady-state method respectively. Results show that the effective diffusivity of carbon dioxide and iodine through dry tuff increased with temperature. The effective diffusivity of carbon dioxide decreased as the moisture content of the "G" tunnel tuff increased. An empirical correlation was obtained to estimate the effective diffusivity of carbon dioxide as a function temperature and the percent saturation. Specific surface area and pore volume of the samples were determined using a mercury porosimeter. A scanning electron microscope was utilized to further characterize the porous structure of the tuff samples.

U11.8

¹⁴C TRANSPORT IN A PARTIALLY SATURATED, FRACTURED, POROUS MEDIUM. W. B. Light, P. L. Chambré, W. W.-L. Lee, and T. H. Pigford, Department of Nuclear Engineering and Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720.

Radioactive gases released from waste placed in the partially saturated rock would have a direct pathway to the biosphere. This presents a new problem in assessing the potential health impacts of such releases, and in complying with regulations.

We analyse the transport of ¹⁴C in an unsaturated, fractured, porous medium with gas-phase advection and dispersion. Gases released into a partially saturated, fractured rock move in the fractures, while pore water is held inside the rock matrix. First we assess the interaction of ¹⁴C in CO₂ with bicarbonate ion in ground water as a possible retardation mechanism. Then we treat the combined fracture and pore matrix as an equivalent porous medium with local carbon-distribution equilibrium between the gas and liquid phases.

Our results indicate that liquid in the rock matrix between fractures will reach essentially the same equilibrium concentration as the liquid at the fracture walls when the modified Peclet number $Lq_0/\epsilon K_D D_l$ is much less than unity, where L is half the distance between fractures, q_0 is the gas Darcy velocity, ϵ is the porosity, K_D is the equilibrium distribution coefficient defined as the molar concentration of liquid-phase carbon divided by the molar concentration of gas-phase carbon, and D_l is the liquid-phase diffusion coefficient.

We then solve the equation for the transport of ¹⁴C in an equivalent porous medium. With the retardation just described the advection velocity v and dispersion coefficient D obtained for ¹⁴C are

$$v = \frac{q_s}{\epsilon(1-S) + SK_D}$$

$$D = \frac{(S)D_f + SK_D D_i}{(1-S) + SK_D}$$

where S is the liquid saturation and D_f is the dispersion coefficient for the gas phase. The solution is based on space-time-invariant values for ϵ , S , K_D , q_s , D_f , and D_i . Using parameter values from the Yucca Mountain SCP we predict peak ^{14}C concentrations at the ground surface comparable to the USNRC limit for unrestricted areas of $10^{-7} \mu\text{Ci}/\text{cm}^2\text{-Air}$. In the paper we present predicted ^{14}C concentrations from point or plane sources, with either an impulse or band-release source term.

U11.9

THE APPLICATION OF A COUPLED CHEMICAL TRANSPORT MODEL IN A TRIAL ASSESSMENT OF DEEP DISPOSAL OF LOW AND INTERMEDIATE LEVEL RADIOACTIVE WASTE

Steve Liew, Vea Economides, Adrian Dawes and David Read. WS Atkins Engineering Sciences, Woodcote Grove, Ashley Road, Epsom, Surrey, United Kingdom KT18 5BW.

The UK Department of the Environment is developing an independent capability to evaluate proposals made for the deep underground disposal of low and intermediate level radioactive wastes. Coupling of chemical processes with hydrodynamic transport has been identified as an important element of the assessment strategy and a suite of models has now been developed which fully couple thermodynamic mass action expressions to advection-diffusion terms.

This paper illustrates the use of the CHEMTARD (Chemical Transport Adsorption Redox and Decay) code by reference to studies on waste disposal and natural analogue sites within the UK. The role of such methods within the overall DOE methodology is highlighted through a trial assessment of deep disposal beneath Harwell, Oxfordshire.

The feasibility of employing a mechanistic approach to quantifying sorption processes is explored and comparisons drawn with more simple analytical models based on linear adsorption isotherms. The implications for risk assessment practices reliant on the assumption of "conservative" parameter distributions or worst case estimates is discussed.

U11.10

ANALYSIS OF MASS TRANSPORT IN AN ENGINEERED BARRIERS SYSTEM FOR THE DISPOSAL OF USED NUCLEAR FUEL. Nava C. Garisto and Dennis M. LeNeveu, Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, Canada ROE 1L0.

The Vault Model has been developed to assess the performance of engineered barriers in a conceptual geological disposal vault for used nuclear fuel. It represents container failure, release of radionuclides from used fuel and mass transport of released radionuclides through the clay-based sealing materials surrounding the waste containers. This paper focuses on mass-transport processes represented by the Vault Model, including diffusion, convection and retardation.

In particular, we present results of several scoping calculations carried out with the Vault Model. We consider cases where the clay-based barriers are represented by either a one- or a two-layer system adjacent to an intact rock and a case where the two clay-based barriers are adjacent to a highly fractured rock.

These calculations provide insight into the model and produce test cases for comparison with both relatively simple analytical estimates and similar computer codes, as they become available. The analytical estimates generally support the Vault Model results and thus enhance our confidence in the accuracy of the Vault Model calculations.

U11.11

ATTEMPTED VERIFICATION OF MATRIX DIFFUSION IN GRANITE BY MEANS OF NATURAL DECAY SERIES DISEQUILIBRIA. W.R. Alexander, Paul Scherrer Institute, 5232 Villigen, Switzerland; I.G. McKinley, NAGRA, 5401 Baden, Switzerland; A.B. MacKenzie, R.D. Scott, SURRC, Glasgow G75 0QU, Scotland and

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According to the Swiss concept for the disposal of radioactive waste, the material will be placed in deep rock formations to ensure that only small amounts, if any, of radionuclides released from the waste packages ever reach the surface and so enter the biosphere. It is, however, likely that the rock formation will be fractured and that advection along the fractures will be the dominant mechanism of radionuclide transport from the repository.

It has been suggested that, in systems where such advective flow is dominant, radionuclides might gain access to the rock surrounding the fractures by diffusion in a connected system of pores or microfractures - the so called "matrix diffusion".

Matrix diffusion is difficult to study in the laboratory due to the very slow transport rates involved but one approach which can circumvent this and other problems involves the study of the natural decay series in profiles perpendicular to water bearing fractures. The preferential mobility of U and Th daughters relative to their parents can enhance their removal from the bulk rock, by diffusion, to the fractures. This transport of natural decay series radionuclides is thus analogous to the diffusion of solute from a fracture into the rock as considered in safety analysis models.

In this paper we present a detailed study of a rock core in which there are clear signs of water-rock interactions in and around a fracture with an especially striking indication of Radium remobilisation across the fracture. The geochemical data are interpreted with the aid of a detailed mineralogical examination of the core in conjunction with data from laboratory sorption experiments. A more realistic definition of matrix diffusion is presented and the implications of the results with respect to mathematical representations of such mechanisms in safety assessment models are discussed.

CORROSION BEHAVIOR OF ZIRCONIUM ALLOY NUCLEAR FUEL CLADDING

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ABSTRACT

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

INTRODUCTION

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

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

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

treatment, and in selected tests, crevice corrosion was evident after exposure to the tests.

MATERIALS AND METHODS

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

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

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

Microstructures of the Zircaloy-2 and -4 wrought materials are shown in Figures 1 and 2. Test specimens were cut from the raw materials and from the cladding tubes. The size of the cut specimens ranged from 0.5 to 0.6 cm² and after masking for corrosion testing, the corrosion test specimen size ranged from 0.4 to 0.5 cm². Specimens from the wrought material received from the Teledyne Wah Chang Company, were cut so that the exposed area was a transverse microstructural section. These specimens were mechanically polished through 300 to 600 grit SiC papers and then with 6 um and 1 um diamond paste and were given a final polish with 0.05 um Al₂O₃. Following the polishing, the specimens were washed with water and then ethyl alcohol to remove any polishing material or contaminants.

Specimens from all of the cladding tube materials were cut to expose longitudinal microstructural sections, and both inner and outer tube sections were tested. Two different surface preparation procedures were used for the cladding tube specimens. Some specimen surfaces were polished with 0.05 um Al₂O₃, washed with water and ethyl alcohol and dried. Other specimen surfaces were prepared only by washing in acetone, ethyl alcohol and water. Test specimens were connected to a titanium lead using with a conducting epoxy or by spot welding, mounted in a glass tube and surrounded with a high temperature epoxy. Specimens of 0.5 cm² were tested one day after preparation or were stored in a desiccator.

Specimens of all types of materials were prepared for microscopic study. These specimens were mounted and polished as described and then were etched in a mixture of 20 ml Lactic acid, 5 ml HNO₃, 5 ml H₂O₂, 2 ml HF and swabbed for 10 to 30 seconds. Representative photomicrographs of the specimen microstructures were taken using light microscopy.

The testing environment for these specimens was a simulated well water found at Yucca Mountain, Nye County, Nevada. The Brookhaven National Laboratories[3] developed a procedure for preparing artificial J-13 well water that had the following chemical content in terms of mg/L; lithium, 0.05, sodium, 51.0; potassium, 4.9; barium, 0.003,; iron, 0.04; aluminum, 0.03; silica, 61.0 fluoride, 2.2; chloride, 7.5; bicarbonate, 120.0; sulfate, 22.0; nitrate, 5.6; and phosphate, 0.12. The same procedures were used to prepare the water for the present study except that the composition was adjusted to one that was concentrated ten times. Some tests were run in this water diluted to the unconcentrated form. The water is heated but not boiled for mixing, and is saturated with some of the chemicals as indicated by the undissolved particles in the container. The pH of this concentrated water is 8.5 at 22°C. The pH of

the unconcentrated water[3] was given as 7.1. The pH of the diluted water to a concentration of one prepared in this was 8.3.

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

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

RESULTS AND DISCUSSION

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

Microstructures

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

The cladding tubes were sectioned to show the microstructure in both the longitudinal and the transverse directions. The longitudinal section of the Zircaloy-2, of Figure 3, did not show much grain elongation due to the drawing. The precipitates in the Zircaloy-2 seem to be randomly distributed with some being at the grain boundaries. The Zircaloy-4 cladding, of Figure 4, was more affected by the production of the cladding tubes, and as evidenced in the elongated grain structure. Some precipitates were randomly located and others were at grain boundaries.



Figure 1. Zircaloy-2, etched.



Figure 2. Zircaloy-4, etched.

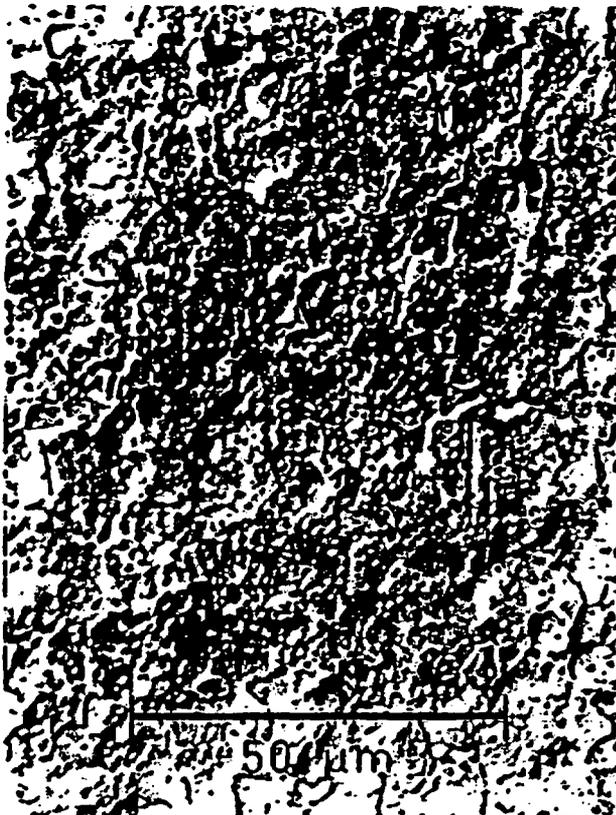


Figure 3. Zircaloy-2 cladding, longitudinal section, etched.

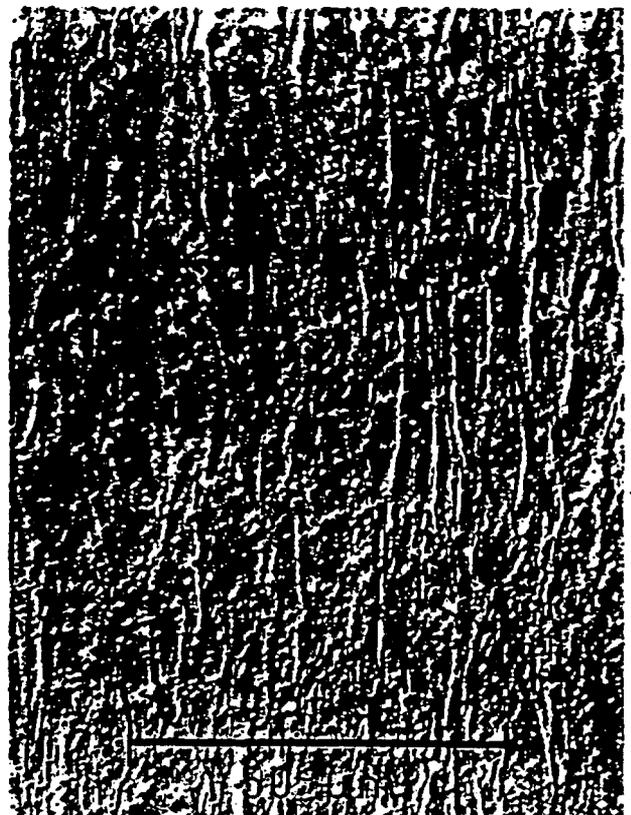


Figure 4. Zircaloy-4 cladding, longitudinal section, etched.

Passivity

Specimens were immersed in the testing solution (not deaerated) of the J-13 water shown in Table 2 that was held at 95°C and had a pH of 8.5. Upon immersion, the specimens of the wrought Zr-2 and Zr-4 would tend to passivate. This was indicated by the increase in the open circuit electrode potential when monitored versus time. For example, if the initial potential were -0.573 V, it could change to -0.473 V after five to fifteen minutes and to -0.250 V after twelve hours. This change of electrode potential in the positive direction indicates passivation. Specimens for all polarization tests using this material also showed this positive trend for the open circuit potential after the fifteen minute waiting period prior to testing. Specimens of the cladding material, both inside and outside of the tubing, that had the surface polished lightly with 0.05 μm Al_2O_3 , also showed an a positive trend in the potential after the fifteen minute waiting period. Specimens of the tubing that were washed in acetone and alcohol using the ultrasonic cleaner, but which did not have the surface polished, did not show this positive trend. This information indicated that the surface preparation or surface exposure affects the initial passivation of the Zircaloy.

Polarization

Cyclic polarization measurements, showing the current versus the applied potential, were made on the materials to determine the passive region, the breakdown potential and other features of the corrosion behavior of the Zircaloy materials. The breakdown potential, marked by a sharp rise in current, for the Zircaloy bulk materials ranged from 0.800 V to 1 V. The Zr-2 cladding with the oxide coating did not appear to breakdown until reaching 1.6 to 2.2 V. There was some variation in the breakdown potentials of these materials. The polarization curves for the bulk materials exhibited a wide range of passivity, extending over approximately 1200 millivolts. Passive regions and breakdown potentials for the cladding tubes were less distinct. Figures 5 and 6 are cyclic polarization curves for Zr-2 and Zr-4, respectively, in J-13 water at 95°C, and were produced using a scan rate for applying the potential of 0.05 V/sec. The hysteresis present can be interpreted as indicating susceptibility to localized corrosion, but this is not necessarily always true since other factors such as the environment and scanning rate of applying the potential during the test can cause this effect. There were some problems with mounting and shielding the Zircaloy specimens for the tests at the higher temperature. There often was a visual indication of crevice corrosion at the mounting/specimen interface and of limited pitting. In other tests, there was no indication of localized corrosion.

Some tests were conducted in unconcentrated J-13 water, and Figures 7 and 8 are cyclic polarization curves for Zr-4 at temperatures of 22°C and 95°C, respectively. The specimen was kept at a temperature of 22°C for twenty five days. Raising the temperature to 95°C caused a change in the curves indicated by hysteresis and a shift in the corrosion potential as is shown in Figure 8. The curve in Figure 7 that was measured at 22°C shows the return portion to have lower current indicating increased passivity. Representative results of cyclic polarization tests on the inner and outer surfaces of the cladding tubes are given in Figures 9 through 12. The hysteresis in these curves is less than that for the wrought specimens. The current in the passive region is increased and breakdown potential is not sharply defined for the cladding materials.

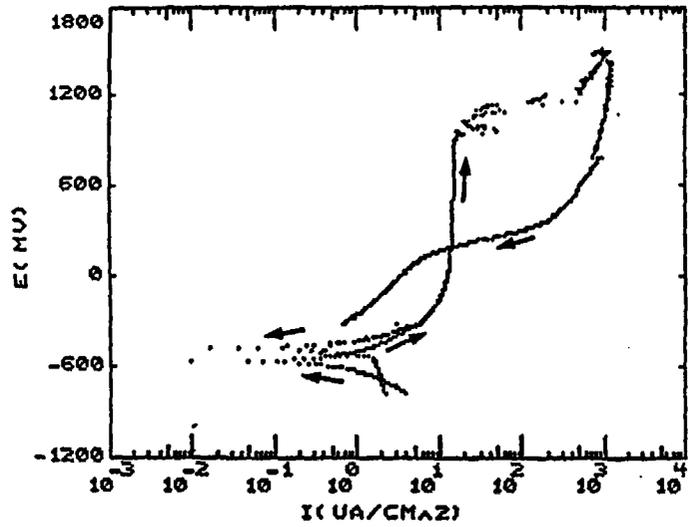


Figure 5. Cyclic polarization curve for Zircaloy-2 in J-13 water, pH = 8.5, 95°C.

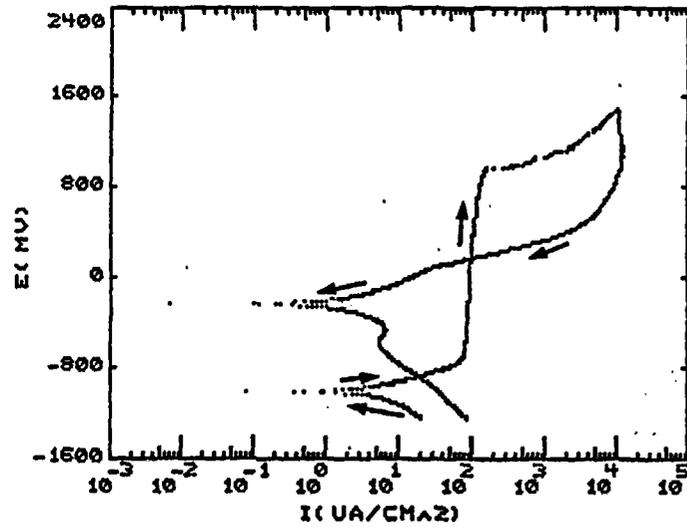


Figure 6. Cyclic polarization curve for Zircaloy-4 in J-13 water, pH=8.5, 95°C.

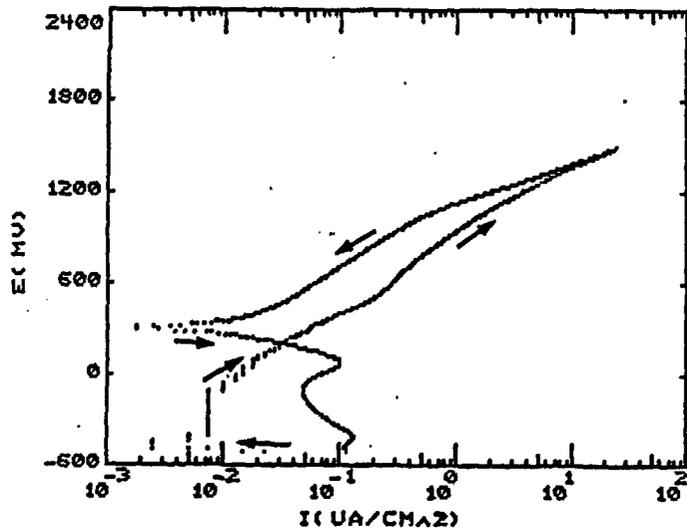


Figure 7. Cyclic polarization curve for Zircaloy-4 in J-13 water, pH=8.3, 22°C

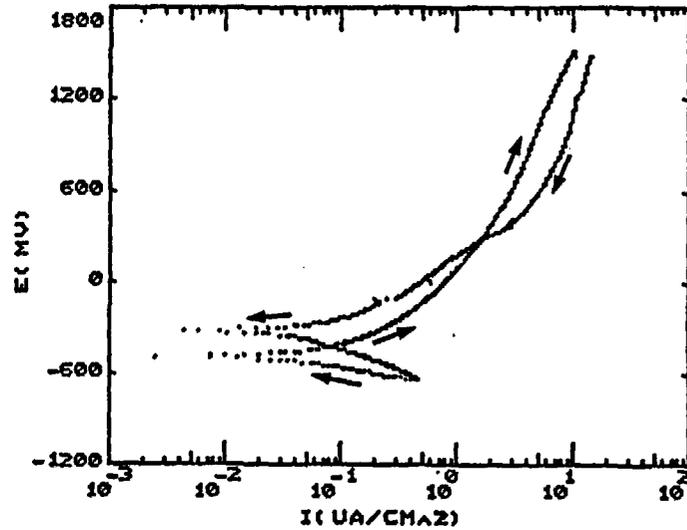


Figure 8. Cyclic polarization curve for Zircaloy-4 in J-13 water, pH=8.3, 95°C.

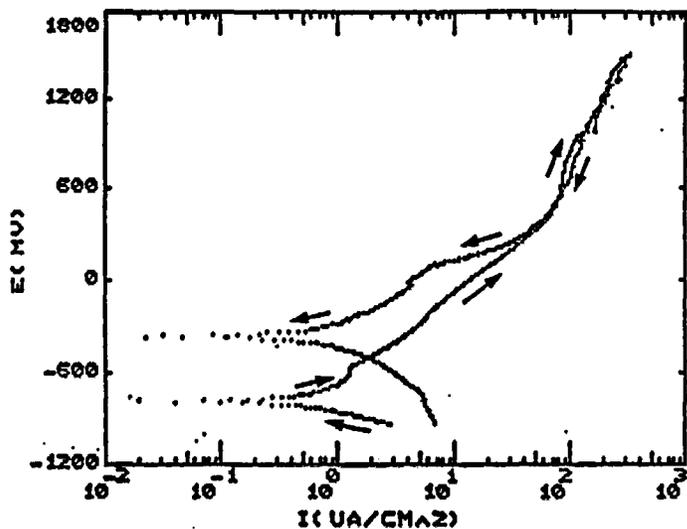


Figure 9. Cyclic polarization curve for inner surface of Zircaloy-2 cladding tube in J-13 water, pH=8.5, 95°C.

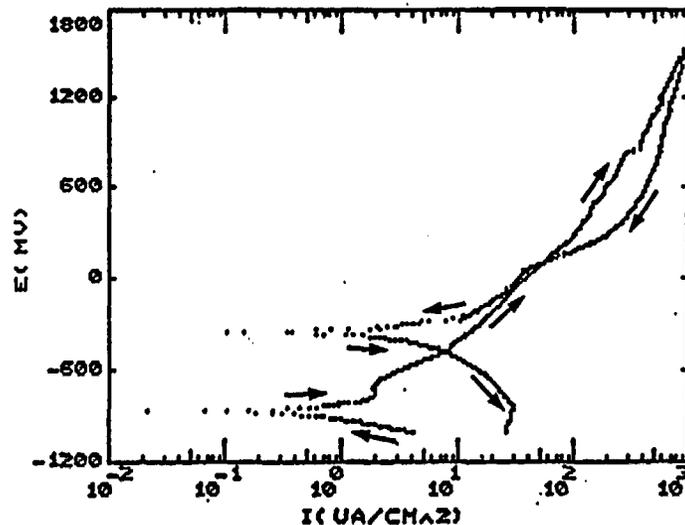


Figure 10. Cyclic polarization curve for outer surface of Zircaloy-2 cladding tube in J-13 water, pH=8.5, 95°C.

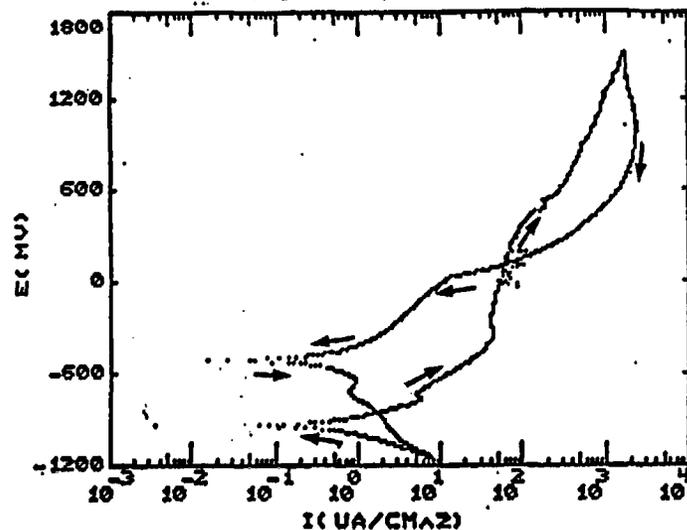


Figure 11. Cyclic polarization curve for outer surface of Zircaloy-4 cladding tube in J-13 water, pH=8.5, 95°C.

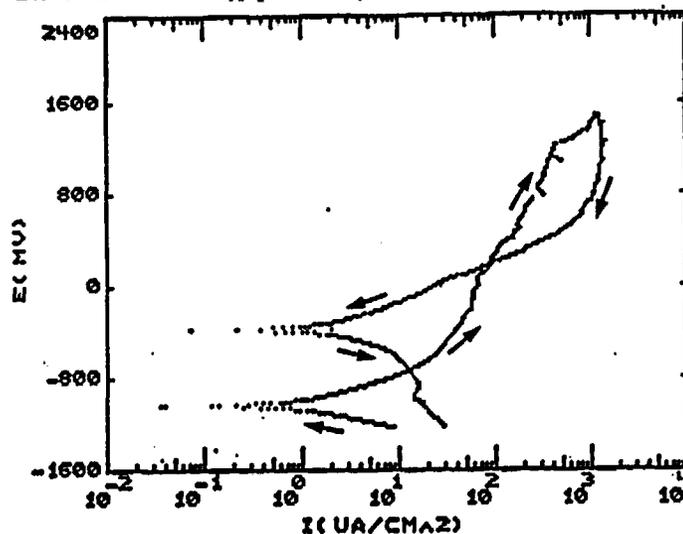


Figure 12. Cyclic polarization curve for inner surface of Zircaloy-4 cladding tube in J-13 water, pH=8.5, 95°C.

SUMMARY

Cyclic polarization measurements were made on the alloys, Zircaloy-2 and Zircaloy-4 in simulated Nye County, Nevada J-13 well water at 95°C. These measurements were made to obtain data on corrosion of Zircaloy under conditions which could occur in the nuclear waste repository. Overall, the Zircaloy shows a low or negligible corrosion rate under all of the conditions tested, but there is evidence of localized corrosion in the electrochemical data and at crevice corrosion sites resulting from the specimen mount.

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

1. Exposure of wrought Zircaloy-2 and -4 materials to J-13 water or concentrated (10X) J-13 water results in passivation of the surface as indicated by the corrosion potential shift in the noble direction.
2. Zr-2 and Zr-4 cladding tubes passivate but not as much as the bulk material, and various surface treatments will alter passivation.
3. Some cyclic polarization measurements of Zr-2 and Zr-4 in J-13 water, at 95°C show no evidence that localized corrosion would occur. Other measurements show evidence of localized corrosion, but the protection potential is over 1000 mV more noble than the corrosion potential.
4. The breakdown potential for the wrought materials occurred within the range of +0.800 V to +1 V vs. S.C.E. and higher in some cases, and that for the tubing ranges from +0.300 V to +0.750 V vs. S.C.E. Surface preparation techniques have a strong influence on the breakdown potential.

REFERENCES

1. Title 10 Code of Federal Regulations (CFR) Part 60-Disposal of High-Level Radioactive Wastes in Geologic Repositories: Section 60.113(a)(11)(B), United States Nuclear Regulatory Commission, (1988).
2. Anna C. Fraker, Corrosion Behavior of Zircaloy Spent Fuel Cladding in a Repository, Nat. Inst. Stds. Tech. (NISTIR)-89-4114, July, (1989).
3. P. Soo, Ed., Review of Waste Package Verification Tests, NUREG/CR-3091, BNL-NUREG-51630, Vol. 6, July, (1985), pp. 138-139.
4. ASTM F 746-87, Standard Test Method for Pitting and Crevice Corrosion of Metallic Surgical Implant Materials, Annual Book of ASTM Standards, Medical Devices, Vol. 13, Am. Soc. for Testing and Mater., Philadelphia, PA 19103, (1988), pp. 221-226.
5. B. Cheng and R. B. Adamson, Mechanistic Studies of Zircaloy Nodular Corrosion, Presented at Am. Soc. for Test. and Mater. 7th Internl. Conf. on Zirconium in the Nuclear Industry, Strasbourg, France, June 24-27, (1985).

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