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

July 10, 1989

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

Re: Monthly Letter Status Report for January 1989 (FIN-A-4171-9)

Dear Mr. Peterson:

Enclosed is the January 1989 monthly progress report for the project "Evaluation and Compilation of DOE Waste Package Test Data" (FIN-A-4171-7). The financial information is attached to this letter.

The names of reviewers have been omitted from these draft reviews despite your several requests made over the past months for inclusion of these names. This policy was established when we undertook this review activity and we have not changed our view on the appropriateness of making the reviewer blind to readers from outside the NIST. Please discuss this at our next program review if you still feel it necessary to see the name of the reviewer on the draft review.

Sincerely,

Charles G. Interrante
Program Manager
Corrosion Group
Metallurgy Division

Enclosures

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Monthly Letter Report for January 1989

Published July 1989

(FIN-A-4171-9)

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

Appended to this report are the following Draft Reviews not previously submitted (see p. 8 to 18). Comments by the NRC and its contractors are solicited.

1. UCRL-95961, "Copper Corrosion in Irradiated Environments. The Influence of H_2O_2 on the Electrochemistry of Copper Dissolution in HCl Electrolyte," December 1986.

2. DP-MS-87-157, "Prediction of Glass Durability as a Function of Glass Composition and Test Conditions: Thermodynamics and Kinetics", a paper proposed for Presentation at the Conference on Advances in the Fusion of Glass, Alfred, NY, June 14-17, 1988.

3. UCRL-53449, "Containment Barrier Metals for High-Level Waste Packages in a Tuff Repository," October 1983.

STATUS OF DATABASE

	Current Month	Previous Month
Number of citations	1040	1025
Number of completed reviews	78	

Status of Recently Listed Reviewable Documents

Reviewable documents are classified as follows: papers currently being reviewed (Category 1), review when time permits (Category 2) and file with cross reference(s) to related report(s) (Category 3).

NNWSI

- 6 NNWSI reports currently under review (Category 1).
- 19 NNWSI reports to review when time permits (Category 2).
- 1 NNWSI reports to file with cross reference(s) to other reports (Category 3).
- 3 NNWSI reports identified and not yet categorized.
- 9 NNWSI reports received and not yet categorized.

GLASS -- VITRIFIED WASTE FORM

- 1 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 the month of December 1988 include NTIS, Metadex, Engineering Abstract, and DOE Energy. Examples of the search conducted for each of these databases are in this report (see p. 19 to 22).

STATUS OF REVIEWS OF NNWSI REPORTS

NNWSI -- Reports recently identified for review

Three reports have been identified for review. Two are on the subject of container design and the third is on the performance of Zircaloy cladding.

The first report is a historical review of the selection process used in the choice of the six candidate metals presently being considered for the waste package container. The report covers the period from 1980 to 1981 and includes an appendix with data and correspondence that impacted on the choice of the six materials [McCright 1988].

The second report considers physical designs of the waste container, and discusses the constraints and considerations taken into account in these designs. Thus, several alternative packages are described to meet the needs of waste containment, however, at the time of the study, copper and its alloys were not yet being considered as container materials [O'Neal 1984].

The last report in this group describes results of the study on the stress-corrosion susceptibility of Zircaloy-4 in C-ring configuration exposed in J-13 water at 90°C and a stress level of 90% of the elastic limit for the material. Failures were observed in 25 to 64 d [Smith 1988].

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

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

3. Smith, H. D., "Initial Report on Stress-Corrosion-Cracking Experiments Using Zircaloy-4 Spent Fuel Cladding C-Rings," WHC-EP-0096 (formerly HEDL-7665), September 1988.

NNWSI --

Category 1 -- Reports currently being reviewed

1. HEDL-TME 85-22, "Results from Cycles 1 and 2 of NNWSI Series 2 Spent Fuel Dissolution Tests," May 1987.

2. UCRL-21019, SAN-662,-027, "Recent Results from NNWSI Spent Fuel Leaching/Dissolution Tests," April 1987.

3. UCRL-21013, "Summary of Results from the Series 2 and Series 3 NNWSI Bare Fuel Dissolution Tests," November 1987.

4. ANL-88-14, "The Reaction of Glass During Gamma Irradiation in a Saturated Tuff Environment, Part 3: Long-Term Experiments at $1x10^4$ rad/hr," February 1988.

5. Ringas, C. and Robinson, F., "Corrosion of Stainless Steel by Sulfate-Reducing Bacteria - Total Immersion Test Results," NACE, Corrosion, Vol. 44(9), September 1988.

6. UCRL-97805, "An Approximate Calculation of Advective Gas Phase Transport of ^{14}C at Yucca Mountain, Nevada," December 1987.

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
HEDL-TME 85-22	11/22/88			
UCRL-21019	12/06/88			
UCRL-21013	06/21/88			
UCRL-95961	07/14/88			
ANL-88-14	12/22/88			
Ringas, 1988		1/30/88		
UCRL-97805	*			

*Document to be reassigned.

Category 2 -- Review as time permits

None this month.

Category 3 -- File and cross reference

1. UCID-20450, "Concept of Waste Package Environment Tests in the Yucca Mountain Exploratory Shaft," May 1985.

2. Gregg, D. W. and O'Neal, W. C., "Initial Specifications for Nuclear Waste Package External Dimensions and Materials," UCID-19926, September 1983.

3. Buscheck, T. A. and Nitao, J. J., "Preliminary Scoping Calculations of Hydrothermal Flow in Variably Saturated, Fractured, Welded Tuff During the Engineered Barrier Design Tests at the Yucca Mountain Exploratory Shaft Test Site," UCID-21571, November 1988.

4. HEDL-TC-2353-2, "Test Plan for Spent Fuel Cladding Containment Credit Tests," November 1983.

OTHER REPORTS ON VITRIFIED WASTE FORM --

Category 1 -- Reports currently being reviewed

1. PNL-5157, "Final Report of the Defense High-Level Waste Leaching Mechanisms Program," August 1984.

Status of Reviews not yet sent to NRC and WERB

Document No.	Assigned to Reviewer	First Draft Completed	Lead Worker	Program Manager
PNL-5157 Chapter 4	6/20/88	1/28/89		

Category 2 -- Review as time permits

None this month.

Category 3 -- File and cross reference

None this month.

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

It is observed that the branch-crack formation in two specimens (ST2v and ST5v), which had Rockwell C hardness values equal to about 37 and 23, respectively, were attributable, at least in part, to the sharp v-shaped notches that they contained. The root radius of the 45-degree notch that was machined into the sides of these specimens was of the order of 0.007 inches. An earlier unpublished study by R. Heady and C. Interrante concluded that a larger radius of 0.025 was less likely to cause branch cracking. Thus, two specimens were sent to the shop to be remachined using a cutter with an 0.025-inch root radius.

Tasks to complete prior to the next test include (1) purchasing a replacement tank of hydrogen sulfide and (2) programming required for computations associated with the comparison of detected acoustic energy and strain energy released in the test. The successful test of specimen ST5v prompted selected changes in the program used for collection of data during the test. In addition, with the advent of a data file on specimen ST5v, which contained valid data, it now becomes desirable to create programs that are needed for analyses of the amount of energy and the crack extension that are associated with a single event of crack extension in this test specimen. After a fully successful test is conducted a plan will be made for any future tests of similar or other not so similar tests.

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

The improvement in control of the environment in the second series of experiments has resulted in data that is more reproducible. The results of oxygen transport measurements show that particle size is not as important as particle shape. For spherical particles, the ratio of pore volume to particle volume is constant and is independent of particle size. If large and small particles are mixed, then the relative pore volume decreases. Similarly, if the shapes of the particles allow tighter packing, then the relative pore volume is reduced. A smaller relative pore volume results in a decrease in the rate of oxygen transport. The effect of these factors is being examined in this second set of experiments, and the improved reproducibility of the data makes it easier to compare the data for sand of one size particles with that for another size.

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

The software for the test equipment was upgraded. Additional improvements in the equipment and software are planned and are in process. Preparations are underway for the Zircaloy specimens needed for future testing.

An outline was prepared based on the literature review on "Corrosion of Zircaloy" which was conducted as part of this project. The title was changed to "Corrosion of Zircaloy Spent Fuel Cladding in a Repository". The paper will be rearranged according to the outline, and some additional material will be added. Additional material on corrosion of zirconium alloys has been received from Michael Maguire of Teledyne Wah Chang Albany, Albany, Oregon, from Materials Characterization Center Reports and from other sources.

Future plans for this project include publication of the review paper on Zircaloy corrosion, studies of long term exposure, studies of welded materials, electrochemical studies of the surface oxide, investigation of effects of solution pH, and various ions and application of additional tests to study localized corrosion.

Table 1. Open circuit potential for Zircaloy-2 in J13 water at 95°C

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

It was noted on Dec. 21, 1988 that the specimen no longer had a good electrical connection, and the test was discontinued.

TASK 4 -- GENERAL TECHNICAL ASSISTANCE

On January 22-25, 1989, in Orlando, Florida, Dr. C. Interrante participated in a meeting of ASTM Committee C26.13 on Nuclear Fuel Cycle. His trip report for that meeting is attached.

Dr. Ugo Bertocci visited Bill Murphy and Prasad Nair of the Center for Nuclear Waste Regulatory Analyses in San Antonio, Texas on January 26-28, 1989 to discuss repository conditions.

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

DATA SOURCE

(a) Organization Producing Report

Lawrence Livermore National Laboratory, Livermore CA. For the NNWSI Project, U.S. DOE.

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

Smyrl, W. H., Bell, B. T., Atanososki, R. T., and Glass, R. S., "Copper Corrosion in Irradiated Environments. The Influence of H_2O_2 on the Electrochemistry of Copper Dissolution in HCl Electrolyte," UCRL-95961, December 1986.

DATE REVIEWED: 1/25/89.

PURPOSE

To study the effect of H_2O_2 on the anodic dissolution of Cu in HCl.

KEY WORDS

Experimental data, general corrosion, electrochemical, laboratory, Cl, acidic solution (ph <7), ambient temperature, copper base, Cu, corrosion (general).

CONTENTS

12 pages, 7 figures, 13 references.

TEST CONDITIONS

Deaerated solutions at 25°C.

UNCERTAINTIES IN DATA

According to the authors the experimental results are reproducible.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

CONCLUSIONS OF AUTHOR

At low H_2O_2 concentrations the behavior is identical to that in the presence of oxygen, which indicates that the mechanism is the same. Deviations observed at H_2O_2 concentrations higher than 0.01 M, can be due, according to the authors, either to direct reaction of H_2O_2 with the metal, or to an indirect mechanism which enhances the formation of a CuCl film.

COMMENTS OF REVIEWER

The experimental work is O.K., but there is little more than already known in the literature. The tentative explanation given to the high H_2O_2 concentration results is very likely invalid, but it is described in such vague terms that it is difficult to discuss. A more reasonable interpretation would probably entail consideration of chloride transport toward the electrode, since the so-called anomalous results are observed at the higher current densities.

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

(a) Relationship to Waste Package Performance Issues Already Identified

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

(b) New Licensing Issues

(c) General Comments

AUTHOR'S ABSTRACT

Five metals that best satisfy the requirements for use as high-level waste containers were chosen. The reference canister and overpack metal is AISI 304L, and alternative alloys are AISI 321, AISI 316L, Incoloy 825, and 1020 carbon steel for borehole liners.

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

DATA SOURCE

(a) Organization Producing Report

Lawrence Livermore National Laboratory, Livermore CA. For the NNWSI Project, U.S. DOE.

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

Russell, E. W., McCright, R. D., and O'Neal, W. C., "Containment Barrier Metals for High-Level Waste Packages in a Tuff Repository," UCRL-53449, October 1983.

DATE REVIEWED: 1/15/89.

PURPOSE

To select candidate metals for the containment of nuclear waste.

KEY WORDS

Data analysis, literature review, scoping test, elongation, tensile strength, yield strength, ductility, corrosion (crevice), corrosion (general), corrosion (intergranular), corrosion (pitting), corrosion (stress cracking) SCC, hydrogen embrittlement.

CONTENTS

26 pages, 4 figures, 10 tables, and 17 references.

AMOUNT OF DATA

No new data. All data taken from the literature. These data consist of 1) a summary of the waste package environment, 2) composition of 17 candidate metals, 3) deterioration rates for several mechanisms of 17 candidate metals, 4) relative costs of 17 metals, 5) mechanical and weldability properties of 17 metals, ranking of 17 metals considering corrosion resistance, mechanical properties, weldability, and cost.

TEST CONDITIONS

No testing conducted.

UNCERTAINTIES IN DATA

None given.

DEFICIENCIES/LIMITATIONS IN DATABASE

None given.

CONCLUSIONS OF AUTHOR

"The results of our analysis show the five metals that best satisfy the requirements for disposal of high-level waste at the NNWSI-posed repository at Yucca Mountain. Testing is presently planned or in progress on these metals for further development of the waste package design for the unsaturated zone. The reference canister and overpack metal is AISI 304L stainless steel, but alternative metals will also be considered for reasons previously discussed. The primary alternative metals have been selected from the list of the 17 candidate metals discussed in this report. They are AISI 321, AISI 316L, Incoloy 825 for canisters and overpacks, and 1020 carbon steel for borehole."

COMMENTS OF REVIEWER

This is the first report summarizing the procedure used in selecting five metals, out of seventeen that were considered, for laboratory testing as candidates for nuclear waste container. At this stage, copper and copper alloys were not included in the list of seventeen metals evaluated. The report does not discuss the methods used in arriving at weighing factors for each of the properties considered.

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

(a) Relationship to Waste Package Performance Issues Already Identified

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

(b) New Licensing Issues

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AUTHOR'S ABSTRACT

Five metals that best satisfy the requirements for use as high-level waste containers were chosen. The reference canister and overpack metal is AISI 304L, and alternative alloys are AISI 321, AISI 316L, Incoloy 825, and 1020 carbon steel for borehole liners.

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

DATA SOURCE

(a) Organization Producing Data

E.I. du Pont de Nemours & Co., Savannah River Laboratory

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

Jantzen, C. M., "Prediction of Glass Durability as a Function of Glass Composition and Test Conditions: Thermodynamics and Kinetics", DP-MS-87-157, a paper proposed for Presentation at the Conference on Advances in the Fusion of Glass, Alfred, NY, June 14-17, 1988.

DATE REVIEWED: 1/12/89.

PURPOSE

"The relative role of kinetics and thermodynamics in predicting the long-term durability of glasses will be examined" by theoretical modeling and experiments.

KEY WORDS

Theory, experimental data, (thermodynamics, precipitation reaction), leaching, solubility, inductively coupled plasma (ICP) atomic adsorption (AA), laboratory, ASTM TYPE I high-purity water, basic (alkaline) solution (pH>7), neutral solution (pH=7), static (no flow), 55 nuclear waste glasses (West Valley Defense, and unspecified) and 100 natural and man-made glasses including 4 ancient glasses, monolith, crushed to various mesh sizes, hydration, matrix dissolution.

CONTENTS

This report consists of 17 pages which include abstract, an introduction, 7 figures, 12 equations, and the following number of pages covering each topic listed:

Topic	Pages
Theoretical:	
Glass Durability: A Function of Glass Composition	1.5
Glass Durability: A Function of Glass Structure	1.0
Glass Durability: A Function of Test Parameters	2.5
Experimental Results:	1.0
Glass Durability: A Function of Glass Composition	1.5
Glass Durability: A Function of the Kinetic (SA/V)t Parameters	1.0

Topic	Pages
Discussion and Conclusions	1.0
References	1.5
Figures	4.0

AMOUNT OF DATA

There are seven figures. Four figures are normalized mass losses with three figures showing ranging from 0.1~10000g/m^2 versus free energy of hydration -20 to 10 Kcal/mole and a fourth figure showing the normalized mass on a scale of .01 to 1000 g/m^2 versus -20 to 10 Kcal/mole. Another figure shows Silicon release of 0.1 to 10000 ppm versus surface area/solution-volume x time (0 ~ 400 days/cm). The final two figures are three dimensional: free energy of hydration (-13.49 ~ 4.96) versus surface area/solution x time (70 ~ 163082) versus log (silicon release) (-0.82 ~ 3.44).

TEST CONDITIONS

Modeling

- Isotropic assumption was used for thermodynamic approach and
- One-dimensional analysis while varying the ratio of glass surface to solution volume, for glass leaching and precipitation.
- Glasses have various compositions, structures, and surface layers. They can be monolith or crushed glasses.
- The thermodynamic approach requires the thermodynamic equilibrium between glasses and aqueous environments, but does not require determination of the time dependent kinetics of leaching processes.
- Concentrations are assumed to be proportional to the ideal ion activities in the thermodynamic treatment. The overall free energy of hydration of glass is a summation of fractional functions of that of individual silicate and oxide components.
- The free energies of hydration of glasses are correlated with both the ionic potential and the ionic field strength, and glass structure is not considered to be an additional parameter affecting glass durability.
- The kinetic approach has nth (unspecified) order dissolution rates for forward reaction and for precipitates reaction as backward reaction. Both rates are proportional to nth power of proton activity.
- The precipitation rates can be expressed with an equilibrium constant, concomitantly and with free energy change associated with the precipitation.

Experiment

ASTM Type I high-purity water was used at 90°C. Four (4)cm2 surface area of glass monoliths and 1.5g of crushed glasses to various mesh sizes were immersed in 40m3 solutions. The test duration was 28 days.

UNCERTAINTIES IN DATA

Modeling

The quoted error bars in thermodynamic approach are as follows: "95% upper and lower confidence limits determined for the combinations of free energy of hydration, log (normalized Silicone release), log (normalized Boron release), and pH. The primary contribution to the 95% was from free energy of hydration and errors in glass analysis are more significant than errors in leachate analyses." There was no specification of error associated with kinetic parameters such as rate constants of dissolution and precipitation, and the free change associated with precipitation.

Experimental

"All glass compositions have errors of 100 + 5%." The detailed analyses of errors in experiments are not given.

DEFICIENCIES/LIMITATIONS IN DATABASE

Modeling

"Since the hydration thermodynamic approaches assume that glass structure is a primary function of glass composition, glass structure is not considered as an additional parameter affecting glass durability."

Experimental

"The solutions were not filtered and the fines were not removed from the crushed glass by an alcohol wash. This is thought to contribute to some of the observed variability in the data." Concentrations were assumed to be proportional to ideal activities in thermodynamic treatment. (Underlines are made by reviewer)

CONCLUSION OF AUTHOR

There are sections entitled (1) Discussion and Conclusions, and (2) Abstract. Conclusions drawn from the contents of these sections are as follows:

The durability of a glass is a function of its thermodynamic and kinetic stability in solution. Glass durability has been shown to be a function of thermodynamic free energy of hydration which can be calculated from the glass composition. Hydration thermodynamics also furnish a quantitative frame of reference to understand how the various test parameters affect the glass durability.

Different test conditions result in different kinetic parameters and this would be true for the following variables: the exposed glass surface area, the leachant solution volume, and the length of

leaching time. The relative durabilities of glasses define a plane in three-dimensional -- free energy of hydration, concentration, glass surface area·time·solution volume -- space. At constant kinetic conditions, the three-dimensional plane is intersected at a constant value of the parameter glass-surface-area·time/solution-volume and the plotting of the free energy of hydration versus concentration has a similar slope.

The combined kinetic and thermodynamic contributions to glass durability have been verified experimentally by defining a plane in the above dimensional space at constant temperatures. The experimental data obtained from nuclear waste, commercial, and ancient glasses.

COMMENTS OF REVIEWER

This report contains much useful information in both modeling and experimental work on glass durability. The most impressive merits are: (1) an excellent correlation between glass durability and free energy of hydration despite a large disparity of materials in which Si losses differ by a factor greater than 300, (2) numerous data for 155 glasses including nuclear waste, ancient, and man-made glasses; and, (3) a new kinetic model incorporating a precipitation reaction as a backward reaction. However, some areas should be clarified and need to be studied further.

The correlation of the material's loss with free energy of hydration is an approach of reversible thermodynamics, while kinetic description is an approach of irreversible thermodynamics. The former is a static situation while the latter is a dynamic situation. It is very unclear how these two approaches are adopted in interpreting experimental data. Did the proposed equilibrium arrive at 90°C after 28 days? Are the quoted data obtained by Newton and Paul at 25°C for 24 hours comparable to the present data? Further, material's loss was found to be dependent on the ratio of surface area to solution volume. Does this imply that concentration cells formed in crushed glass and, concomitantly, the solution is not at equilibrium? The correlation of leach rates with reversible thermodynamic terms should be independent of kinetic parameters.

Work by Grambow and his co-workers is based on the equilibrium between crystalline precipitates and solutions to justify the continuously dissolving glasses even in saturated solutions. The glasses may never reach the equilibrium state because of their metastability. The present work uses the equilibrium between glasses and solutions in the calculation of free energy, using a simple fractional addition of each free energy of hydration of glass constituents, or by using bond energy calculation. How can the author justify the continuous glass dissolution in light of the work by Grambow and his co-workers?

In the calculation of free energy of hydration, several aspects need to be considered and justified; if it can be correlated with both the ionic potential and the ionic field strength, it is consequential to take into account the ionic strength of solution. Is the present correlation valid in repository solutions other than DI water? The fractional addition of each free energy of hydration does not explain the mixed alkali effects

where the durability of glass does not change linearly following the variation of glass composition. While the free energy of hydration is a fractional addition from that of each component at approximately neutral pH, the correlation at high pH is absolutely empirical. Further, the author does not address the high dissolution at low pH and the time-dependent pH. No glass structure was taken into consideration in the calculation. There are varieties not only of atomic structures but also of microstructures such as phase separation.

In the kinetic formulation; the incorporation of leachant concentration in reaction constant is absent; the mentioned parabolic curve is far from the derived equation (11) which itself is strange due to the double exponential term in temperature expression; the pH dependence on the rate equation is highly empirical; and the precipitation rates do not have any term of activation energy and the factor m (deviation from equilibrium) implies the kinetic control.

Although the work with ancient glasses is appreciated, it may be premature to conclude that waste glasses are durable over geological time. Actually, we need information on material's loss during geological times in ancient glasses in light of NRC regulation of the controlled release rate of radionuclide. Work by Newton and Paul is highly desirable in measuring glass loss in geological time.

In experiments, the author stated the possibility of the involvement of glass powder obtained from glass crushing. This seems to be significant considering precipitation products.

More work is needed in most of the major areas discussed in the report. Areas specifically recommended are as follows:

- The validity of thermodynamic approach should be clarified to be independent of kinetic parameters. For instance, time variation in experiments would be a way to prove it.

- The correlation of glass durability with free energy of hydration should incorporate the mixed alkali effect, solution ionicites, glass structure including atomic-and micro-structures, activity coefficient, and mechanistic pH effect (particularly at low pH).

- Precise and accurate description of the kinetic equation is required, specifically in (1) precipitation rates including activation energy, (2) Arrhenius activation energy of the overall kinetics is of a double exponent term, and (3) the mechanistic pH effect (particularly at low pH).

- In experiments, (1) the monolith and crushed glasses are recommended to be compared at a fixed surface area; (2) solution replenishment or flow rates need to be studied; (3) dating (or materials loss/century) data are more valuable than laboratory test data in ancient glasses; and (4) caution should be given to the contribution of powdered glasses from crushing and are not to be mixed with precipitation products.

RELATED HLW REPORT

1. R.G. Newton and A. Paul, Glass Technology, 21, 307 (1980) has a correlation of free energy of hyrdration with the thickness loss (mm/century) of ancient glasses.

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

(a) Relationship to Waste Package Performance Issues Already Identified

2.3.2.1.1, which waste form dissolution mechanisms are most likely?
2.3.2.1.2, what are the rates of dissolution associated with the potential waste form dissolution mechanisms?
2.3.2.2, what non-radioactive dissolution products are likely to be produced from the waste form?
2.3.2.3, what are the solubilities of the radionuclides released from the waste form?
2.3.2.4, what will be the chemical species of the radionuclides released from the waste form?

Related to ISTP issues

Theoretical Glass durability - a function of glass composition.
a function of glass structure.
a function of test parameters.

Experimental
Leaching test - 55 nuclear waste glasses, and 100 natural and man-made glasses.

(b) Licensing Issues

- Predictive model combining thermodynamic and kinetic approaches.
- The correlation of leaching with free energy of hydration of glass components and pH effect.
- Leaching of ancient glasses.

(c) Comments Related to Licensing

This report provides predictive models and supporting data which need to be better formulated and understood prior to licensing waste package.

ABSTRACT

The long-term durability of nuclear waste glasses can be predicted by comparing their performance to natural and ancient glasses. Glass durability is a function of the kinetic and thermodynamic stability of glass in solution. The relationship between the kinetic and thermodynamic aspects of glass durability can be understood when the relative contributions of glass composition and imposed test conditions are delineated. Glass durability has been shown to be a function of the

thermodynamic hydration free energy which can be calculated from the glass composition. Hydration thermodynamics also furnishes a quantitative frame of reference to understand how various test parameters affect glass durability.

Linear relationships have been determined between the logarithmic extent of hydration and the calculated hydration free energy for several different test geometries. Different test conditions result in different kinetic reactivity parameters such as the exposed glass surface area (SA), the leachant solution volume (V), and the length of time that the glass is in the leachant (t). Leachate concentrations are known to be a function of the kinetic test parameter (SA/V)t. The relative durabilities of glasses including pure silica, obsidians, nuclear waste glasses, medieval window glasses, and frit glasses define a plane in three dimensional G_{hyd}-concentration-(SA/V)t space. At constant kinetic conditions, e.g. test geometry and test duration, the three dimensional plane is intersected at constant (SA/V)t and the G_{hyd}-concentration plots have similar slopes. The slope represents the natural logarithm of the theoretical slope, (1/2.303 RT), for the rate of glass dissolution.

SDI006, UD 8904, SER. DD016

File(s) searched:

File 6:NTIS - 64-89/ISS04
(COPR. 1989 NTIS)

Sets selected:

Set	Items	Description
1	6	WASTE(W)PACKAGE?
2	7	CANISTER?
3	29	CORROSION
4	13	LEACHING
5	68	GLASS
6	8	VITRIFICATION
7	107	S3-S6/OR
8	4	HIGH(W)LEVEL(W)WASTE?
9	78	RADIOACTIVE(W)WASTE?
10	12	NUCLEAR(W)WASTE?
11	5	(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
21jan	00:45EST	PR 11/5/1-25 (items 1-5)

Total items to be printed: 5

DIALOG INFORMATION SERVICES, INC.

SDI032, UD 8902, SER. DD022

File(s) searched:

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

Sets selected:

Set	Items	Description
1	3	HIGH()LEVEL()WASTE? ? OR RADIOACTIVE()WASTE? OR NUCLEAR()WASTE?
2	1751	STEEL? ? OR ZIRCALOY? ? OR TITANIUM? ? OR COPPER
3	2	1*2
4	0	ANNA FRAKER, 223, B-254, X6009

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

Date	Time	Description
14jan	21:47EST	PR 3/5/1-25 (items 1-2)

Total items to be printed: 2

SDI293, UD 8902, SER. DD023

File(s) searched:

File 293:Engineered Materials Abs 86-89/Feb
(Copr. 1989 ASM INTERNATIONAL)

Sets selected:

Set	Items	Description
1	1	HIGH()LEVEL()WASTE? ? OR RADIOACTIVE()WASTE? OR NUCLEAR()WASTE?
2	272	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
28jan	19:27EST	PR 3/5/1-25 (no items to PRINT)

Total items to be printed: 0

SDI103, UD 8902, SER. DD017

File(s) searched:

File 103:DOE ENERGY - 83-89/JAN(ISS02)

Sets selected:

Set	Items	Description
1	4	WASTE(W)PACKAGE?
2	3	CANISTER?
3	112	CORROSION (1974 DEC)
4	24	LEACHING (1974 DEC)
5	55	GLASS (1974 DEC)
6	6	VITRIFICATION (1974 DEC)
7	187	S3-S6/OR
8	4	HIGH(W)LEVEL(W)WASTE?
9	87	RADIOACTIVE(W)WASTE?
10	10	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
28jan	19:20EST	PR 11/5/1-25 (no items to PRINT)

Total items to be printed: 0

Trip Report -- Meetings of Committee C26.13 in Orlando, Florida
January 23 and 24, 1989

by

Charles G. Interrante

The only task of this subcommittee is writing a document on "Prediction of Long-Term Behavior to Aid in Performance Assessment of Waste Package Materials for Geologic Disposal of High-Level Nuclear Waste. As a follow-on to several meetings of a task group working on this document over the past six months, a pre-meeting of the Tuesday (Jan. 24) meeting of C26.13 was held on Monday (Jan. 23). Work on the document through all of Monday afternoon by the task group and on Tuesday morning and afternoon by the subcommittee resulted in substantial agreement on figures that have been the topic of debate for the past year. The content of figures that have been controversial and difficult to agree upon were accepted by vote of the subcommittee and it is my firm hope that no further discussion of these agreed upon items will be needed until after the committee C26 has been balloted. In addition, the terminology, selected terms and their definitions have now been widely accepted. My participation in the preparation of this document has centered on three areas related to the terminology for this document: (1) Recording any task-group consensus on terminology, (2) Interpretation of task-group views in terms of ASTM's recommendations, which are given in "Part E -- Preparation and Use of Terminology in ASTM Standards," Form and Style for ASTM Standards, 7th Edition, March 1986, (3) Development of definitions for various terms used in the document. The latest version of this terminology is attached to this trip report. For additional details on these meetings, see also the minutes of this meeting made available recently by C. Peterson.

DRAFT Terminology -"Recommended Practice for the Prediction of Long-Term Behavior to Aid in the Performance Assessment of Waste Package Materials for Geologic Disposal of High-Level Nuclear Waste," under jurisdiction of ASTM Subcommittee C26.13 on Mined Geologic Repository Waste Package Materials Testing

NOTES FOR THOSE WHO PREPARE DRAFTS FOR USE BY THIS TASK GROUP -- Various terms presently used in this method will have to be modified by the terms preclosure, preacceptance, postclosure and postacceptance. These should be liberally used without the need for definitions of compound terms in which any of these terms are included. Definition for compound terms are needed only when some special (non-implicit) meaning in conferred or intended.

The terminology currently being used by this task group is attached. Twice since the July 1988 meeting of C26 in Toronto, this terminology has received votes of acceptance from those present at task group and subcommittee meetings held since then. Thus, agreement is slowly being reached on a terminology for the recommended practice under development by the subcommittee. For many of the definitions, my editorial notations and recommendations are given as suggestions for consideration at future meetings.

The definitions given below are divided into two groups. The first group contains terms and definitions that, in my perception, reflect the usage intended by the task group, as expressed at various meetings, including views expressed at the Orlando meeting. Every effort has been made to express (translate) this group's views in terms of ASTM's recommendations, which are given in "Part E -- Preparation and Use of Terminology in ASTM Standards," Form and Style for ASTM Standards, 7th Edition, March 1986. In addition, definitions for each of about nine of these terms were adopted by votes taken at the subcommittee meeting in Orlando, 1989. For a few of these nine, the editorial notes indicate that the definition presented in the minutes of the Orlando meeting differs from that shown here, and so these differences should be resolved at the start of the next meeting. Each of those definitions is marked as follows: (v - Jan. 24, 1989).

Appended to the terminology agreed upon in these various ways, there is a second group of definitions and these are presented below a line labeled "OTHER RELATED DEFINITIONS FOR CONSIDERATION." This group includes

(1) dictionary definitions that might be useful references for the task group during deliberations.s
(2) incipient definitions worthy of consideration by the group.
(3) definitions marked [CP], which were taken from Chairman Peterson's working draft document used at the Orlando meeting.

6. Definitions

6.1 accelerated test -- a test that results in rates of alterations that are greater than the rates that occur in service.

Discussion -- In this practice, consideration must be given as to whether or not the mechanism of alteration for the accelerated test and the long-term behavior are the same. Examples of parameters that might be varied to accelerate processes might include temperature, electrochemical potential, mechanical stress, radiation level, and surface-to-volume ratio. (v -- Jan. 24, 1989)

[Ed. Note -- the minutes of the Orlando meeting shows a version of this definition created from Peterson's handout. It is significantly different from the above, which was taken from my hand written notes on the versions adopted.

6.2 alteration -- any change in the properties of a material.

*[Ed. Note -- "The act or process of altering" is Webster definition for alteration. Thus, Webster builds on the root verb alter, which is defined as follows: alter -- to make different without changing into something else. [Webster] I would suggest that we follow this practice and substitute alter for alteration as our item 6.2. Then we won't need to define alteration.]

6.2.1 alteration mode -- in nuclear waste storage, a particular form of alteration, e.g. passivation or general corrosion.

6.2.2 alteration mechanism -- in nuclear waste storage, the fundamental chemical or physical processes by which alterations occur.

[Ed. Note -- Due to the task group decision to switch from emphasis on degradation to alteration, this term was substituted for degradation mechanism. However, the meaning of this compound term is self evident, when given the definitions of its two simple terms, alteration and mechanism. Therefore, the ASTM Standing Committee on Terminology is likely to recommend that this term not be defined in our recommended practice. Thus, I see no need for this definition and I would suggest we eliminate it from our terminology.]

6.3 bounding condition -- in this practice, the extreme credible value that might be expected for an independent variable.

6.4 characterization test -- in high-level radioactive waste, any test conducted principally to furnish information for a mechanistic understanding of degradation. Examples include polarization tests, potential-pH (Pourbaix) diagrams, solubility analyses, XRD of corrosion layers, etc.

Discussion -- A characterization test might be conducted under conditions that exceed those expected for a repository setting.
6.5 confirmation test - in high-level radioactive waste management, a test that provides data that becomes available subsequent to the validation stage of the model and would normally be intended to provide confirmation data for the model predictions. (v -- Jan. 24, 1989)

6.6 degradation -- any change in the properties of a material, which adversely affects the behavior of that material, i.e. an adverse alteration. (v -- Jan. 24, 1989)

[Ed. Note -- This is slightly different from that given in the minutes for the Orlando meeting.]

6.7 disposal -- in nuclear waste storage, the isolation of radioactive waste from the accessible environment and the public.

6.8 engineered barrier system -- in high-level waste storage, the waste packages and the underground facilities [10 CFR 60.2] used to increase the time lapsed prior to release of radionuclides to the accessible environment.

6.9 geologic repository -- a system for the permanent disposal of radioactive waste in (excavated) geologic media.

6.10 high-level radioactive waste -- 1: irradiated reactor fuel 2: liquid wastes from reprocessing of irradiated reactor fuel 3: solid waste (e.g. glass) into which liquid high-level radioactive wastes have been incorporated.

6.11 long-term test -- in high-level radioactive waste management, a test of duration normally greater than about five years. (v -- Jan. 24, 1989)

6.12 mechanism -- the fundamental physical or chemical processes <u>or sequence of</u> processes involved in or responsible for an action, reaction, or other natural phenomenon.

[Ed. -- The underlined part was added in Orlando at the insistence of several present. The Webster definition is the part not underlined. ASTM recommends that technical committees take the ASTM standard definitions, i.e. Webster's, when it seems to fit our needs, and I would recommend against adding the underlined parts, since they contribute very little to the description of the concept.]

6.13 model -- 1: a mathematical representation of a process 2: a system of postulates, data, and inferences presented as a mathematical description of an entity or state of affairs [Webster] 3: a simplified representation of a system or phenomena, with any hypotheses required to describe the system or explain the phenomenon, often mathematically [McGraw-Hill] 4: a description or analogy used to help visualize something (as an atom) that cannot be directly observed [Webster].
6.13.1 bounding model -- in high-level radioactive waste management, a model that predicts more adverse alterations of materials than those predicted from existing mechanistic or semi-empirical models.
(v -- Jan. 24, 1989)

[Ed Note -- An Orlando vote on this item is not acknowledged in the Orlando minutes.]

6.13.2 bounding calculation -- a calculation that uses bounding conditions for parameters that affect a process.

6.13.3 empirical model -- a model based only on observations or data from experiments, without regard to mechanism or theory.

6.13.4 mechanistic model -- a model based on one or more mechanisms.
(v -- Jan. 24, 1989)

6.13.5 semi-empirical model -- in high-level radioactive waste management, a model based on a partial mechanistic understanding of available observations or data from experiments. (v -- Jan. 24, 1989)

[Ed. Note -- The above differs significantly from the definition shown in the minutes of the Orlando meeting.]

6.14 service-condition test -- in high-level waste storage, a test for evaluation of behavior under actual or simulated conditions in service.

[Ed. Note -- Because the definition gives no hint concerning radioactivity, I would suggest adding the word radioactive in the delimiter, "high-level radioactive waste storage." This would permit the definition to better stand alone.]

6.15 short-term test -- in high-level radioactive waste management, a test conducted over a period normally less than five years. (v -- Jan. 24, 1989)

6.16 waste form -- in nuclear waste storage, radioactive waste materials and any encapsulating or stabilizing matrix. [10 CFR 60.2]

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* Editorial notes are given for consideration of the Subcommittee. They are, of course, not intended for inclusion in this terminology.

OTHER RELATED DEFINITIONS FOR CONSIDERATION

accelerated test -- a test in which the values of the independent variables are set at or near the values for service conditions, with allowances for anticipated changes in service conditions. [CP]

analog -- 1. of, relating to, or being an analogue 2. variation of ANALOGUE [Webster]
analogue -- 1. something that is analogous or similar to something else
2a. chemical compound structurally similar to another but differing often by a single element ... [Webster]

analog -- in this recommended practice, a natural material that is believed to be similar to a man-made material. The composition and history of environmental exposure of the analog are believed to be close enough so that observations of the analog, can be used to infer behavior of the man-made material.

analog -- in this Recommended Practice, a material whose composition, and environmental history are similar enough to those of the materials of interest to permit use of conclusions about it to be applied to the materials of interest. Alternatively, a process that is similar enough to the process of interest to be used in this manner. [CP]

analogue process -- in high-level radioactive waste management, a process that is understood to an extent that permits other processes to be understood by analogy.

behavior -- the response of a material to the environment in which it is placed. [CP]

confirm -- 1: to make firm or firmer : STRENGTHEN 2: to give approval to : RATIFY 3: to give new assurance of the validity of : remove doubt about by authoritative act or indisputable fact. [Webster]

extrapolate -- to infer (values of a variable in an unobserved interval) from values within an already observed interval 2a: to project, extend, or expand (known data or experience) into an area not known or experienced so as to arrive at ... 2b: to predict by projecting past experience or known data.. [Webster]

extrapolate -- to project known data or experience into an area not known or experienced so as to arrive at a usually conjectural knowledge of an unknown area by inferences based on assumed continuity, correspondence or other parallelism between it and what is known. [CP]
input -- information used to make an analysis or to develop a model. It may include data, correlations, models, expertise, and judgement. [CP]

in-service conditions -- the normal conditions to which a system and its components will be exposed during their operational lifetimes. [E722, E44]

in-service test -- a test in which building components or materials are exposed to degradation factors under in-service conditions. [E632, E6]

in situ -- in position ; in the natural or original position. [Webster]

in situ test -- a test conducted in the environment in which a material or waste form will be emplaced. [CP]

normal test conditions -- conditions in which the values of the independent variables are set at or near the values for service conditions, with allowance for anticipated changes in service conditions. [CP]

predict -- to declare in advance; esp : foretell on the basis of observation, experience, or scientific reason. [Webster]

response test -- a test to observe or measure the response of a material to a particular stimulus, such as leach rate, anodic polarization, or magnetic hysteresis. A further objective may be to elucidate alteration. [Should these types of tests be included in with characterization tests?] [CP]

service conditions -- conditions in which the values of the independent variables characterizing the service environment for a material are the mean values expected in actual service. [CP]

service term -- the period of time for which predictions of behavior are to be made. [prediction time?] [CP]

short-term test - any test (1) conducted over a period of normally less than about 5 years, or (2) completed before validation of the model used for long-term prediction of materials behavior.

validate -- 1: to make legally valid 2: to support or corroborate on a sound or authoritative basis, e.g. experiments designed to validate his hypothesis.

validation test -- in high-level radioactive waste management, a test that gives legal support for or corroboration of the soundness of a model that is used to predict the expected behavior of a material in repository service.

verify -- to establish the truth, accuracy or reality of.
SYN see confirm. [Webster]

waste package -- the waste form and any containers, shielding, packing and other absorbent materials immediately surrounding an individual waste container. [CP]