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

March 30, 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 November 1988 (FIN-A-4171-7)

Dear Mr. Peterson:

Enclosed is the November 1988 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.

Sincerely,

Charles G. Interrante
Program Manager
Corrosion Group
Metallurgy Division

Enclosures

Distribution:
WM Docket Control Center (1-original)

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8904030138 890330
PDR WMRES EUSNBS
A-4171 PDC

WM-1
A4171
NH14

Monthly Letter Report for November 1988

Published March 1989

(FIN-A-4171-7)

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). Comments by the NRC and its contractors are solicited. We do not intend, to continue reviewing reports like these, which deal with general topics on performance assessment, aqueous models and leaching models.

1. UCRL-53761, "Waste Package Performance Assessment: Deterministic System Model Program Scope and Specification," October 1986.

2. UCRL-52658, "Calculation of Chemical Equilibrium between Aqueous Solution and Minerals: the EQ3/6 Software Package," February 1979.

3. Chapter 6, Phenomenological Models of Nuclear Waste Glass Leaching," from "Final Report of the Defense High-Level Waste Leaching Mechanisms Program" compiled by J.E. Mendel, PNL-5157, UC-70, August 1984.

Status of Database

1020 Document citations in HLW database.
78 Completed reviews in HLW database (taken from Vols. 1 to 4).
15 Draft and completed reviews for Vol. 5.

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

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

GLASS -- VITRIFIED WASTE FORM

2 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 November 1988 include the National Technical Information Services (NTIS), DOE Energy Database and Metadex. Examples of the search conducted for each of these databases are in this report.

STATUS OF REVIEWS OF NNWSI REPORTS

NNWSI -- Reports recently identified for review. These reports will not be assigned for review, as our current mission precludes the NIST from initiating reviews on topics that will not relate directly to interpretive reports to be written under Task I. These reports will be entered into the NIST/NRC database as citations only.

The chemical reaction of glassy tuff and J-13 water at 150°C and 250°C, 100 bars pressure, was studied in the laboratory. Modeling results, using the EQ3/6 modeling program, indicate relatively good agreement between the laboratory and the modeling predictions [Knauss, 1986].

A mathematical analysis of temperature, displacement, and stress resulting from heat generated by simulating a heater in a Yucca Mountain exploratory shaft, has been carried out. These data are to be used for planning of an experiment whereby heaters are placed in a Yucca Mountain exploratory shaft [Montan, 1987].

This is a description of the waste form testing program designed to characterize the rate of release of radionuclides from the engineered barrier system. Preliminary results (60 d exposure) indicated that release rates for spent fuel and waste glass would be below 1 part in 10^5 per year [Oversby, 1983].

Spent fuel dissolution results from Canada and Sweden are compared with the results from the NNWSI project. Analysis of the results indicates that the mechanism for radionuclide dissolution is multistaged and depends on the chemistry of the solution and the fugacity of the system. Analytical problems in carrying out the analyses are described [Oversby, 1987].

1. Knauss, K. G., "Zeolitization of Glassy Topopah Spring Tuff Under Hydrothermal Conditions," UCRL-94664, December 1986.

2. Montain, D. N., "Thermomechanical Calculations Pertaining to Experiments in the Yucca Mountain Exploratory Shaft," UCID-21100, April 1987.

3. Oversby, V. M., "The NNWSI Waste Form Testing Program," UCRL-89477, November 1983.

4. Oversby, V. M. and Shaw, H. F., "Spent Fuel Performance Data: An Analysis of Data Relevant to the NNWSI Project," UCID-20926, August 1987.

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

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

6. UCID-21323, "Preliminary Technique Assessment for Nondestructive Evaluation Certification of the NNWSI Disposal Container Closure," November 1987.

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

8. ANL-88-14, Abrajano, T. A., Bates, J. K., Gerding, T. J. and Ebert, W. L., "The Reaction of Glass During Gamma Irradiation in a Saturated Tuff Environment, Part 3: Long-Term Experiments at $1x10^4$ rad/hr," February 1988.

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	x			
UCRL-21019	x			
UCRL-21013	x			
UCRL-95961	x			
UCID-20450	x			
UCID-21323	x			
ANL-88-14	x			

Category 2 -- Review as time permits

1. UCRL-95962, "Hydrogen Speciation in Hydrated Layers on Nuclear Waste Glass," January 1987.

2. UCRL-94658, "Integrated Testing of the SRL-165 Glass Waste Form," December 1986.

3. UCRL-91258, "Leaching Savannah River Plant Nuclear Waste Glass in a Saturated Tuff Environment," November 1984.

4. ANL-84-81, "NNWSI Phase II Materials Interaction Test Procedures and Preliminary Results," January 1985.

5. HEDL-7540, "Technical Test Description of Activities to Determine the Potential for Spent Fuel Oxidation in a Tuff Repository," June 1985.

6. HEDL-SA-3627, "Predicting Spent Fuel Oxidation States in a Tuff Repository," April 1987.

7. UCRL-15976, SANL-522-006, "Microstructural Characteristics of PWR Spent Fuel Relative to its Leaching Behavior", April 1985.

8. UCRL-96702, "Geochemical Simulation of Reaction Between Spent Fuel Waste Form and J-13 Water at 25°C and 90°C," November 1987.

9. UCRL-53702, "Spent Fuel Test - Climax: An Evaluation of the Technical Feasibility of Geologic Storage of Spent Nuclear Fuel in Granite," March 1986.

10. UCID-21274, "Plan for Integrated Testing for NNWSI Non EQ3/6 Data Base Portion," May 1987.

11. UCRL-94721, "Leaching of Actinide-Doped Nuclear Waste Glass in a Tuff-Dominated System," UCRL-94721, January 1987.

12. UCRL-90044, "Waste Package for a Repository Located in Tuff," November 1983.

13. UCRL-89475, "Post Emplacement Environment of Waste Packages," November 1983.

14. UCID-21323, "Preliminary Technique Assessment for Nondestructive Evaluation Certification of the NNWSI Disposal Container Closure," November 1987.

15. WHC-EP-0107, "Measurement of the Oxidation of Spent Fuel Between 140° and 225°C by Thermogravimetric Analysis," September 1988.

16. UCRL-93735, "Estimates of Radionuclide Release from Glass Waste Forms in a Tuff Repository and the Effects on Regulatory Compliance," April 1986.

17. UCRL-15801, "NNWSI Waste Form Testing at Argonne National Laboratory," March 1986.

Category 3 -- File and cross reference

None this month.

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.

Chapter 4, "Dissolution of Specific Radionuclides," has been assigned and no draft has been received to date. The other chapters of PNL-5157 have already been reviewed by NBS.

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.

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	x			
DP-MS-87-157			x	

Category 2 -- Review as time permits

1. "Large Scale Leach Testing of DWPF Canister Sections," Proceedings of the Materials Research Society Symposium, "Scientific Basis for Nuclear Waste Management X," December 1986.

2. "Waste Glass Leaching: Chemistry and Kinetics," Proceedings of the Materials Research Society Symposium, "Scientific Basis for Nuclear Waste Management X," December 1986.

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

4. DOE/NE/44139--34, "Preliminary Results of Durability Testing with Borosilicate Glass Composition," January 1987.

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

On November 1, the test of specimen ST5v was initiated. Hardness of the test specimen (estimated from data taken on the plate from which it was machined) was Rockwell C 22.8 and initial stress-intensity was 43 ksi-in$^{1/2}$. As part of this test, a two-channel audio recording of the amplified signal from the acoustic transducer was made. One channel recorded the amplified acoustic event and the other recorded the root mean square (rms) of that signal. The rms signal is squared when it is used to represent the energy of an acoustic

event. The recording practice used here met with partial success. While the acoustic events were successfully recorded, switching noises (associated with the apparatus used for the electric-resistance measurements of crack length) were themselves recorded as "events." Nevertheless, these acoustic tracks did furnish some reliable records of the cracking behavior for this test specimen, for periods of six hours per record. However, due to the presence of the switching noises on these records, it would be very difficult to play them back in an attempt to recreate the cracking events, that is to recreate them with the intention of recalculating the energy released during the periods that the tapes represent. However, an operator could manually reject the switching noises from the record, as these noises are easily distinguished (with an oscilloscope) from cracking events.

The test of Specimen ST5v was completed on November 7, 1988. A later optical examination of the specimen revealed a crack growth of about 0.40 inches. Initial crack length of 1.42 inches extended to 1.82 inches before any significant branch cracking occurred. Data taken after branch cracks from have no apparent value. When a branch crack did form, it extended through 3/4 of the thickness of each of the two beams of the double beam specimen. Thus, the crack of this test specimen had extended for a full 0.40 inches and during this extension period, the data on crack length was recorded along with data on the acoustic events. Further, the audio record of the acoustic events contains time marks needed to match this data with electric-resistance measurements of crack length. There is an aspect of this test that was regarded as only a partial success, and it is the acoustic record. The records of several previous tests were very sensitive, i.e. the rms voltage from the acoustic transducer was large even for small calibration taps (of a piano wire) onto the external surfaces of the specimen chamber. After this test had been initiated with a very sensitive transducer, the sensitivity of this particular transducer suffered a dramatic decrease. While this transducer problem was neither desired nor understood at that time, the test was considered to be successful enough to complete (which required that the transducer could not be exchanged for another one). Any attempt to rectify the problem during the test would have required dismantling of the test apparatus and the reinitiation of the test. It was reasoned that even with a transducer that was less sensitive, the same computational methods must be used in development of data analysis techniques, and so this data could prove useful. During this test many fewer events were recorded -- perhaps four per hour, as opposed to as many as five per minute (very rough preliminary estimate) in previous tests. Further, in previous tests the events seemed to occur in clusters, and this clustering of events was not noted during this test, which is another indication that sensitivity was below normal.

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

The influence of corrosion in the soil environment on the surface roughness of steel samples is being characterized. A diamond stylus, whose vertical movement is measured and monitored, is drawn across the face of the steel specimen. The diameter of the stylus is 10 μm; it is drawn across the specimen surface for a distance of 15 mm. The maximum vertical displacement

of the stylus is expressed in μm as a maximum roughness. The five greatest excursions along the 15 mm trace are averaged and defined as an average roughness. In addition to this measurement, the surface of the specimen is examined at 50x using an optical microscope to determine the number and distribution of pits. Weight loss is determined from data on the original and final weight. Preliminary evaluation of data from the first experiment indicates that the electrochemical results underestimate the actual weight loss by approximately 10 percent.

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

The studies involving possible localized corrosion of A27 steel will be prepared in the coming months for submission for publication in a journal. Additional reading and literature references have been collected on the corrosion of this and similar steels.

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

The corrosion equipment and test procedure were checked for accuracy and proper function using 316L stainless steel in 0.9 percent NaCl solution. A test was prepared and started on Nov. 28, 1988 that exposed Zircaloy-2 to 10 times concentration J-13 water at 95°C and a pH of 8.25. The initial open-circuit potential was -.573 volts vs. a saturated calomel electrode (S.C.E.). All voltages in this report are in reference to the S.C.E. The open-circuit potentials (V vs. SCE) for this specimen versus time are given in Table 1.

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

On Nov. 28, 1988, cyclic polarization measurements were made and the potential was applied at a rate of 5 mv/s. This specimen in these conditions had a passive region extending from -0.300 V to +0.935 V where breakdown occurred. The return half of the scan showed that the current remained higher than the current in the first half of the scan, and the protection

potential was +0.180V. It is clear that Zircaloy exhibits passivity in the J13 water at 95°C, but the large hysteresis observed in these measurements indicates a potential susceptibility to localized corrosion. As a result, more experiments will be required before we can fully understand the corrosion behavior of Zircaloy in this environment.

TASK 4 - GENERAL TECHNICAL ASSISTANCE

As part of our efforts to coordinate the activities at the NIST with those at the Center for Nuclear Waste Analyses, Dr. Charles Interrante and Dr. Neville Pugh visited Prasad Nair and his associates at the Center for Nuclear Waste Analyses on November 11 - 12, 1988.

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

DATA SOURCE

(a) Organization Producing Data

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

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

O'Connell, W. J. and Drach, R. S., "Waste Package Performance Assessment: Deterministic System Model Program Scope and Specification," UCRL-53761, 1986.

DATE REVIEWED: 8/22/88; Revised 10/31/88; 11/5/88.

PURPOSE

"We describe the principal processes affecting the waste package's long-term performance and the models developed for these processes." The report also includes the identification of the principal processes.

KEY WORDS

System performance computer code, Monte Carlo, general corrosion, pitting, solubility, Radiation Model, Thermal Model, Mechanical Model, Waste Package Environment Model, Waste Form Alteration Model, Waste Transport Model, System Drive Model, TACO2D, ORIGEN2, WAPPA, TOUGH-A, MORSE-L, field, Yucca Mountain, air, tuff composition, Cl, tuff, alpha radiation field, gamma radiation field, ambient temperature, ambient pressure, lithostatic pressure, cladding, stainless steel, weld, spent-fuel-rod without defects, glass (not specified). high-level-waste (not specified), spent fuel (not specified), actinides, fission products, neutron, gamma rays (not specified), density, modules of elasticity, thermal conductivity, thermal expansion, yield strength, corrosion (general), deformation (elastic), leaching (radiation enhancement), leaching (spent fuel), matrix dissolution (glass).

CONTENT

This report consists of 52 pages which include an executive summary, an abstract, and introduction, a list of contents, a list of figures, 21 figures, a list of tables, 9 tables, a glossary, and the following number of pages covering each topic listed:

Topic	Pages
Waste Packages and Processes Affecting Waste Package Performance:	
Waste Forms and Waste Packages	0.5
Processes Affecting the Waste Package	2.5
Earlier Programs of Similar Scope	2.0
PANDORA Models Description:	
Waste Package Model	0.5
Radiation Model	6.5
Thermal Model	3.0
Mechanical Model	4.5
Waste Package Environment Model	2.5
Corrosion Model	1.0
Waste Form Alteration Model	2.0
Waste Transport Model	0.5
Drive Model	8.5
Conclusions:	1.0
References:	1.0
Appendix A. WAPPA's Gamma Ray Attenuation Model	2.0
Appendix B. PANDORA's Gamma Ray Dose Model	4.0

AMOUNT OF DATA

There are 10 schematics of waste package, 9 flow diagrams, one temperature versus the radius of waste package, a schematic of water flow patterns, 6 lists of elements of data diagrams, and 3 lists of elements of mechanical model.

The dimension of the presented data are:

Gamma Ray Flux (Photons/sec·Cm^2) (o to 5 x 10^n) versus container Radius (Cm) (0 to 30).

Effective Gamma Ray Absorption Coefficient (m^2/kg) (0 to 1.6 x 10^{-2}) versus Gamma Ray Energy (MeV) (0 to 1.2).

TEST CONDITIONS

The present system modeling is based on the existing code, WAPPA, developed earlier in the ONWI program. There are modifications for the application of this code to the NNWSI waste package. "The model geometry for an appropriate degree of simplification has essentially one dimension of variation, the radial direction in a cylindrical geometry."

"Each annular element in the waste package is described by its inner and outer radii and a materials name.: Besides the component annuli, the PANDORA adds corrosion-layer annuli, a gas gap annulus and Zircaloy cladding as an additional barrier protecting the spent fuel waste form."

"The properties of waste-form annuli may be space-averaged properties, actual properties of the solid waste form, or total quantity per waste package," depending on each submodel.

"There are seven process models: (1) radiation model, (2) thermal model, (3) mechanical model, (4) waste package environment model, (5) corrosion model, (6) waste form alteration model, and (7) waste transport model. Each model may consist of several interacting or mathematically related submodels. The driver model treats the interactions of the models and the sequencing of these interactions."

Radiation Model

The source model uses code ORIGEN2 which has been developed for the burnup calculation of nuclear fuel, and "interpolates in the time variable."

The gamma ray dose model uses "MORSE-L which calculates radiation transport using a Monte Carlo method."

"The gamma ray absorbed dose rate at waste form surface assumes that the outer-most waste form annulus is a thick self-shielding source and the dose rate at its outer surface comes from that source alone."

"The mass energy-absorption coefficients between 0.4 and 1.0 ev are nearly equal for main constituents of glass and metal barriers, and that for spent fuel is dominated by the major constituent, uranium by weight."

"The alpha particle dose model gets the alpha particle generation rate from the radiation source model."

"The fission dose model functions similarly to the alpha particle dose model."

Thermal Model

"The model assumes steady-state radial heat transfer, cylindrical symmetry and homogeneous material within an annulus."

Mechanical Model

"The principal elements are waste forms and metal barriers. Other element types account for corrosion and gaps. The elements are assumed to be free to expand in the axial direction."

Waste Package Environment Model

"The simplified model assumes that all the water flux passing through a certain area above the waste package will flow into the emplacement hole and contact the waste package. However, the likely flow at an emplacement hole is around the hole rather than into the hole. After the water's influx to the emplacement hole, we simply assume that the water can keep part of the package wet."

Corrosion Model

"The first-generation corrosion model considers general corrosion in two environments: (1) air-steam, and (2) air-water vapor."

Waste Form Alteration Model

"We assume that activation products contained in the cladding material or stainless steel and Inconel components are converted into mobile form congruent with the corrosion, except for zirconium and nickel."

"We assume that matrix dissolution rate is the limiting factor for the contained elements' release rate. We condense all of the fast-release fraction of a fuel rod, which may actually be released over several years, into its first year after the full rod cladding fails."

"For the matrix-limited component of waste release, we assume that this release begins at its full rate when the first fuel rod cladding is breached. This assumes that the release is limited by water flow and/or matrix solubility rather than the fraction of the fuel rods exposed to the water flow."

"For a radionuclides with a fast-release fraction of x %, we assume that the last x % of the matrix has none of this nuclide, and the first (100-x) % has a concentration of this nuclide determined from the total inventory of the nuclide divided by the total inventory of uranium."

"For a glass waste form, it is assumed that release of all elements is controlled by the matrix alteration rates."

Waste Transport Model

"It is assumed that the water flux out equals the water flux in and that any gases mobilized after the first breach are immediately available for transport beyond the boundary of the waste package."

UNCERTAINTIES IN DATA

Radiation Model

"The gamma ray dose model has a reasonable degree of accuracy and additional MORSE-L runs must be performed to explore the degree of accuracy achievable."

"A threshold gamma ray energy is perhaps 0.2 Mev for glass waste forms and 0.3 Mev for spent fuel. Below the threshold gamma ray energy, a high probability of absorption takes place."

"Thermal model can compare limited variations in waste package design where heat transfer is altered."

DEFICIENCIES/LIMITATIONS IN DATABASE

Radiation Model

"The gamma ray dose model has some limitations in accuracy compared to the full situation because of the simplifying approximations we use:

1. Mass energy-absorption coefficients for materials across a range of atomic numbers are not quite equal.

2. The sources are thick but not infinitely thick: a small effect of radius was noted.

3. Some waste form shapes are only coarsely approximated by a cylinder.

4. Spent fuel in the form of fuel assemblies could have some streaming effect in the open channels between rows of fuel rods. It is nonuniform scattering with a spatial variation."

Thermal Model

"If the waste package design departs from cylindrical symmetry and homogeneous material within an annulus, 2-D or 3-D models are necessary. For a horizontally emplaced waste package, the k_e/k ratio is greater than or equal to one, and is not continuous."

"Mechanical model did not evaluate (1) fallen rocks on the horizontal waste package, (2) pinhole penetration through fuel rods which can heat the water intruded exerting an interior pressure, (3) stresses associated with individual rod, and (4) inter-rod forces. The maintenance of cylindrical symmetry is an uncertain assumption when the yielding is significant. Finally, fracture criterior for ductile materials are not of use."

Corrosion Model

"The PANDORA model will take conservative envelope of the sensitivity and localized corrosion modes."

Waste Form Alteration Model

The element release rate did not take into account the constraint imposed by solubility limit. The total release for a group of containers will be deferred to future work.

Waste Transport Model

"Transport is to the borehole wall and future work includes that at some distance into the rock."

CONCLUSIONS OF AUTHOR

"We have developed the first generation of conceptual models for the long-term performance assessment of a nuclear waste package to be emplaced in a repository in an unsaturated tuff environment. The models of the processes and their interactions provide the specification for a first-generation computer program. The purposes of the first generation development are (1) to guide later generations of development and (2) to get first-approximation results examining interactions among the processes and evaluating proposed designs.

Our conceptual models use present knowledge and indicate an agenda for future information needs.

The radiation source model is a standard one and is implemented by data tables from a detailed model. Our gamma ray attenuation model is a new approximation of a well-understood but complex process. The goals of the approximation are simplicity and reasonably accurate results in variations or sensitivity analysis. We will need to do validation of this approximation.

Our thermal model uses steady-state heat transfer to determine the temperature field. Earlier studies using a time-varying heat transfer code have shown only small departures from the steady-state results.

The mechanical model uses well-understood principles for the elastic stress-strain range and somewhat conservative models for the limits of elasticity and for failure modes.

Future needs in the radiation, thermal, and mechanical areas include modeling of effects near the ends of the waste package, validating simplified models and evaluating the achievable values in the simplification/accuracy trade-off.

The waste package environment excludes liquid water in early years after repository closure, when the local temperature is above the boiling point of water. The groundwater flow details near the waste package are presently unknown for the proposed emplacement geometry and the unsaturated, thermally changing conditions. We have greatly simplified model which in conservative, possibly by orders of magnitude.

We include general corrosion in the first model, but defer localized corrosion modes such as pitting and stress corrosion cracking. It is unclear whether we can model these modes by establishing conservative bounds on go/no-go thresholds or whether we will need models including microscopic initiation and subcritical growth over the long time period of interest to waste package performance.

Waste form alteration and transport of waste to the waste package boundary are modeled by data tables to be developed from experiments. When the details of groundwater movement through a partially degraded waste package are developed, the corresponding responses of waste form alteration and waste transport processes may require more detailed models to describe the range of possible flow patterns and responses.

Our first generation computer code will be able to examine the interactions of processes affecting the waste package. Interactions among heat source, heat transfer, fluid flow, mechanical stress, and general corrosion are included in the first-generation model. Gamma radiation effects on corrosion can be included via data tables. The magnitudes of different radiation types-gamma rays, alpha particles, spontaneous fissions, and neutrons--will be calculated over time; their relative magnitudes can guide modeling of their effects in alter generations of the model. The first-order effects of progressive degradation of barriers upon fluid flow will be calculated. The effects of fluid flow, temperature, and radiation upon waste form alteration and waste transport to the boundary of the waste package will be calculated.

Calculations with the first-generation computer code will quantify some (but not all) of the important consequences of design choices. Calculations will also indicate which processes and interactions modeled are most important. Calculation of magnitude of effects, sensitivity, and estimates of uncertainty or suspected bias (hopefully in a conservative direction) can identify present model simplifications most in need of refinement in the next generation model."

COMMENTS OF REVIEWER

This report outlines the framework of computer codes for the deterministic system's performance of waste package, based on the existing code, WAPPA, developed earlier in ONWI. It has minor modifications of WAPPA made for NNWSI projects. The system code has to be developed for the requirement of NRC regulations and this work is certainly a unique basis and reasonably written for this purpose. Although the authors insist that the code is intentionally simplified to develop the underlying framework, there are many areas of inconsistency, incompatibility, omissions, inefficiency, and wrong or vague descriptions of the framework itself. Much more work is necessary in future and it is prudent to wait for the real implementation.

The present code, PANDORA, is weakly modified version of the WAPPA code for NNWSI projects. They discarded the performance of backfill, included groundwater input data containing gas release and the treatment of spent fuel. However, the underlying framework has not progressed much. Rather, it discarded important issues treated in WAPPA, even though they are considered to be important in NNWSI environments. Those issues include: (1) container oxidation in air/steam conditions, (2) gamma ray attenuation model (will be discussed more below), (3) stress corrosion cracking and creep of containers, and (4) glass leaching.

Also, when each model adopts the existing relevant codes, the authors did not evaluate the basic assumptions used in those codes and their applicability in

NNWSI. For instance in code MORSE-L or ORIGEN-2, cross-section track or geometric effects were neglected, which may be important in NNWSI. The most serious one is the effect of time scale since ORIGEN-2 or MORSE-L are based on the short-term performance. Therefore, the existing codes may not be able to be used when the alteration of waste package or of environments is significant. Neither WAPPA nor the current code provides specific prescriptions for time-dependent boundary conditions such as cracked glasses, plastically deformed containers,breached containers and time-dependent rock temperature. In these circumstances, currently quoted submodels are also considered to be no longer applicable. Such examples are rigorous description of elastic stresses, heat transfer or stress relief in the deformed waste package.

As a first approximation, thermal or mechanical models are unnecessarily extensive, while corrosion models, waste transport models or waste package environment models are too simplified.

The code PANDORA is based on the deterministic model of waste package performance. However, there are codes available based on probabilistic model (the Aerospace Corporation, 1985) or on the combined model with deterministic and probablistic approaches (Commissariat ν l'Energie Atomique and Ecole Nationale Supιrieure des Mines de Paris, 1988). Each approach has its unique advantages in licensing the waste packages. Therefore, it is desirable for the authors to compare their approach with the probablistic one.

More detailed comments are given about each model below:

Radiation Model

Radiation source is presumed to be a line source. This is only valid when the observation distance is far from the source. The current model does not consider radiation far away in rocks from the waste package but the space between bore-hole wall and the waste package which is a very short distance for the use of line source assumption.

(defined as the depth such that the attenuation of the primary gamma ray flux from the equivalent line source to the point of observation) is simply a monotonically increasing function of the radius of waste package while the radiation flux is inversely proportional to the sum of z and the distance of observation (according to reactor-shielding design). Therefore, WAPPA's description is correct.

The assumption of the uniform waste form misleads many conceptually defined quantities such as Z or L" (half of the gamma ray energy existing in the waste form surface originates from the zone within a depth L" from the surface). During the manufacturing of the waste package, glasses are cracked and those quantities, therefore, may need to be modified accordingly.

Descriptions are needed for the treatment of activation products, decay daughters, prior accumulation of radionuclides to the emplacement of waste packages, alpha- and gamma-radiolysis, radiation embrittlement, and dose-rate effect.

Thermal Model

There are heat losses which were not considered in the model. Examples are heat of vaporization (or condensation) or heat loss through the fractured rock.

Many constants used in the formulation are dependent on temperature and radiation field. They include thermal conductivity, rock temperature, gas or liquid density, volume expansion coefficient, viscosity, and active length of waste form.

Mechanical Model

Descriptions in the plastic regime should be explored. Creep deformation can take place for many years at low stress levels.

Both compressive and tensile stress concentrations can be present from waste package geometry and weldments. They are not necessarily associated with existing precracks.

Many equations were described incorrectly in the elastic regime. For instance, equations 3.4-12 and 3.4-16 will also lead to three directional displacements, and equations 3.4-12, 3.4-16 and 3.4-34 use incorrect definitions.

Any fracture taking place may lead to new stress to adjacent components or parts by building stress concentration as far as the stresses of the whole system are reduced. It does not necessarily relieve all the local stress concentrations.

Many elastic constants may also depend on radiation field or temperature. An example is the modification of Young's modulus by radiation embrittlement.

Waste Package Environment Model

More dangerous species are present in groundwater other than chloride ions. They are fluoride ions, carbonate (or bicarbonate) ions, and radicals generated by radiolysis. Also, solution pH is a time-dependent quantity as glasses interact with water and radiation field.

Corrosion Model

Very little effort is given to model localized corrosions. Also, there are unmentioned failure modes such as salt-cracking, microgalvanic corrosion, wet-dry cycle effect, and inside oxidation of container.

Waste Form Alteration Model

The containers may age for extended periods. For instance, carbides may continuously grow or containers may slowly become embrittled by radiation.

Displacement damage in waste form has not been ruled out based on a technical assessment from the dominance of thermal crack. It may lead to a significant alteration of the radionuclide transport model.

It is encouraging to have a distribution of container pits. However, the subsequent release modes of radionuclide will vary significantly due to the distribution.

Waste Transport Model

To describe the waste transport properly, it is necessary to include leach models, or, at least, justifications are necessary stating that solubility limit, diffusion or flow rate is a dominant factor controlling the release rate of waste form. There are many realistic models in waste transport which are available and recommended to be used.

Drive Model

The model describes every event from the beginning, making a gigantic code. It may be desirable to have a subroutine to pick up necessary models to consider in a given time interval. In this way, the system will be organized more efficiently.

Once any failure occurred, there was no time delay. This seems to be too conservative. For many instances, it takes a while to achieve such a condition. For example, the situation of a single pin-hole is quite different from that of a complete breaching of a container in waste form release. It is hard to believe in the complete instantaneous breaching of a container.

Direct reversible directions (figure 3-14) are confusing since those reversible modifications are also made by the system-loop.

RELATED HLW REPORT

1. INTERA Environmental Consultants, Inc., WAPPA: A Waste Package Performance Assessment Code, Battelle Memorial Institute, Office of Nuclear Waste Isolation, Columbus, OH, ONWI-452 (1983).

2. Boyars, C., Fuller, G., Moller, R., Stephens, K., and Zarembra, L., "Demonstration of Methodology for Waste Package Performance Assessment," The Aerospace Corporation, WPR-86(6810-01)-01, (1985) and related reports.

3. Lewi, J., Mejon-Goula, M. J., Goblet, P. and Cernes, A., Berlin Conference

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

(a) Relationship to Waste Package Performance Issues Already Identified

2.1, when, how, and at what rate will brine penetrate the packing around the waste package and contact the container?

2.1.3.1, how will the chemical characteristics of the brine reaching the waste package container be affected by radiolysis?
2.1.3.2, how will the chemical characteristics of the brine contacting the waste package container be affected by chemical reaction with the packing and container materials?
2.2.1, what will the physical properties of the waste package container materials be as affected by temperature, radiation, interaction with the packing materials, brine migration, and other effects?
2.2.2, what will the chemical properties of the waste package container materials be as affected by temperature, radiation, interaction with the packing materials, brine migration, and other effects?
2.2.3.1.1, what will be the magnitude of the lithostatic/hydrostatic loads on the waste package container and the resultant stress developed within the container as a function of time?
2.2.3.1.2, what will be the magnitude of the thermal stresses developed within the waste package container as a function of time?
2.2.4.1, what are the rates of corrosion as a function of time for the various corrosion modes of the waste package container?
2.2.4.2.1, what is the predicted rate of radiolytic generation of hydrogen, oxygen, and other species due to gamma radiation in the vicinity of the waste package container?
2.2.5, what are the anticipated physical dimensions of waste package container breach as a function of time?
2.2.6, what will be the physical characteristics (e.g., temperature, pressure, and flow rates) of the brine penetrating the waste package container and reaching the waste form as a function of time?
2.2.7, what will be the chemical characteristics (e.g., Eh, ph, and chemical constituents of the brine penetrating the waste package container and reaching the waste form as a function of time?
2.2.8, how will the design of the waste package container accomodate all potential natural and waste package-induced conditions?
2.3.1, what are the physical, chemical, and mechanical properties of the waste form, how do those properties of the waste form change with time, and how will such changes alter the ability of the waste form to contribute to the overall performance of the repository system or impact the performance of other barrier materials and properties of the site?
2.3.2.4, what will be the chemical species of the radionuclides released from the waste form?
2.3.5, how will packing, container materials (including overpacks, canisters, and any special corrosion-resistent alloys or spent fuel rod cladding, if applicable) and/or their alteration products interact with the waste form to cause its alteration and/or effect release of radionuclides?
2.3.6.1, what is the predicted rate of failure of each of the potential failure mechanisms for spent fuel.
2.3.6.2, what is th predicted size of cladding breach associated with each of the potential spent fuel cladding failure mechanisms?
2.4.1, what will be the convective flows in the waste package as a function of time?
2.4.3, how will the radionuclide species (i.e., particles, colloids, and solubles) change with time in the waste package?

(b) New Licensing Issues

(c) Comments Related to Licensing

This report provides a predictive computer code of waste package performance which need to be better formulated prior to licensing waste package.

ABSTRACT

"Integrated assessments of the performance of nuclear waste package designs must be made in order to qualify waste package designs with respect to the containment time and release-rate requirements set by the NRC in the Code of Federal Regulations (10 CFR 60). PANDORA is a computer-based model of the waste package and the processes affecting it over the long term, specific to conditions at the proposed Yucca Mountain, Nevada, site. The processes PANDORA models include: changes in inventories due to radioactive decay, gamma radiation dose rate in and near the package, heat transfer, mechanical behavior, groundwater contact, corrosion, waste for alteration, and radionuclide release. The model tracks the development and coupling these processes over time. The process models are simplified ones that focus on major effects and on coupling. This report documents our conceptual model development and provides a specification for the computer program. The current model is the first in a series. Succeeding models will use guidance from results of preceding models in the PANDORA series and will incorporate results of recently completed experiments and calculations on processes affecting performance."

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

DATA SOURCE

(a) Organization Producing Data

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

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

Wolery, T. J., "Calculation of Chemical Equilibrium between Aqueous Solution and Minerals: the EQ3/6 Software Package," UCRL-52658, February 1979.

DATE REVIEWED: 9/30/88; Revised 10/31/88; 11/5/88.

PURPOSE

"The purposes of this report are to announce the availability of the EQ3/6 software package, to discuss the application of EQ3 and EQ6 to solve problems in aqueous geochemistry, to compare these with other available programs, and to present the mathematical and numerical approaches adopted in program EQ6."

KEY WORDS

Theory, computation development, Monte Carlo, Newton-Raphson, relaxation, reaction path, flow-through model, SOLMNEQ, WATEQ, REDEAL, MINEQL, PATHI, SOLSAT, TOTH, field, simulated field, Salton Sea Water, groundwater, simulated groundwater, pH=3 HCl solution, acid solution (pH <7), ambient pressure, ambient temperature, basic (alkaline) solution (pH >7), high pressure, high temperature, neutral solution (pH = 7), redox condition, static (no flow).

CONTENTS

This report consists of 41 pages which include an abstract, an introduction, a glossary of symbols, 9 tables, 8 figures, and the following number of pages covering each topic listed:

Topic	Pages
Capabilities of Programs EQ3 and EQ6	1.5
Equilibrium calculations in Aqueous Geochemistry:	
Nature of Chemical Equilibrium Problems	1.0
Development of Models for Aqueous Systems	2.0
Applying the Newton-Raphson Method to the class II Equilibrium Calculation:	
Basic Development	13.0
Under-Relaxation Techniques	0.5
Optimizing Starting Estimates	0.5
Finding the Correct Phase Assemblage	4.0
Computing Reaction Path Models:	
Types of Models	1.0
Use of Finite Differences	1.5
The Flow-Through Model	1.0
Example: Dissolution of Microcline	1.5
Example: Heating of Salton Sea Water	5.0
References	3.0
Appendix A. Contents of the EQ3/6 Software Package	1.5
Appendix B. Sample Request Form to Obtain the Package from the National Energy Software Center	1.0
Appendix C. Note on Thermodynamic Data	0.5

TEST CONDITIONS

The author adopted three general steps commonly used in solving a chemical equilibrium problem. They are "(1) to define the model in terms of its physical and thermodynamic nature, (2) to manipulate this original set of equations into a desirable form, and (3) to solve the remaining simultaneous equations."

Many trial and error methods are developed to solve non-linear equations and to determine the system with the best guess based on the limited amount of known input information and numerical solutions.

Particularly in many instances, this work is based on the model developed by Helgeson and his coworkers. Helgeson's program was modified to improve the treatment of (1) supersaturation, (2) drift error involved in the integration of differential equations, and (3) long and costly execution.

EQ3/6 is composed of two separate works, EQ3 and EQ6. "EQ3 computes the concentration, thermodynamic activity of each chemical species, and the saturation state of the fluid with respect to all relevant mineral phases." "EQ6 first equilibrates the input system by calculating a new model of modified fluid plus precipitates, and then computes reaction progress models of compositional evolution and mass transfer in a closed or open (flow-through) system containing this aqueous solution (with or without any initial precipitates.)"

"Data files support model calculations in the temperature interval, 0-350°C, either at pressures on the 1 atm-steam saturation curve (0-100°C at 1 atm and 100-300°C with the steam saturation) or at a constant pressure of 500 bars."

UNCERTAINTIES IN DATA

"We lack sufficient understanding of these parameters (activity coefficients) at high temperatures and pressures, but the present assumption of unit activity coefficients for such species appears reasonable."

"EQ6 test for convergences by comparing each of βmax (the largest residual sector) as δmax (the largest Newton-Raphson correction term) with a user-specified tolerance parameter (usually in the range 10-6 to 10_{-10})."

DEFICIENCIES/LIMITATIONS IN DATABASE

"The activity coefficient approximations for aqueous species are not suitable to describe aqueous solutions of concentration greater than about 1 molal ionic strength."

"log k values in no way represent a critical and comprehensive compilation, and uncertainties in complex dissociation data are in general much greater than for mineral dissolution data."

Solid solution might be modeled as "ideal solutions, but many are obviously quite non-ideal."

To treat the divergence of Newton-Raphson iteration and the singularity of the ill-condition of Jacobian matrix, special techniques and modification were made. However, "some are specific to the chemical equilibrium calculation dealt with here."

When the maximum precipitable mass of each phase is very small the scaled affinity of the phase is arbitrary reduced. "If a tie exists after scaling the affinities, one must make an arbitrary choice, such as deleting the phase with the lowest numerical index."

"I shall assume that, once a satisfactory phase assemblage has been found, no further question of uniqueness need be considered." However, "it may not be true when some popular non-ideality relations are applied."

In the example of "heating Salton Sea Water", there was a discussion of the realistic appearance of colloid particles or met a stable phases.

CONCLUSIONS OF AUTHOR

There is no formal section entitled CONCLUSIONS. The following is quoted from the content as reviewers' conclusion.

"The newly developed EQ3/6 software package computer equilibrium models of aqueous geochemical systems. The package contains two principal programs: EQ3 performs distribution-of-species calculations for natural water compositions; EQ6 uses the results of EQ3 to predict the consequences of heating and cooling aqueous solutions and of irreversible reaction in rock-water systems."

"The calculation predicts in detail the changes in fluid composition, the identity, appearance, and disappearance of secondary minerals, and the values of reaction progress at which the fluid saturates with reactants."

"The methods used in EQ3 have been discussed in detail by Wolery and Waters, and were used in a computer program called SALT. This document therefore concentrates on presentation of the mathematical derivations used in EQ6 and discussion of some of the important numerical techniques adopted."

"The EQ6 uses the Newton-Raphson method to solve the governing equations of chemical equilibrium for a system of specified elemental composition at fixed temperature and pressure. Convergence is aided by optimizing starting estimate and by under-relaxation techniques. The minerals present in the stable phase assemblage are found by several empirical methods. Reaction path model may be generated by using this approach in conjunction with finite-differences. This method is analogous to applying high-order predictor-corrector methods to integrate corresponding set of ordinary differential equations, but avoids propagation of error."

"The programs are valuable for studying such phenomena as the formation of core bodies, scaling and plugging in geothermal development, and the long-term disposal of nuclear waste."

COMMENTS OF REVIEWER

This report describes methods developed for use in the determination of aqueous geochemical systems. Emphases are on the developing methods to solve non-linear equations and on the empirical methods to determine the system with the best guess based on the limited amount of known input information and numerical solutions. The author improved existing codes such as those made by Helgeson and his co-workers. He provided many useful methods, including various tricks which often are important for the users and difficult to identify. The following is the reviewer's comments for future study which have not been addressed fully in the content.

> "The involvement of kinetics is the issue to be discussed in irreversible reactions. This is particularly important in nuclear waste management where the time frame is very long. The time sequence in precipitation, evaporation, or condensation is a good example. Also, as mentioned by the author too, metastable phases actually do exist. How do we incorporate these phases in the chemical model?"

"There are many unclear and less specific descriptions of chemical reactions. The users may need more specific examples for a better understanding and for finding the applicability of the present methods to their problems."

"The methods are based on trial and error, and are quite empirical. Therefore, they should be organized in a better way for user-specific cases. Sometimes, they are very risky for users. For instance, the divergence of numerical iteration is not necessarily the key criterion to determine the phases present: the divergence can be from other sources as well. Also, there must be ways to prove these methods either experimentally or with the aid of other numerical methods such as the calculus of variation (free energy minimization)."

"Regarding many models of activity coefficients in solid solution and aqueous solute species, the author should be more realistic in choosing those candidates or developing his own models. Too many models were presented without identifying specific advantages to various users' problems."

"Finally, the controversy of system redox should be discussed. There is no system redox in a complex system. How do we deal with individual redox in conjunction with system parameters?"

RELATED HLW REPORT

1. Walters, L.J., Jr., and T.J. Wolery, A monotone-sequences algorithm and FORTRAN IV program for calculation of equilibrium distributions of chemical species, Comp. Geosci., 1, 57-63, 1975.

2. Wolery, T.J., and L.J. Walters, Jr., Calculation of equilibrium distributions of chemical species in aqueous solutions by means of monotone sequences, Math. Geol. 7, 99-115, 1975.

3. Viani, B., "Interim Report on Modeling Sorption with EQ3/6," UCID-21308, Revision 1, January 1988.

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

(a) Relationshp to Waste Package Performance Issues Already Identified

1.1.2.3, how and to what extent is local groundwater flow affected by structural, stratigraphic, and lithologic discontinuities and heterogeneities?
2.1.2, what will be the physical characteristics (e.g., temperature, pressure, and flow rates) of the brine reaching the waste package container as a function of time.

2.1.3, what will be the chemical characteristics (e.g., Eh, pH, and chemical composition) of the brine reaching the waste package container as a function of time?

3.1.1.2, what is the present amount of interstitial and bound water and its chemistry in the host rock (intracrystalline and intercrystalline inclusions, hydrous materials?

(b) New Licensing Issues

(c) General Comments

This report provides methods to predict geochemical environemtns which need to be better formulated prior to licensing waste package.

ABSTRACT

"The newly developed EQ3/6 software package computes equilibrium models of aqueous geochemical systems. The package contains two principal programs: EQ3 performs distribution-of-species calculations for natural water compositions; EQ6 uses the results of EQ3 to predict water systems. The programs are valuable for studying such phenomena as the formation of ore bodies, scaling and plugging in geothermal development, and the long-term disposal of nuclear waste.

EQ3 and EQ6 are compared with such well-known geochemical codes as SOLMNEQ, WATEQ, REDEQL, MINEQL, and PATHI. The data base allows calculations in the temperature interval 0-350°C, at either 1 atm-steam saturation pressures or a constant 500 bars. The activity coefficient approximations for aqueous solutes limit modeling to solutions of ionic strength less than about one molal.

The mathematical derivations and numerical techniques used in EQ6 are presented in detail. The program uses the Newton-Raphson method to solve the governing equations of chemical equilibrium

for a system of specified elemental composition at fixed temperature and pressure. Convergence is aided by optimizing starting estimates and by under-relaxation techniques. The minerals present in the stable phase assemblage are found by several empirical methods. Reaction path models may be generated by using this approach in conjunction with finite-differences. This method is analogous to applying high-order predictor-corrector methods to integrate a corresponding set of ordinary differential equations, but avoids propagation of error ("drift")."

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

DATA SOURCE

(a) Organization Producing Data

Pacific Northwest Laboratory, Richland, Washington

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

Chapter 6: "Phenomenological Models of Nuclear Waste Glass Leaching," from "Final Report of the Defense High-Level Waste Leaching Mechanisms Program" compiled by J.E. Mendel, PNL-5157, UC-70, August 1984. Available from NTIS.

DATA REVIEWED: 7/20/88; Revised 10/31/88; 11/5/88.

PURPOSE

Chapter 6 of this report reviews and discusses mathematical models describing the mechanisms of nuclear-waste glass leaching under a wide range of environmental conditions. The models will serve the purpose of providing long-term predictions of nuclear-waste-glass leaching.

KEY WORDS

Literature review, model, leaching, altered glass-surface, gel-layer and precipitate-layer, interactive leach-model, diffusion, matrix dissolution, ion migration, electric double layer, hydration energy, thermodynamic equilibrium, crystalline silicates, mineral dissolution, rock weathering, adsorption and description, phenomenological model, Quarts, Muscovite, K-Feldspar, Diopside, Forsterite, Nepheline, SRL-131, DI water, dispersion, leachant renewal time, Peclet number, flow, Pyrex, Obsidian, CUA, NBS borosilicate, window glass, CAS, SRL-165C, M3, M5, M7, IDAHO-1277, LLNL-529, PNL 76-68, Frit, ESF.

CONTENTS

Chapter 6 of this report consists of 16 pages which include an executive summary, a background, 1 table, 8 figures, 27 equations, and the following number of pages covering each topic listed:

Topic	Pages
Kinetics of Aqueous Attack	2.0
Interactive Modeling Approaches	1.5
Thermodynamic Models	1.5
Reaction Kinetic Models	2.0
Mathematical Phenomenology of Glass Leaching: a Non-Mechanistic Model	4.0
Diffusion - Controlled Dispersion of Leach Products	2.0
References	2.0

AMOUNT OF DATA

The calculated data with experimental verification are included in 4 figures and 2 places in the content. The dimensions of the presented data are:

$\log_10[kg/0 \cdot t]$ (-4 to 4) versus leach rate slope (0 to 1.2)
where K is the high-dilution rate constant for silica dissolution,
D is the silicon species diffusion coefficient in the protective layer of thickness ℓ, and
q is the proportionality constant in the relationship between the amount of silica leached and ℓ.

Free Energy of Hydration, Kcal/mol (3 to -18) versus Normalized Si Loss, g/m^2 (0.4 to 10^3)

Total Immersion Time, day (10 to 10^3) versus Leachant Concentration, mg/L (10 to 10^3).

Leachant Renewal Time, $day \cdot m^{-1}$ (10 to 10^5) versus Normalized Concentration mg/L (1 to 10^4).

Immersion Time, day (10 to 10^3) versus concentration, mg/L (10^2 to 10^3).

TEST CONDITIONS

In most cases, one-dimensional analysis was performed using a leaching source (glasses) of a fixed concentration in (1) infinitely diluted leachants, (2) leachants with varying concentration, and (3) saturated leachants. Occasionally, the glass surface had layers of protection, gel and precipitates. In rare cases, two-dimensional analysis was performed using cylindrical coordinates in intact or fractured glasses with infinitely diluted leachants.

The following summarizes assumptions, the state of waste forms, environmental conditions, and main leaching-mechanisms.

(1) classical approach

o The diffusion of mobile ions through the glass network.

o Matrix dissolution and surface layer mass transfer.

(2) A protective layer formation

The processes described in (1) classical approach quickly reach their equilibrium, after which protective layers form on the glass surface. These are the porous alteration (gel) and the protective precipitation-layers. At a steady state, silicon-containing species are diffused through the protective layer, balancing the rate of silicon dissolution.

(3) Interactive modeling approach

Leaching is highly sensitive to leachant concentrations which can vary up to the solubility limit at low or even moderate flow rates. The solubility limit can be predicted by thermodynamics.

(4) Thermodynamic approach

Since the contact-time of leachant with glasses is very long in repository, the leachant is expected to be saturated with respect to surface precipitates, arriving at a thermodynamic equilibrium state.

(5) Reaction kinetic approach

The kinetics of mineral dissolution are used in waste glasses because the precipitate-layer on the glasses is crystalline and both have similar base-structure of silicates. Glass dissolution is rate-controlled by surface reaction because of low solubility. Precipitation rates can be added, as the rates of backward-reaction, to the overall reaction rates.

(6) A non-mechanistic approach

A semi-empirical description is presented both with one's intuition and conclusions regarding the importance of specific processes. One example of such processes is the concentration overshoot of leachants. The leachant concentration is the time-integral of accumulation rates of dissolved species. In interactive cases, the accumulation rates can be any function of the integral itself.

(7) Dispersion of leach-product approach

The dissolved species are dispersed by diffusion and convection from intact or cracked glasses to stagnant or low flow-rate groundwater.

UNCERTAINTIES IN DATA

The stated uncertainties in adjustable parameters or subsequently calculated results using these parameters are:

(5) Reaction kinetic approach: The silicon dissolution rates are proportional to nth power of proton activity. The exponent n varies from -0.2 to 0.6 in basic solutions.

(7) Dispersion of leach-product approach: the backfill porosity is 10~20%.

Many parameters have uncertainty ranges, though not stated by the authors. Such parameters include diffusivities of mobile species in solid and liquid, reaction-rate constants, the thickness of altered layer, supersation parameter, and waste form dimension.

DEFICIENCIES/LIMITATIONS IN DATABASE

The authors state following deficiencies/limitations in models. More comprehensive evaluation by the reviewer is given in the section entitled GENERAL COMMENTS.

(1) Classical Approach

Diffusion-controlled kinetics are inadequate to account for the observed leaching data. The modification with moving boundary conditions still do not represent the fundamental physical and chemical processes. The formulation is only credible under conditions of an extremely diluted leachant.

(2) A protective layer formation

A carefully constructed treatment of the interplay of protective-film formation and solubility-controlled dissolution must be incorporated into a realistic model of leaching process.

(3) Interactive modeling approach

- Michiels and Pescatore: The effects of temperature and pH need to be described independently, and alteration layer and precipitation should be considered.

- Michiels and Sullivan: The evolution of surface layer has not been integrated with an approach that accounts for changes in solution chemistry.

- Grambow: The rates of formation or the distribution of precipitates within the layer have not been considered.

(4) Thermodynamic approach

- The choice of structural units in calculating free energies of hydration is arbitrary.

- Species interactions, such as the formation of alumino-silicates, are ignored.

- The application of equilibrium thermodynamic considerations to a fundamentally dynamic situation is only justifiable post-hoc.

- The use of MCC-1 tests without some definite stages of interaction may invalidate the model.

(5) Reaction kinetic approach

After the initial fast dissolution of preferentially attacked glasses, the rates slow down to those of bulk materials, but the overall rates curve of linear kinetics was misinterpreted by parabolic kinetics.

(6) A non-mechanistic approach

The non-linear response functions were approximated to be an elementary product form. Each element of the product uses empirical exponential-decay-form without justifications.

Quantitative prescription is lacking for evaluating the long-time limiting concentration of various elements.

(7) Dispersion of leach product approach

The diffusivity of mobile species in the contacting leachant is too slow, leading to a very short leachant-renewal-time.

CONCLUSION OF AUTHOR

There is not a conclusion section in this report. The following is from the Executive Summary and several discussions in content.

1. The continued leaching of waste glass under almost any given set of conditions ultimately leads to steady-state (or quasi steady-state) concentrations of all leached species.

2. The models developed depend largely on dissolution-rate-constants, effective diffusion coefficients, saturation concentration and identity of alteration products.

3. No comprehensive model is available for the prediction of leaching in geological times. It may be a zero-exponent time-law in saturated conditions, deduced from 1/2 and 1 exponent time-laws in short-term kinetics.

4. The saturated condition in geological times can be predicted through the calculation of the thermodynamic equilibrium state.

5. The observed concentration-overshoot can also be predicted by a semi-empirical approach, which includes the expansion of accumulation rates with respect to the total concentration.

6. The diffusion and convection are equally important in the long-term dispersion of radionuclides from glasses to surrounding environments.

COMMENTS OF REVIEWER

The classification and evaluation of leaching models made by authors are very good, showing the distinctive scientific-merits of representative models: classical leaching-kinetics, the role of protective layer(s), the effect of leachant concentrations, the thermodynamic prediction, the non-mechanistic approach, and the dispersion model. However, some areas need to be reorganized or complemented for better understanding.

The relevant data in generic glasses need to be addressed. Phase separation is an example which was not considered seriously in waste glasses. When the phase-separated microstructures are interconnected, they are likely to be preferentially attacked along easily susceptible phases. Other localized attacks are pits observed in ancient glasses and the spallation of precipitates or gel layers. The authors need to address how these phenomena are viewed or explained with respect to existing models.

The report should be more comprehensive regarding the extent to which each article was evaluated, particularly, in its assumptions, applicabilities or limitations. The concentration overshoot or the decrease of dissolved-ion concentration in long-term have been modeled in at least three different ways: solubility limit by Apted, supersaturation by Harvey, and semi-empirical correlation by Macedo group. Certainly all of them fit the experimental data well. Therefore, it is desirable to understand each model by developing a more comprehensive evaluation to find out reasons for such a coincidence.

The author did not address the time-dependence of glass surface area which may be significant as the amount of precipitates are increased. Also, the growth kinetics of precipitates layer need attention. Any modifications in the growth kinetics may alter leaching kinetics significantly. Many works in solid state chemistry provide mechanistic kinetics rather than a linear correlation to total leachant concentration. Such an example is the diffusion-controlled kinetics of oxide scale growth. Also the possibility of homogeneous precipitates should be considered in leach models. Incorporation of surface precipitates in leach rates are briefly considered in crystalline silicates by authors and in the model developed by Wallace and Wick. More extensive evaluation is necessary, including homogeneous precipitates in solution. Classical theory and works by Harvey or McCoy and Markworth do not include surface or bulk precipitates. The authors need to find out how these models are justified without them.

The solution effects may need to be evaluated more specifically, though mentioned briefly as a controversy using thermodynamics in dynamic equilibrium. When solubility limit is used in multicomponent glasses, the solubility limit for one component will affect the dissolution rates of others which are not yet at saturated conditions. Therefore, verifying the model with short-term tests in unaltered solutions may not be valid.

Also, the solution pH is a time-varying function caused by either the hydrolysis process or by the occluded cell formation in severely cracked glasses. This concept was not considered in any models quoted.

The role of flow rates was analyzed quantitatively by Hughes group. It shows several regimes of flow-rates where diffusion-rates, flow-rates, or leach-rates are dominant. Perhaps it would be worth while for the authors to point out whether conditions made by Hughes group can limit the use of each model described in the content. Furthermore, other relevant models for flow-rates effects were not included. An example of this type of work was developed by McCoy and Markworth.

The authors should have informed us that it was unclear as to whether the glass surface was in contact with the saturated leachant or not. Pigford group assumed that the leachant was saturated on the glass surface while other groups (Wick, Harvey and Lasaga) did not. Are the kinetic effects responsible for the unsaturated leachant on the glass surface? For instance, during precipitations, the leachant concentration near precipitates or in leachant solution are not necessarily saturated in diffusion-limited kinetics for geological times. The unsaturated region can extend to a longer distance in leachants.

The author may need to address the justification of leach-rates equations in interactive cases. There is no reason why the leach-rates are first-order kinetics, and should not be formulated as second-order kinetics which are closer to the experimental values observed by Harvey.

Works on the geometric effect of waste form or leaching paths have been neither considered nor mentioned, except for one-dimensional analysis; Such examples are formulations in the performance of the whole waste package known to us by the codes WAPPA and PANDORA (even though they are very primitive codes).

Radiation decay or radiolysis is largely missing. These radiation effects may lead to the modification of existing models or to the development of completely new one. To obtain this knowledge, the author needs to evaluate the codes WAPPA and PANDORA.

The real scenario of waste glass leaching needs to be addressed. An example of this is the modification of the Pigford model, considering glass wetting through a pin-hole in a container. Also, the authors should extend their evaluations to the up-to-dated and modified Pigford model by McVay group, incorporating temperature, pH and Eh.

The introduction part in <u>6.6 non-mechanistic model</u> is lengthy because it reiterates previous formulations and underlying mechanisms made by others. Perhaps the statement beginning with (6.13) along with a detailed discussion of figure 6.6 is sufficient to explain this model.

In the calculated results, very little attention was given to uncertainty analysis caused by doubt associated with physical parameters.

More specific comments not evaluated by authors are as follow for each classification of models:

6.2 Kinetics of aqueous attack

- The picture of gel-layer and the precipitates-layer are opposite to that made by Aagaard.
- In obtaining the exponent of time-law, caution should be given: such a plot is only valid asymptotically when viewed over a long time period.
- It has not been confirmed that leach rates are decreased with the increased surface area at low leachant concentrations

6.3 Interactive model

In the model made by Harvey, leach rates can be zero, according to the authors' evaluation. There is no justification for the existence of supersaturation.

6.4 Thermodynamic models

Following the normalization of leachant concentration with silicon concentration, we should also normalize the axis of solution pH). It is well known that leachant concentration versus solution pH has a minimum value of leachant concentration approximately at pH=7, in short-term testing rate-controlled by diffusion or matrix dissolution. Therefore, both the kinetic model and the thermodynamic model predict the same results. The authors should explain this coincidence.

6.5 Reaction Kinetic Model

In working forward or backward reactions, it may not be possible to have a precipitate reaction if the leachant concentration is far from equilibrium on which the dissolution kinetics were formulated.

6.6 Non-mechanistic Model

In long-term extrapolation of phenomenological equations, the probability of obtaining misleading results due to uncertain parameters is greater than that which exists in the mechanistic model. This is because the uncertainties associated with the mechanistic model can be estimated, while those associated with non-mechanistic model can not.

6.7 Diffusion-controlled dispersion

In Hughes model, leach rates should be time-dependent, which will alter the calculated domains significantly. The model is valid in a very large amount of leachant. Are the extreme values derived from the model at increased flow rates consistent to other models?

RELATED HLW REPORT

This report is a comprehensive summary of existing literature in leaching model. Therefore, all reports or papers quoted should be included in data base, separately.

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

(a) Relationship to Waste Package Performance Issues Already Identified

Related to NNWSI ISTP issues.

6.2 Classical leaching model
6.2 Role of protective layer in leaching
6.3 Role of solution concentration in leaching
6.4 Thermodynamic model of leaching in confined and stagnant solutions
6.7 Dispersion of leach products

(b) New Licensing Issues

6.5 Leaching kinetics of crystalline silicates as complementary tools for glass leaching

6.6 Application of non-mechanistic model

(c) General Comments on Licensing

The Chapter 6 of this report summarizes and evaluates a number of pertinent leach models which need to be better formulated prior to licensing waste package.

SDI103, UD 8821, SER. DD017

File(s) searched:

File 103:DOE ENERGY - 83-88/NOV(ISS21)

Sets selected:

Set	Items	Description
1	17	WASTE(W)PACKAGE?
2	18	CANISTER?
3	245	CORROSION (1974 DEC)
4	62	LEACHING (1974 DEC)
5	166	GLASS (1974 DEC)
6	35	VITRIFICATION (1974 DEC)
7	467	S3-S6/OR
8	19	HIGH(W)LEVEL(W)WASTE?
9	389	RADIOACTIVE(W)WASTE?
10	67	NUCLEAR(W)WASTE?
11	9	(S1 OR S2) AND S7 AND (S8 OR S9 OR S10)
12	0	ANNA FRAKER RM. B-106 BLDG. 223 X6009
13	0	JILL RUSPI

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

Date	Time	Description
15nov	13:45EST	PR 11/5/1-25 (items 1-9)

Total items to be printed: 9

DIALOG INFORMATION SERVICES, INC.

SDI103, UD 8822, SER. DD017

File(s) searched:

File 103:DOE ENERGY - 83-88/OCT(ISS22)

Sets selected:

Set	Items	Description
1	9	WASTE(W)PACKAGE?
2	13	CANISTER?
3	114	CORROSION (1974 DEC)
4	41	LEACHING (1974 DEC)
5	93	GLASS (1974 DEC)
6	17	VITRIFICATION (1974 DEC)
7	243	S3-S6/OR
8	10	HIGH(W)LEVEL(W)WASTE?
9	190	RADIOACTIVE(W)WASTE?
10	29	NUCLEAR(W)WASTE?
11	11	(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
26nov	20:23EST	PR 11/5/1-25 (items 1-11)

Total items to be printed: 11

DIALOG INFORMATION SERVICES, INC.

SDI006, UD 8823, SER. DD016

File(s) searched:

File 6:NTIS - 64-88/ISS23
(COPR. 1988 NTIS)

Sets selected:

Set	Items	Description
1	3	WASTE(W)PACKAGE?
2	7	CANISTER?
3	57	CORROSION
4	17	LEACHING
5	86	GLASS
6	6	VITRIFICATION
7	153	S3-S6/OR
8	6	HIGH(W)LEVEL(W)WASTE?
9	161	RADIOACTIVE(W)WASTE?
10	29	NUCLEAR(W)WASTE?
11	6	(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
05nov	15:30EST	PR 11/5/1-25 (items 1-6)

Total items to be printed: 6

DIALOG
INFORMATION SERVICES, INC.

SDI006, UD 8824, SER. DD016

File(s) searched:

File 6:NTIS - 64-88/ISS24
(COPR. 1988 NTIS)

Sets selected:

Set	Items	Description
1	7	WASTE(W)PACKAGE?
2	1	CANISTER?
3	63	CORROSION
4	18	LEACHING
5	88	GLASS
6	8	VITRIFICATION
7	162	S3-S6/OR
8	8	HIGH(W)LEVEL(W)WASTE?
9	141	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

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

Date	Time	Description
20nov	20:34EST	PR 11/5/1-25 (items 1-3)

Total items to be printed: 3

SDI032, UD 8812, SER. DD022

File(s) searched:

File 32:METADEX 66-88/DEC
(Copr. 1988 ASM International)

Sets selected:

Set	Items	Description
1	3	HIGH()LEVEL()WASTE? ? OR RADIOACTIVE()WASTE? OR NUCLEAR()WASTE?
2	2147	STEEL? ? OR ZIRCALOY? ? OR TITANIUM? ? OR COPPER
3	1	1*2
4	0	·ANNA FRAKER, 223, B-254, X6009

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

Date	Time	Description
14nov	03:20EST	PR 3/5/1-25 (items 1-1)

Total items to be printed: 1