RIBUTION
s/f
WMGT r/f
NMSS r/f
REBrowning
MBell
JOBunting
MRKnapp
WLDam & r/f
RJStarmer & r/f
PDR

WM-RES
WM Record File
A-1756
B-0287
SNL
Distribution:
(Return to WM, 623-SS)

WM Project 10,11,16
Docket No.
PDR ✓
LPDR B,N,S

3013.1/109.9/WLD/84/10/30

- 1 - 5

JAN 08 1984

MEMORANDUM FOR: Malcolm R. Knapp, Chief
Geotechnical Branch
Division of Waste Management, NMSS

FROM: R. John Starmer, Section Leader
Geochemistry Section
Geotechnical Branch
Division of Waste Management, NMSS

William L. Dam
Geochemistry Section
Geotechnical Branch
Division of Waste Managment, NMSS

SUBJECT: TRIP REPORT, OAK RIDGE, TENNESSEE, OCTOBER 1-5, 1984

Three primary activities took place during the week of October 1 in Oak Ridge, Tennessee. On Monday, Bill attended a meeting of the thermochemical data base committee for the A1756 contract. On Tuesday through Friday, we both attended the workshop on geochemical modeling of HLW. We also met with ORNL staff who are involved in sampling mill tailings sites for the Uranium Recovery Field Office.

The data base committee (attachment 1) lists the attendees, reviewed plans specified in the A1756 contract "Geochemical Sensitivity Analysis." The committee expressed the need to improve the quality of any geochemical data base by critical evaluation and selection of internally consistent data. Other improvements should reflect the "pedigree" of, and uncertainties in, the data. The meeting notes were given to Walt Kelly who is the project manager for A1756.

The workshop on geochemical modeling was very successful. The workshop program (attachment 2) and a list of attendees (attachment 3) is enclosed. The workshop was sponsored through contract B0287 "Technical Assistance in Geochemistry" with ORNL. Susan Whatley and Gary Jacobs of ORNL did an excellent job organizing the workshop. The workshop proceedings will be published as a NUREG-CR in early 1985. It will contain abstracts and comments by the chairman for each of the five subject area sessions.

It was evident from the workshop that communication among laboratory workers, modelers and other researchers could be greatly improved. This workshop provided a forum for scientists who make laboratory measurements to discuss data problem with the modelers who use the data. In general, many geochemical computer modelers are not experienced with problems inherent in obtaining high

OFC	:WMGT	:WMGT				
NAME	:WLDam;mt	:RJStarmer				
DATE	:85/01/	:85/01/	:	:	:	:

1253

quality thermochemical data. This may result in misleading interpretations of the modeling results due to inaccurate thermochemical data.

For geochemistry codes the following specific problems were cited (as they have been in the past), 1) definition of uncertainty in the thermodynamic data input to models and correct handling of those uncertainties during calculations, 2) activity coefficient corrections are not optimal (although it was not made clear that this is a problem of more than academic interest), 3) problems resulting from lack of agreement on standard states, 4) handling metastability and 5) non-equilibrium systems.

One of the topics discussed at the workshop was the importance of kinetics. Kinetics is one of the most important, yet least understood, controls on chemical reactions. For instance, the rates of precipitation and dissolution are generally not the same. An example discussed at the workshop was a field study which revealed unexpectly high plutonium concentrations in the groundwater. In this field study the plutonium was predicted to precipitate out of solution based on classical thermodynamics and was assumed to be stable. However, as it turned out, the precipitated radionuclide redissolved at a faster rate than predicted and was very mobile.

Peter Ortoleva and Craig Moore presented the basics of a coupled transport/kinetics-based chemical reaction code and some applications. Their main conclusion is that when kinetics are included in the coupled transport/chemistry type code, the system is seen to be unstable. Ortoleva stated that "...instabilities pop up everywhere when you couple reactions [grain growth] with transport." The question of calculational versus actual system stability was not adequately addressed during the talks or discussions. The applications presented were interesting but rather hap-hazard and the audience left with the feeling that they were seeing the successful application of an operator-biased monte carlo simulation rather than proof that the kinetic approach was the reason for the successful simulation. In other words, there must be some combination of twenty seven input variables that will produce a "fit" to the observations from the field.

A second example concerning the importance of kinetics involves redox reactions. Heavy metals generally oxidize faster than they reduce. This is because strong covalent bonds are formed by the oxygen atoms. The activation energy required to break these strong bonds is very large so that reduction reactions are much slower. Different rates of redox reactions influence the migration of contaminants. For example, heavy metals are rapidly oxidized during uranium milling and solution mining. In contrast, heavy metal complexes will be much slower to precipitate out of solution even under highly reducing conditions. Allowing contaminants to migrate into reducing zones as a means of

OFC	:WMGT	:WMGT	:	:	:	:	:
NAME	:WLDam;mt	:RJStarmer	:	:	:	:	:
DATE	:85/01/	:85/01/	:	:	:	:	:

removing the heavy metals from solution may not be effective based on slow rates of reduction. In addition, it seems that the handling of REDOX conditions in presently available geochemical codes is not adequate. Since the reactions involved are strongly kinetics controlled and uncoupled, the (necessary) assumption of equilibrium is seldom, if ever, met. Calculations assuming equilibrium may be valid and therefore the calculated radionuclide speciation/solubility must be carefully evaluated, not just accepted at face value.

It was a proposed that laboratory experimentation for proposed waste disposal alternatives will be difficult to defend because of problems of scale. Scale problems could cause a problem of transferability of laboratory results to the field. An example was given of a laboratory experiment where the physical scale factor was 2:1 but where it would be impossible to keep a viscosity ratio of 2:1 and retain the original solution chemistry. It became obvious that the scale problems were most severe where dynamic processes were involved, the classic realm of "THMC" coupled models. The solution to the problem of scale correspondence was suggested to be "mathematical modeling" of the various phenomena involved. Unfortunately, while it is theoretically possible to write a conceptual model which describes the system and develop scenarios that exercise the model, there are still some basic problems involved in demonstrating that the physics/chemistry is indeed comprehensive and correct, in obtaining the necessary physical correspondences, and the necessary input data for the models. Verification and validation further complicate the picture for complex coupled models.

John Weare showed how the ionic activity correction problem may be approached using a combination of more classical ion-pairing techniques and the more modern specific interaction models. He observed that "A computer should not be used when intuition is better.", something that we should all keep in mind. Information presented on the EQ3/EQ6 code package suggests that this philosophy may not be the driving force behind that code development effort.

Denis Strachan of PNL gave an impromptu presentation (see Scientific Basics for Nucelar Waste Management VII-1983 pages 623-624 for details) which showed how the judicious use of computers and intuition can work together to produce an understanding of experimental results by analysis of the data and that the modeling can highlight potentially bad data and help guide future experiments. More papers of this type illustrating the use of computer modeling would have been welcome.

On Thursday and Friday afternoons, we met with the ORNL staff who are sampling uranium mill tailings ponds. We discussed how the URFO work might be helpful

OFC	:WMGT	:WMGT	:	:	:	:	:
NAME	:WLDam;mt	:RJStarmer	:	:	:	:	:
DATE	:85/01/	:85/01/	:	:	:	:	:

to the 10 CFR Part 41 rulemaking. In particular, we discussed their plans to sample the Petrotomics ponds and other ponds in the future. Analysis includes TOC (total organic carbon) and TOX (total organic hologen). Analysis of other organic constituents may be performed depending on the results of these indicators.

Original Signed By

William L. Dam
Geochemistry Section
Geotechnical Branch
Division of Waste Managment, NMSS

Original Signed By

R. John Starmer, Section Leader
Geochemistry Section
Geotechnical Branch
Division of Waste Managment, NMSS

Enclosures:
As Stated

OFC	:WMGT WLD	:WMGT RJS	:	:	:	:	:
NAME	:WLDam;mt	:RJStarmer	:	:	:	:	:
DATE	:85/01/8	:85/01/8	:	:	:	:	:

ATTACHMENT 1

Attendees of the Thermochemical Data Base Committee Meeting:

Sidney Phillips	Lawrence Berkley Labs
Vijay Tripathi	Stanford University
Gary Jacobs	Oak Ridge National Labs
Ken Krupka	Pacific Northwest Labs
Howard White	National Bureau of Standards
Vivian Parker	National Bureau of Standards
Malcolm Siegel	Sandia National Labs
Bill Dam	Nuclear Regulatory Commission

Attachment 2

PROGRAM

The Application of Geochemical Models to High-Level Nuclear Waste Repository Assessment

October 2–5, 1984

Pollard Auditorium
Oak Ridge Associated Universities
Oak Ridge, Tennessee

Sponsored by: U.S. Nuclear Regulatory Commission
and
Oak Ridge National Laboratory

Tuesday morning, October 2

10:30 Coffee and Registration

Tuesday afternoon, October 2

1:00 Welcome and Introduction—**G. K. Jacobs**, Oak Ridge National Laboratory, Oak Ridge, Tennessee; **J. R. Starmer**, Nuclear Regulatory Commission, Washington, D.C.

Session I. Solution Chemistry: Theory, Code Development, Non-Repository Applications

Chairman: H. L. Barnes, The Pennsylvania State University, University Park

G. K. Jacobs

1:30 Thermodynamic Problems in Speciation Modeling—**H. L. Barnes**, The Pennsylvania State University, University Park

2:15 Prediction of Mineral Solubilities in High-Temperature and High-Ionic-Strength Solutions—**J. H. Weare**, University of California, San Diego

3:00 Intermission

3:15 Summary and Discussion—Panel and Participants

4:15 Announcements and Adjournment

Wednesday morning, October 3

Session I. Solution Chemistry: Theory, Code Development, Non-Repository Applications

Chairman: H. L. Barnes, The Pennsylvania State University, University Park

Dennis Stratman

8:30 PHREEQE: Status and Applications—~~L. N. Plummer~~, U.S. Geological Survey, Reston, Virginia

9.15 MINTEQ: Status and Applications—**J. R. Morrey** and **K. M. Krupka**, Pacific Northwest Laboratory, Richland, Washington

10:00 Intermission

10:15 EQ3/EQ6: Status and Applications—**T. J. Wolery**, Lawrence Livermore National Laboratory, Livermore, California

11:00 Summary and Discussion—Panel and Participants

12:00 Lunch

Wednesday afternoon, October 3

Session II. Data Base Development

Chairman: G. R. Choppin, Florida State University, Tallahassee

Silva

1:00 Complexes of Actinides with Naturally Occurring Organic Compounds—**G. R. Choppin**, Florida State University, Tallahassee

1:30 Experimental Determination of Stability Constants of the Carbonate Complexes of Uranium and Neptunium—**Leon Maya**, Oak Ridge National Laboratory, Oak Ridge, Tennessee

2:00 Temperature Dependence of Actinide Solubilities and Speciation—**R. J. Silva**, Lawrence Berkeley Laboratory, Berkeley, California

2:30 Intermission

2:45 Neptunium and Technetium Behavior in Geologic Systems—**R. E. Meyer**, Oak Ridge National Laboratory, Oak Ridge, Tennessee

3:15 Thermodynamic Properties of Geologic Materials: Status and Future—**J. L. Haas**, U.S. Geological Survey, Reston, Virginia

3:45 Summary and Discussion—Panel and Participants

4:45 Announcements and Adjournment

Thursday morning, October 4

Session III. Coupled Processes: Thermodynamic, Kinetic, and Transport

Chairman: P. Ortoleva, Indiana University and Geochem Research Associates, Inc., Bloomington, Indiana

8:30 Mathematical Reaction-Transport Modeling of Nonequilibrium Water/Rock Interactions—**P. Ortoleva**, Indiana University and Geochem Research Associates, Inc., Bloomington, Indiana

9:15 Coupled Geochemical and Fluid-Flow Code Development—**J. R. Morrey**, Pacific Northwest Laboratory, Richland, Washington

9:45 Intermission

10:00 Comparison of Dissolution Versus Precipitation Kinetics in Silicates—**A. C. Lasaga**, Yale University, New Haven, Connecticut

10:30 Modeling of Reaction Processes and Fluid Flow in Complex Systems—**C. H. Moore**, Geochem Research Associates, Inc., Bloomington, Indiana

11:00 Summary and Discussion—Panel and Participants

12:00 Lunch

Thursday afternoon, October 4

Session IV. Repository Applications of Geochemical Models

Chairman: G. E. Grisak, Geologic Testing Consultants, Ltd., Ottawa, Ontario, Canada

1:00 Canadian Program—**N. C. Garisto**, Atomic Energy of Canada, Ltd., Pinawa, Manitoba, Canada

1:30 Basalt Waste Isolation Project—

Applications of Geochemical Modeling to High-Level Nuclear Waste Disposal at the Hanford Site, Washington—**T. O. Early, J. Myers**, Rockwell Hanford Operations, and E. A. Jenne, Pacific Northwest Laboratory, Richland, Washington

2:00 Nevada Nuclear Waste Storage Investigation Project—

Modeling Matrix Diffusion Coefficients for the NNWSI Waste Package Environment—**K. G. Eggert**, Lawrence Livermore National Laboratory, Livermore, California

Application of Geochemical Modeling to Site Characterization and Radionuclide Transport in the NNWSI Project—**J. F. Kerrisk**, Los Alamos National Laboratory, Los Alamos, New Mexico

2:30 Intermission

~~2:45 Office of Crystalline Rock Development Project—E. S. Petera, Department of Energy, Chicago Operations Office, Argonne, Illinois~~ } canceled

3:15 Office of Nuclear Waste Isolation Project—

Chemical Modeling of Nuclear Waste Repositories in the Salt Repository Project—G. Jansen, G. Raines, J. Kircher, and **N. Hubbard**, Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, Ohio

Ion Interaction Modeling of Deep Brines, Palo Duro Basin—**D. Melchior**, Earth Technology Corporation, Long Beach, California, and N. Hubbard, Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, Ohio

3:45 Summary and Discussion—Panel and Participants

4:00 Announcements and Adjournment

Friday morning, October 5

8:30–12:30 **Session V. Summary and Conclusions**

Chairman: G. K. Jacobs, Oak Ridge National Laboratory
Oak Ridge, Tennessee

This session will include brief summary statements by each panel member concerning his/her respective session. The floor will then be opened for discussion (arranged according to session order) for each of the key topics and issues that were prepared prior to the workshop. Approximately 45 minutes of discussion will be allowed for each session topic. At the end of the discussion, a consensus statement will be developed by the pertinent member of the panel. Unless opposition remains on the floor, this statement will be taken to be a conclusion of the workshop. If extreme opposition should continue, then a compromise statement will be prepared, or both positions will be duly recorded.

12:30 Closing Comments and Adjournment

Program Committee

G. K. Jacobs
S. K. Whatley
J. G. Blencoe
A. D. Kelmers
Oak Ridge National Laboratory

H. L. Barnes	The Pennsylvania State University
G. R. Choppin	Florida State University
G. E. Grisak	Geologic Testing Consultants, Ltd.
P. Ortoleva	Indiana University

OF PARTICIPANTS

R. D. Aines
Lawrence Livermore National Laboratory
P.O. Box 808, L-202
Livermore, California USA 94550

M. J. Apted
Pacific Northwest Laboratory
P.O. Box 999
Richland, Washington USA 99352

J. W. Ball
U.S. Geological Survey
Water Resources Division
345 Middlefield Road, MS 421
Menlo Park, California USA 94025

H. L. Barnes
Department of Geosciences
The Pennsylvania State University
University Park, Pennsylvania USA 16802

G. F. Birchard
Waste Management Branch
Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission
Washington, D.C. USA 20555

D. L. Bish
Los Alamos National Laboratory
MS-J978
Los Alamos, New Mexico USA 87545

J. G. Blencoe
Oak Ridge National Laboratory
P.O. Box X, Bldg. 4500S
Oak Ridge, Tennessee 37831

D. S. Brown
Athens Environmental Research Laboratory
U.S. Environmental Protection Agency
College Station Road
Athens, Georgia USA 30613

G. Cederberg
Los Alamos National Laboratory
P.O. Box 1663
Los Alamos, New Mexico USA 87545

G. R. Choppin
Department of Chemistry
Florida State University
Tallahassee, Florida USA 32306

I. D. Colton
IT Corporation
2340 Alamo Street, S.E.
Suite 306
Albuquerque, New Mexico USA 87106

W. Dam
Geotechnical Branch
Office of Nuclear Materials
Safety and Safeguards
U.S. Nuclear Regulatory Commission
Willste Building
Washington, D.C. USA 20555

J. M. Delaney
Lawrence Livermore National Laboratory
P.O. Box 808
Livermore, California USA 94550

C. J. Duffy
Los Alamos National Laboratory
MS-J514
Los Alamos, New Mexico USA 87545

T. O. Early
Rockwell Hanford Operations
P.O. Box 800
Richland, Washington USA 99352

K. G. Eggert
Lawrence Livermore National Laboratory
P.O. Box 808, L-202
Livermore, California USA 94550

K. L. Erickson
Sandia National Laboratory
P.O. Box 5800
Albuquerque, New Mexico USA 87185

J. S. Fruchter
Pacific Northwest Laboratory
P.O. Box 999
Richland, Washington USA 99352

N. C. Garisto
Atomic Energy of Canada Ltd.
Whiteshell Nuclear Research Establishment
Pinawa, Manitoba, ROE ILO CANADA

C. S. Haase
Oak Ridge National Laboratory
P.O. Box X, Bldg. 3504
Oak Ridge, Tennessee USA 37831

J. Hadermann
Swiss Federal Institute for
Reactor Research
CH55303 Würenlingen
SWITZERLAND

G. R. Helz
Chemistry Department
University of Maryland
College Park, Maryland USA 20742

J. S. Herman
Department of Environmental Sciences
University of Virginia
Clark Hall
Charlottesville, Virginia USA 22903

N. Hubbard
Battelle Memorial Institute
Office of Nuclear Waste Isolation
505 King Avenue
Columbus, Ohio USA 43201

D. Isherwood
Lawrence Livermore National Laboratory
P.O. Box 808, L-204
Livermore, California USA 94550

G. K. Jacobs
Oak Ridge National Laboratory
P.O. Box X, Bldg. 3504
Oak Ridge, Tennessee USA 37831

B. S. Jensen
Chemistry Department
Riso National Laboratory
DK - 4000 Roskilde
DENMARK

A. D. Kelmers
Oak Ridge National Laboratory
P.O. Box X, Bldg. 4500S
Oak Ridge, Tennessee USA 37831

J. F. Kerrisk
Los Alamos National Laboratory
P.O. Box 1663
Group WX-4, MS-G787
Los Alamos, New Mexico USA 87545

N. C. Krothe
Department of Geology
Indiana University
Bloomington, Indiana USA 47401

K. M. Krupka
Pacific Northwest Laboratory
P.O. Box 999
Richland, Washington USA 99352

A. C. Lasaga
Department of Geology and
Geophysics
Yale University
New Haven, Connecticut USA 06520

S. Y. Lee
Oak Ridge National Laboratory
P.O. Box X, Bldg. 3504
Oak Ridge, Tennessee USA 37831

T. P. Malinauskas
Oak Ridge National Laboratory
P.O. Box X, Bldg. 4500S
Oak Ridge, Tennessee USA 37831

L. Maya
Oak Ridge National Laboratory
P.O. Box X, Bldg. 5505
Oak Ridge, Tennessee USA 37831

V. McCauley
Battelle Memorial Institute
Division of Project Management
Office of Nuclear Waste Isolation
505 King Avenue
Columbus, Ohio USA 43201

C. F. McLane
Rockwell Hanford Operations
P.O. Box 800
Richland, Washington USA 99352

D. Melchior
The Earth Technology Corporation
3777 Long Beach Blvd.
Long Beach, California USA 90807

A. Meijer
Los Alamos National Laboratory
INC-7, MS-J519
P.O. Box 1663
Los Alamos, New Mexico USA 87545

R. E. Meyer
Oak Ridge National Laboratory
P.O. Box X, Bldg. 4500N
Oak Ridge, Tennessee USA 37831

C. H. Moore
Geochem Research Associates, Inc.
400 East Third St.
Bloomington, Indiana USA 47401

J. Myers
Rockwell Hanford Operations
P.O. Box 800
Richland, Washington USA 99352

K. L. Nash
U.S. Geological Survey
P.O. Box 25046
MS 424, Denver Federal Center
Denver, Colorado USA 80225

P. Ortoleva
Geochem Research Associates, Inc.
400 East Third St.
Bloomington, Indiana USA 47401

V. B. Parker
Division of Chemical Thermodynamics
National Bureau of Standards
Washington, D.C. USA 20234

S. L. Phillips
Lawrence Berkeley Laboratory
MS 50B-2239
Berkeley, California USA 94720

D. J. Pruett
Oak Ridge National Laboratory
P.O. Box X, Bldg. 4501
Oak Ridge, Tennessee USA 37831

M. A. Revelli
Lawrence Livermore National Laboratory
P.O. Box 808, L-206
Livermore, California USA 94550

J. D. Rimstidt
Department of Geological Sciences
Virgina Polytechnic Institute and
State University
Blacksburg, Virginia USA 24060

P. F. Salter
Rockwell Hanford Operations
P.O. Box 800
Richland, Washington USA 99352

B. Scheetz
Materials Research Laboratory
The Pennsylvania State University
University Park, Pennsylvania USA 16802

M. R. Schweingruber
Swiss Federal Institute for
Reactor Research
CH-5303 Würenlingen
SWITZERLAND

F. G. Seeley
Oak Ridge National Laboratory
P.O. Box X, Bldg. 4500S
Oak Ridge, Tennessee USA 37831

M. Siegel
Sandia National Laboratory
Division 6431
Albuquerque, New Mexico USA 87047

R. J. Silva
Lawrence Berkeley Laboratory
University of California
Berkeley, California USA 94720

E. D. Smith
Oak Ridge National Laboratory
P.O. Box X, Bldg. 1505
Oak Ridge, Tennessee USA 37831

R. M. Smith
Rockwell Hanford Operations
P.O. Box 800
Richland, Washington USA 99352

B. P. Spaulding
Oak Ridge National Laboratory
P.O. Box X, Bldg. 1505
Oak Ridge, Tennessee USA 37831

R. J. Starmer
Geotechnical Branch
Office of Nuclear Materials
Safety and Safeguards
U.S. Nuclear Regulatory Commission
Willste Bldg.
Washington, D.C. USA 20555

S. H. Stow
Oak Ridge National Laboratory
P.O. Box X, Bldg. 1505
Oak Ridge, Tennessee USA 37831

D. M. Strachan
Battelle Pacific Northwest Laboratories
P.O. Box 999
Battelle Blvd., PSL Bldg.
Richland, Washington USA 99352

T. Sullivan
Brookhaven National Laboratory
Bldg. 703
Upton, New York USA 11973

R. W. Tank
Department of Geology
Lawrence University
Appleton, Wisconsin USA 54911

V. S. Tripathi
Department of Applied Earth Sciences
Stanford University
Stanford, California USA 94305

R. R. Turner
Oak Ridge National Laboratory
P.O. Box X, Bldg. 1505
Oak Ridge, Tennessee USA 37831

J. H. Weare
Department of Chemistry, B-014
University of California, San Diego
La Jolla, California USA 92093

D. Wesolowski
Oak Ridge National Laboratory
P.O. Box X, Bldg. 4500S
Oak Ridge, Tennessee USA 37831

S. K. Whatley
Oak Ridge National Laboratory
P.O. Box X, Bldg. 4500N
Oak Ridge, Tennessee USA 37831

W. B. White
210 Materials Research Laboratory
The Pennsylvania State University
University Park, Pennsylvania USA 16802

T. J. Wolery
Lawrence Livermore National Laboratory
University of California
P.O. Box 808
Livermore, California USA 94550

R. G. Wymer
Oak Ridge National Laboratory
P.O. Box X, Bldg. 4500N
Oak Ridge, Tennessee USA 37831

G. T. Yeh
Oak Ridge National Laboratory
P.O. Box X, Bldg. 1505
Oak Ridge, Tennessee USA 37831