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ORNL

WM Project 10, 11, 14
Docket No. _____
PDR _____
LPDR B, N, S

Dr. D. J. Brooks
Geotechnical Branch
Office of Nuclear Material
Safety and Safeguards
U.S. Nuclear Regulatory Commission
623-SS
Washington, D.C. 20555

Distribution: _____
* BROOKS _____

(Return to WMA, 623-SS) _____ 23

Dear Dave:

Enclosed is the progress report for the month of July 1985 for B0287, "Technical Assistance in Geochemistry," with five attachments (MR-287-1, MR-287-2, MR-287-3, LR-287-8, and LR-287-9).

Under separate cover I am sending a printout of the BWIP, NTS, and Salt geochemistry documents that are in the data base and a copy of meeting report, MR-287-4, "NRC/DOE Meeting to Discuss Palo Duro Basin Geology and To Examine Rock Core from Permian Basin," by G. K. Jacobs.

Sincerely,

Susan
S. K. Whatley, Manager
Repository Licensing Analysis
and Support
Chemical Technology Division

SKW:bek

Enclosures:

Monthly Progress Report for June 1985, w/attachments

cc: Office of the Director, NMSS (Attn: Program Support Branch)
Division Director, NMSS Division of Waste Management (2)
M. R. Knapp, Chief, Geotechnical Branch
K. C. Jackson, Geochemistry Section, Geotechnical Branch
Branch Chief, Waste Management Branch, RES
D. G. Brookins, University of New Mexico

W. D. Arnold
J. T. Bell
J. G. Blencoe
N. H. Cutshall
L. M. Ferris
J. R. Hightower
G. K. Jacobs

A. D. Kelmers
D. C. Kocher
A. P. Malinauskas
R. E. Meyer
R. G. Wymer
SKW File (2)

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PDR WMRES EXIORNL
B-0287 PDR

Attachment in pocket # 5A

2291

W/la. dtd. 8/15/85
To: D.S. Brooks
From: S.K. Whatley

SKW
8/15/85

B-0287

MONTHLY PROGRESS REPORT FOR JULY 1985

PROJECT TITLE: Technical Assistance in Geochemistry

PROJECT MANAGER: S. K. Whatley

PROJECT STAFF: J. G. Blencoe, G. K. Jacobs, A. D. Kelmers, and R. E. Meyer

ACTIVITY NUMBER: ORNL #41 37 54 92 4 (FIN No. B0287)/NRC #50 19 03 01

TECHNICAL HIGHLIGHTS:

Task 1 - BWIP Geochemical Technical Assistance

Discussions were held at NRC with the Project Manager on the topical review document, Review and Assessment of Radionuclide Solubility Information for the Hanford, Washington, Candidate HLW Repository Site (meeting report MR-287-1, Attachment 1).

Task 2 - NNWSI Geochemical Technical Assistance

Several staff members attended the NRC/DOE Waste Package Workshop for the Yucca Mountain Candidate Site (meeting report MR-287-3, Attachment 2).

Task 3 - Salt Site Geochemical Conditions

No activity.

Task 4 - Short-Term Geochemical Technical Assistance

G. K. Jacobs attended a three-day ACS short course on the Environmental Chemistry of Groundwater (meeting report MR-287-2, Attachment 3).

A thorough review (letter report LR-287-8, Attachment 4) was made of a recent article by A. Timur and M. N. Toksoz, "Downhole Geophysical Logging," Ann. Rev. Earth Planet. Sci. 13, 315-44, 1985, which describes the most common methods of, and recent developments in, borehole geophysical logging (well-logging technology). The authors provide brief easy-to-read summaries of many of the more important logging methods. However, more importantly for geochemists concerned with radionuclide migration in rock/groundwater systems, the authors also identify the well-logging methods that are used to obtain information on the primary and secondary (fracture) porosities of rocks.

Attachment 5 is a letter report (LR-287-9) in response to S. Phillips' comments on our earlier letter report (LR-290-10).

Task 5 - Project Management

A printout of the current data base for BWIP, NTS, and Salt is being sent under separate cover.

MEETINGS AND TRIPS:

J. G. Blencoe and S. K. Whatley visited NRC in Silver Spring on July 10, 1985, to discuss the topical review document, Review and Assessment of Radionuclide Solubility Information for the Hanford, Washington, Candidate HLW Repository Site.

G. K. Jacobs attended the ACS short course on the Environmental Chemistry of Groundwater on July 17-19, 1985.

G. K. Jacobs, A. D. Kelmers, and S. K. Whatley attended the NRC/DOE Waste Package Workshop for the Yucca Mountain Candidate Site at Lawrence Livermore National Laboratory on July 23-25, 1985.

REPORTS AND PUBLICATIONS:

Meeting report, MR-287-1, "Document Review Meeting," by J. G. Blencoe, July 29, 1985.

Meeting report, MR-287-2, "ACS Short Course on the Environmental Chemistry of Groundwater," by G. K. Jacobs.

Meeting report, MR-287-3, "NRC/DOE Waste Package Workshop for the Yucca Mountain Candidate Site," by G. K. Jacobs, A. D. Kelmers, and S. K. Whatley.

Letter report, LR-287-8, "Evaluation of Article by A. Timur and M. N. Toksoz, Downhole Geophysical Logging', Ann. Rev. Earth Planet. Sci. 13, 315-44 (1985)," by J. G. Blencoe.

PROBLEM AREAS: None

COST/BUDGET REPORT:

Expenditures were \$37.2K for July 1985 and \$298.5K for FY 1985. A detailed cost/budget report will be sent under separate cover.

MEETING REPORT

AUTHOR: J. G. Blencoe
LOCATION: Silver Spring, Maryland
DATE: July 10, 1985
PURPOSE: Document Review Meeting
PROJECT TITLE: Technical Assistance in Geochemistry
PROJECT MANAGER: S. K. Whatley
ACTIVITY NUMBER: ORNL #41 37 54 92 4 (189 #B0287)/NRC #50 19 03 01
PARTICIPANTS: D. J. Brooks (NRC), J. W. Bradbury (NRC),
S. K. Whatley (ORNL), J. G. Blencoe (ORNL)

SUMMARY

This report describes the results of a meeting between Dave Brooks, John Bradbury, Susan Whatley, and the author on July 10, 1985, in Silver Spring, Maryland. The meeting was held in a conference room on the fourth floor of the Willste Building and lasted from approximately 1:20 p.m. to 3:45 p.m. The meeting was convened to consider revisions in the topical review document: Review and Assessment of Radionuclide Solubility Information for the Hanford, Washington, Candidate HLW Repository Site.

DETAILS

NRC had carefully reviewed the report and concluded that the technical material contained therein is satisfactory. However, it was thought that the document could be improved by deleting certain parts of the text and reorganizing the material contained within several other sections. The suggested deletions concern discussions of regulatory aspects of matrix diffusion and making recommendations to the DOE regarding how inadequacies in technical information can be remedied. The subject topical review and all subsequent topical reviews prepared by ORNL should avoid comments concerning whether information possessed by DOE is adequate to satisfy NRC regulations and technical criteria. It was suggested that ORNL recommendations to NRC on how DOE could address inadequacies in technical information should be transmitted as letter reports rather than as part of the topical review. The purpose of topical reviews should be to review and assess the information developed or assembled by DOE that is likely to be utilized to support the licensing of an HLW repository. Furthermore, as indicated above, assessment of this information should be confined to identifying inadequacies in the information; that is, assessments should exclude dialogue that could be interpreted as "prescriptive."

One additional major suggestion was made — namely, that we consider reorganizing the parts of the report that deal with quantitative information on radionuclide solubilities. Basically, this reorganization would result in text wherein quantitative solubility information would be discussed on a radionuclide-by-radionuclide basis. Within this broad framework, the quantitative solubility information would be further divided into discussions of information concerning radionuclide solubilities at "low" temperatures (25-90°C) and at "high" temperatures (90-300°C).

Finally, there were a number of minor comments and questions relating to commentary in specific sections of the text in the topical review.

8/1/85

MEETING REPORT

AUTHOR: G. K. Jacobs, A. D. Kelmers, and S. K. Whatley

LOCATION: Lawrence Livermore National Laboratory, Livermore, California

DATE: July 23-25, 1985

PURPOSE: NRC/DOE Waste Package Workshop for the Yucca Mountain Candidate Site; See Attachment #1 for Agenda.

PROJECT TITLE: Technical Assistance in Geochemistry

PROJECT MANAGER: S. K. Whatley

ACTIVITY NUMBER: ORNL #41 37 54 92 4 (189 #B0287)
NRC #50 19 03 01

PARTICIPANTS: See attachment #2a.

GENERAL COMMENTS

The agenda for the workshop (see attachment #2b) included one day of discussions concerning the design of the waste packages for the Yucca Mountain candidate site and corrosion information for reference canister/overpack materials. The second day emphasized waste form (spent fuel and DHLW glass) testing and release rate modeling. The third day consisted of a short tour through the corrosion laboratory at LLNL. A large amount of information was presented by the staff of NNWSI. The information presented contained both new and previously released data and analyses. Copies of the view-graphs from the presentations were to be mailed to the NRC after the workshop.

A major concern voiced by the NRC and some of its contractors during both days was that NNWSI has not yet adequately bounded the possible range of environmental parameters relevant to the proposed repository at Yucca Mountain. These parameters (e.g., temperature, groundwater resaturation and flow rate, water chemistry, etc.) need to be properly addressed during the testing of waste forms and canister/overpack materials.

The NRC and its contractors experienced in corrosion raised strong objections to the apparent singular emphasis being placed on the testing of austenitic stainless steel as the reference material for the canister/overpack material of the waste package. This concern, initially brought to the attention of DOE by the NRC at a similar workshop during October 1983, is centered around the tendency for austenitic stainless steel to stress corrosion crack in the presence of chloride-bearing solutions. The NRC suggested that more corrosion-resistant materials (e.g., Inconel 825) begin

to be emphasized in the NNWSI testing program. In this way, if austenitic stainless steel is found to be unacceptable at a later date, at least some information will be available on a potentially more acceptable alternative material under repository-relevant test conditions.

Preliminary data on the dissolution of spent fuel was presented by V. Oversby (LLNL) which suggest that the 1 part in 100,000 per year release rate requirement may be met by the dissolution of spent fuel alone. The dissolution of the spent fuel matrix may sufficiently control the release rates of U, Pu, Np, Am, and other elements that are an integral part of the UO₂ matrix. However, the data indicate that credit for a distributed failure of spent fuel rods (i.e., zircaloy cladding corrosion and failure) may be required to meet the release rate requirement for radionuclides of elements such as C, I, and Cs. V. Oversby (LLNL) stated that further tests will be conducted to refine the estimates of release rates. This analysis assumed a groundwater flow rate of 1 mm/yr, a value not well supported by NNWSI or accepted as conservative by the NRC staff and its contractors at the workshop. The groundwater flow rate should be a topic specifically addressed at the hydrology/geochemistry workshop in September.

J. Bates of Argonne National Laboratory (ANL) discussed a newly developed "unsaturated" test intended to be used to investigate realistic interactions between glass waste forms, canister/overpack material, and groundwater with and without the presence of tuff. This test protocol has been just recently developed and has not undergone extensive testing to date. A major concern of ours is that sufficient benchmark and parametric testing of the protocol must be performed before the results from this test can be considered reliable.

SPECIFIC COMMENTS

1. NNWSI has not performed, and apparently has no plans to perform, dissolution tests directed toward establishing at least a qualitative understanding of important mechanisms controlling the release of radionuclides from spent fuel or glass waste forms. It is difficult to envision how DOE plans to extrapolate short-term test data without such a qualitative understanding. Related to this concern is the fact that NNWSI does not agitate the solution in the spent fuel dissolution tests except during the extraction of solution samples and the addition of fresh J-13 groundwater. It is not obvious that these stagnant tests are representative of anticipated conditions in the repository, and stagnant tests are certainly not providing data to help establish a qualitative understanding of the dissolution mechanism. We would suggest that a few parametric tests be performed in which various stirring rates be applied to the solutions to observe the effect, if any, on the steady-state concentrations of elements in solution.
2. There is currently an inconsistency in the waste form testing program of NNWSI. Spent fuel is being tested under saturated conditions, whereas DHLW glass is being tested under unsaturated conditions. It was not clear during the discussions whether both waste forms will eventually be tested under similar conditions. It would seem to be desirable to test both waste forms under repository-relevant conditions.

Based on the thermal analyses presented by NNWSI, the DHLW waste packages would be expected to be contacted by liquid water significantly before the spent fuel packages. Therefore, it seems inconsistent to be testing spent fuel under saturated conditions and the DHLW glass under unsaturated conditions. A second inconsistency in the NNWSI work is that testing with groundwater compositions more concentrated than J-13, which would be representative of emplacement scenarios involving partial or complete evaporation of groundwater during the thermal pulse prior to groundwater ingress, is being carried out with the hot cell tests involving spent fuel, but is not being conducted with the glass waste form testing. If groundwater compositions more concentrated than J-13 are valid for testing with one waste form, then use of these compositions seems equally valid for all waste forms. A third inconsistency is that actual spent fuel is being used in the hot cell work, while only radionuclide-doped glass is being used in the unsaturated condition tests. It was not made clear by NNWSI staff whether actual DHLW glass is planned to be tested or not. Several cogent arguments were advanced by NNWSI to justify the need (and cost) to use actual spent fuel in order to obtain realistic data; these arguments would seem to apply equally to the glass waste form work.

3. V. Oversby (LLNL) stated that determinations of the speciation and valence state (for those radionuclides with multiple valence states) of key nuclides (e.g., Pu and Np) will be made at the termination of waste form tests. This intention is to be commended because this information is needed so that sorption tests being conducted at the Los Alamos National Laboratory (LANL) for the NNWSI can make up starting solutions representative of the solutions that will migrate away from the failed waste packages. In a related subject, V. Oversby described the results of an analysis of the NRC and EPA requirements. Her analysis showed that, if the NRC waste package requirement ($<10^{-5}$ release per year of the 1,000 year inventory of each radionuclide) is met, then the EPA limits for release to the environment are automatically met for all radionuclides except Am, Pu, and Tc, although the sum of all radionuclides released may exceed the EPA standards. Therefore, other radionuclides (e.g., Np, Tc) may require special attention with respect to retardation by the geologic setting in order to provide reasonable assurance that the EPA standards will be met. This analysis is of considerable aid, then, in scoping sorption/solubility studies related to the performance of the geologic setting. To meet regulatory requirements, retardation of radionuclides via sorption/solubility processes would be necessary only for these three elements (Am, Pu, and Tc). Likewise, modeling of the expected performance of the site would have to consider retardation of only these three elements, because expected behavior must equal or exceed regulatory requirements. Only consideration of unexpected, but possible, events would require information on sorption of other radionuclides. If V. Oversby's analysis is accepted by NNWSI, then most of the sorption work conducted at Los Alamos National Laboratory (which has concentrated on Cs, Sr, and Ba) would be of relevance only to the third category of information; possible, but unanticipated events. If the NRC accepts her analysis, then our task to evaluate sorption/solubility information relevant to the geologic setting would be somewhat simplified, and greater emphasis could be directed to evaluation of information for the engineered facility.

4. V. Oversby described the overall strategy of NNWSI to deal with the collection of information related to waste form release rates needed to support repository licensing. She identified three categories of information:
 - a. Information needed to show compliance with regulatory requirements (10CFR60.112 and 60.113) would be of highest priority. It would be essential to meet the requirements and the supporting information must be of high certainty, but not necessarily of high accuracy (i.e., bounding or limiting conditions might be used in many situations). It would only be necessary to prove with certainty that the repository would meet or exceed the regulatory requirements.
 2. 10CFR60.21(c)(1)(ii)(C) requires that the DOE model expected behavior or performance; this analysis would be of secondary importance. The supporting data would not need to be known with as great a certainty as the data to support the analysis showing compliance with the regulatory requirements, and the data could have appreciable error bars.
 3. 10CFR60 also requires consideration of unexpected but possible events. This information would be of still less importance and lower quality and would only need to support the contention that unexpected, but possible, events would not seriously compromise the repository.

This approach seemed logical to us, and we were disappointed that more discussion was not addressed to this topic at the meeting. V. Oversby's suggested approach represents one of the first attempts we are familiar with to develop an overall strategy for the collection of the information needed for repository licensing. If it were possible for the NRC to comment on this approach, or suggest alternate approaches, it would be beneficial to all.

5. There was some discussion of a possible workshop to specifically address the waste form testing program. Such a workshop would be an excellent idea, because the results of this program will likely be central to the licensing application. We suggest that this meeting be held in Richland, Washington, so that the hot cell experimental set-ups of Westinghouse-Hanford Company can be observed.

AGENDA

NNWSI/NRC WASTE PACKAGE MEETING

**July 23-24, 1985
Building 123 - Conference Room A
Lawrence Livermore National Laboratory**

Tuesday, July 23

- 8:30 - Introductions**
 - NRC Participants**
 - DOE & LLNL Participants**
 - Others**

- 8:45 - Meeting Objectives & Agenda Overview**
 - NRC Objectives**
 - DOE/LLNL Objectives**
 - Agenda Overview and Arrangements**

- 9:00 - Update on Package Design Concepts - E. Russell**
 - Alternative Emplacement Geometries**
 - Spent Fuel Internal Configurations**
 - Thermal and Structural Analyses**
 - WV/DWPF Containers**

- 10:00 - Potential Implications of MRS on NNWSI - L. Ballou**
 - Packaging Options**
 - Storage and Transportation Considerations**

- 10:45 - Break**

- 11:00 - Part 60.135(b) Excluded Materials - NRC**
 - Discussion of NRC Intent**
 - Rationale for Implementing Criteria**

- 12:00 - Lunch - LLNL Cafeteria**

- 1:00 - Container Material Testing - D. McCright**
 - Introduction and Overview**
 - NNWSI Environmental Conditions**
 - Anticipated Conditions and Uncertainties**
 - Candidate Materials**
 - Austenitic Stainless Steels and Copper Alloys**
 - Conceptual Corrosion Models**

- 3:00 - Break**

- 3:15 - Material Testing - Continued**
 - General and Localized Corrosion Testing**
 - Stress Corrosion Testing**
 - Planned Testing and Schedules**

- 4:45 - Adjourn**

Wednesday, July 24

8:30 - Waste Form Testing - Spent Fuel - V. Oversby
Approach to Testing & Results to Date
Isotopes of Concern
Release Rates
Cladding Degradation
Fuel Oxidation

10:00 - Break

10:15 - Spent Fuel - Continued
Modeling of Release Mechanisms
Comparison with Performance Objectives
Planned Testing
Discussion of Fuel Population
Proposed Test Matrix - Test Materials
Adequacy of Sampling

12:00 - Lunch - LLNL Cafeteria

1:00 - Waste Form Testing - Glass - V. Oversby
Unsaturated Testing
Procedure Development
Results to Date
Planned Testing
Supporting Tests and Experiments
Modeling of Release Mechanisms

2:30 - Break

2:45 - Reliability Considerations
Discussion of NRC Approach to Interpretation
of "substantially complete"
Approach to Reliability for Containment

3:30 - Summary and Development of Minutes

4:45 - Adjourn

Note to Attendees:

This meeting will be held on the LLNL site. To reach the Laboratory from the San Francisco Area, proceed east on I-580 past Livermore to the Vasco Rd. exit; south to East Ave. (2+ miles); east .1 miles to entrance. Enter Bldg. 123 (Auditorium) just north of West Badge Office. Visitor parking is limited, park in any non-carpool space in the main West Lot.

AGENDA

NNWSI/NRC WASTE PACKAGE MEETING

**July 23-24, 1985
Building 123 - Conference Room A
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Tuesday, July 23

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DOE & LLNL Participants
Others**

8:45 - Meeting Objectives & Agenda Overview

**NRC Objectives
DOE/LLNL Objectives
Agenda Overview and Arrangements**

9:00 - Update on Package Design Concepts - E. Russell

**Alternative Emplacement Geometries
Spent Fuel Internal Configurations
Thermal and Structural Analyses
MV/DWPF Containers**

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Storage and Transportation Considerations**

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MEETING REPORT

AUTHOR: G. K. Jacobs

LOCATION: Denver, Colorado

DATE: July 17-19, 1985

PURPOSE: ACS Short Course on the Environmental Chemistry of Groundwater

PROJECT TITLE: Technical Assistance in Geochemistry

PROJECT MANAGER: S. K. Whatley

ACTIVITY NUMBER: ORNL #41 37 54 92 4 (189 #B0287)
NRC #50 19 03 01

This three day short course reviewed the sampling and analysis of groundwater samples, organic geochemistry, and inorganic geochemistry. The course was taught by M. M. Reddy and E. M. Thurman of the U.S. Geological Survey in Denver, Colorado. The textbooks for the course were "Aquatic Chemistry," by W. Stumm and J. J. Morgan and "Organic Geochemistry of Natural Waters," by E. M. Thurman. An extensive bibliography of other books and journal articles was also furnished. Selected reference lists and title pages, which were provided at the course, are attached.

Topics discussed during the short course included: sampling procedures, analytical procedures, the physical chemistry of aqueous solutions, the hydrogeochemical cycle, biogeochemical processes, the nature of organic carbon in groundwater, and the nature of organic contaminants in groundwater. The content of the course emphasized near-surface (e.g., < 100 m deep) groundwater systems. An enormous amount of material was presented during the three days - allowing the course to cover most of the essential topics related to groundwater geochemistry. Unfortunately, because of the amount of material, only a superficial treatment could be given to each subject area. Therefore, the course, rather than providing any detailed training, mostly provided an introduction and references for further reading for each topic. Most of the material covered relevant to organic geochemistry is contained in the textbook for the course.

The course was worthwhile for me because it introduced topics and references for information relevant to groundwater sampling and organic geochemistry that I had never been exposed to before. I now have a better appreciation for sampling problems and some references to more detailed information. The information I received on organic geochemistry should enable me to more easily familiarize myself with available literature. The ACS short courses are not designed as detailed training courses, but rather to provide a starting point for further investigation and to interact with others working on a variety of problems. I would recommend the course for anyone dealing with groundwater-related problems, but who has little background in actual groundwater geochemistry. However, the course is not designed to provide the information necessary to make one an "expert" in groundwater geochemistry in three days.

"Groundwater" by R.A. Freeze and J.A. Cherry, 1979, Prentice Hall Inc., Englewood Cliffs.

"Aquatic Chemistry" by W. Stumm and J.J. Morgan, 1981, John Wiley and Sons, Inc., New York.

"Marine Organic Chemistry" by E.K. Duursma and R. Dawson, 1981, Elsevier, Amsterdam.

"Identification and Analysis of Organic Pollutants in Water" by L.H. Keith, 1976, 1981, vols. 1 and 2, Ann Arbor Science, Ann Arbor.

"Organic Geochemistry of Natural Waters" by E.M. Thurman, 1985, Martinus Nijhoff-Dr. W. Junk, Dordrecht.

"Organic Chemicals in Natural Waters"

ISBN - 0 - 387 - 96034 - 1

by J W Moore + S R Ramamoorthy

Springer-Verlag, NY

1984

Geochemistry for Ground Water Systems

A review and revision of fundamental concepts and principles

Michael M. Reddy

Annotated bibliography

BREWER, Peter G.

Minor elements in seawater

Chemical Oceanography vol 1, 416-420, (1975)

(A-8)

BURTON, J. D.

Behavior of some trace chemical constituents in estuarine waters.

Pure and Applied Chemistry 56, 385-393, (1978).

(b2p27) "Better understanding of the processes involved in the interactions of dissolved and particulate material is obtainable from environmental studies in which a group of constituents, the behavior of which may be inter-related, is examined, with relevant measurements on particulate fractions. Complete descriptions of chemical speciation in these systems cannot be obtained for the trace constituents by present methods. Analytical resolution of dissolved and particulate material is an area needing further work."

BYRNE, Robert H.

Trace metal complexation in high ligand variety natural media

Marine Chemistry 12, 15-24, (1983).

(from abstract) "Mixed-ligand complexes can dominate the solution chemistry of trace metals in ligand-rich, high ligand variety media. A probable consequence of neglecting mixed-ligand complexation in high ligand variety systems is substantial underestimation of a metals degree of complexation"

CONWAY, B.E.

Ionic hydration in chemistry and biophysics

Elsevier Scientific Publishing Company, Amsterdam,

1981

(B-3)

- CUMME, G. A., A. Horne, and W. Achilles
Metal complex formation and its importance for enzyme regulation
Biol. Med. Germ. 31, 349-364, (1973).
"A computer program is described ... by which the total concentrations may be calculated which are needed to achieve prescribed values of the concentrations of selected free and complex species."
- CURTIS, C. D.
Sedimentary geochemistry: environments and processes dominated by involvement of an aqueous phase
Phil. Trans. R. Soc. Lond. A. 286, 353-372, (1977).
(from abstrcat) . . . "Erosion, sedimentation and diagenesis move weathering products through a succession of chemical environments. . . . It is now possible to present a fairly complete account of the important chemical reactions occurring at each stage of the surface cycle."
- DAVIES, C.W.
Electrochemistry
Philosophical Library Inc., New York, 1967
(C-1)
- FINDLAY, Alexander
The Phase Rule and Its Applications
Dover Publications Inc., N. Y., 1951
(A-1)
- FLETCHER, W. K., G. S. Holmes, and A. G. Lewis
Geochemistry and biological availability of iron and trace elements in the upper Fraser River estuary
Marine Chemistry 12, 195-218, (1983).
(b5p71)
- FLORENCE, T. M.
Trace metal species in fresh waters
Water Research 11, 681-, (1977).
(blp22) Trace metal speciation scheme proposed by the author is said to provide useful information about the forms of the toxic heavy metals (eg. cadmium, copper, lead, and zinc). Author feels that the proposed technique is superior to all others proposed. Discusses advantages and disadvantages of scheme.

FLORENCE, T. M. and G. E. Batley

Trace metal species in sea-water - I. Removal of trace metals from sea-water by a chelating resin

Talanta 23, 179-186, (1977).

(blp86) A significant fraction of cadmium, copper, lead, and zinc in seawater exists in a form not retained by a chelating resin (Chelex-100) or extracted by APDC-MIBK. ASV suggests that a major part of this is adsorbed on, or occluded in, organic and inorganic colloidal particles. Most complexing ions are unimportant. For a very strong chelator (an "EDTA-like" ligand) cadmium, copper, lead, and zinc complexation is entirely controlled by the concentrations of ligand and labile iron(III) and chromium(III) in seawater, since these two ions together will react quantitatively with EDTA. L-cysteine, if present in seawater will also complex trace metals.

FLORENCE, T. M. and G. E. Batley

Determination of the chemical forms of trace metals in natural waters, with special reference to copper, lead, cadmium, and zinc.

Talanta 24, 151-158, (1977).

(blp89) Methods used to differentiate between the various forms of a metal in a natural water are critically reviewed.

FLORENCE, T. M., and G. E. Batley

Chemical speciation in natural water

CRC Critical Reviews in Analytical Chemistry, August, 1980, 219-290.

"In this review, all the important speciation techniques are considered, and the results which have been obtained for several important elements are critically discussed. The many problems involved in this exacting area of trace analysis are enumerated, and recommendations are made for future work.

FOWLER, R.H., and Guggenheim, E.A.

Statistical thermodynamics

Cambridge at the University Press, 1939

(C-2)

GOLDBERG, E. D., Editor

The nature of seawater. Report of the Dahlem Workshop on the nature of seawater

Published by the Dahlem Conference, Berlin, 1975

(blp32) Five conference areas: (1), Chemical speciation; (2), Conventions to describe seawater equilibria; (3), Kinetics; (4), Colloidal and surface phenomena; and (5), Biosynthesis and biodegradation.

GOLDBERG, E. D., Editor

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"In 1948 we had proposed an explanation of the increase in the activity coefficient of many electrolytes at high concentrations in terms of a hydrated-ion model. We treated the solution as one of hydrated cations, free anions, and free water, and assumed that the solution behaved as an ideal solution of these species except for the effects of ion-ion interactions, which were described by the usual Debye-Huckel formula. A valuable modification of the theory was made by Glueckauf, who pointed out that we had implicitly assumed mole fraction ideality for the entropy of mixing of the solvated ions, anions, and free water molecules. He suggested that the entropy of mixing would be more appropriately calculated by the volume-fraction statistics of Flory and Huggins, and showed that this led to a more consistent set of hydration numbers."

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JUL 17 1985
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Techniques of Water-Resources Investigations of the United States Geological Survey

Chapter A1

METHODS FOR DETERMINATION OF INORGANIC SUBSTANCES IN WATER AND FLUVIAL SEDIMENTS

By Marvin W. Skougstad, Marvin J. Fishman, Linda C. Friedman,
David E. Erdmann, and Sandra S. Duncan, Editors

Book 5

LABORATORY ANALYSIS

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JUL 17 1985
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A SUPPLEMENT TO
METHODS FOR THE DETERMINATION OF INORGANIC SUBSTANCES
IN WATER AND FLUVIAL SEDIMENTS

U.S. Geological Survey Techniques of Water-Resources Investigations
Book 5, Laboratory Analysis, Chapter A1

Marvin J. Fishman and Wesley L. Bradford, Editors

OPEN-FILE REPORT 82-272

Denver, Colorado

May 1982

JUL 17 1985

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Techniques of Water-Resources Investigations
of the United States Geological Survey

Chapter A1

METHODS FOR COLLECTION AND
ANALYSIS OF WATER SAMPLES FOR
DISSOLVED MINERALS AND GASES

By Eugene Brown, M. W. Skougstad, and M. J. Fishman

Book 5
LABORATORY ANALYSIS

JUL 17 1985
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Techniques of Water-Resources Investigations
of the United States Geological Survey

Chapter A6

**QUALITY ASSURANCE PRACTICES FOR
THE CHEMICAL AND BIOLOGICAL
ANALYSES OF WATER AND
FLUVIAL SEDIMENTS**

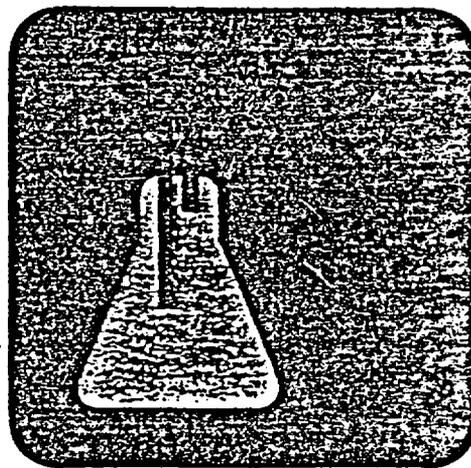
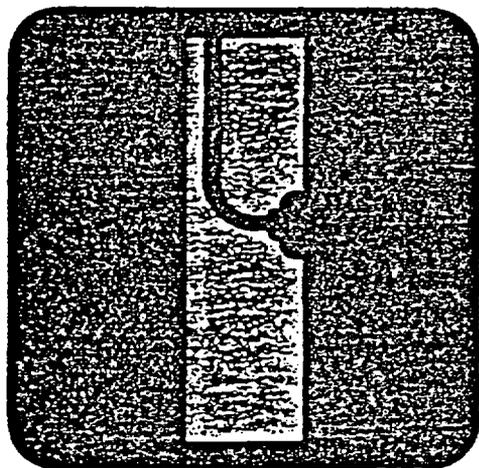
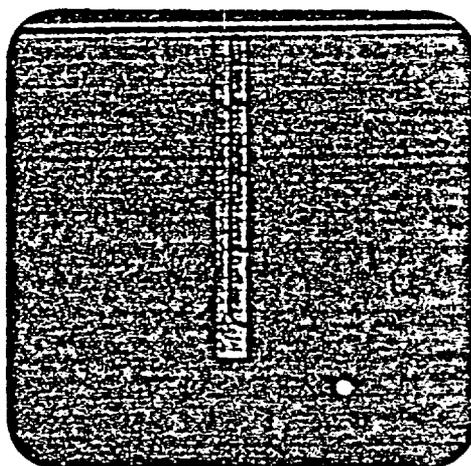
By Linda C. Friedman and David E. Erdmann

Book 5

Laboratory Analysis

Manual of Ground-Water Sampling Procedures

490
M318



by Marion R. Scaif, James F. McNabb, William J. Dunlap,
Roger L. Cosby, John Fryberger
NWWA/EPA Series

TABLE 1. RECOMMENDATION FOR SAMPLING AND PRESERVATION
OF SAMPLES ACCORDING TO MEASUREMENT ^(a)

Measurement	Vol. Req. (ml)	Container ^(b)	Preservative	Holding Time ^(c)
<u>Physical Properties</u>				
Color	50	P,G	Cool, 4°C	24 Hrs.
Conductance	100	P,G	Cool, 4°C	24 Hrs. ^(d)
Hardness	100	P,G	Cool, 4°C HNO ₃ to pH<2	6 Mos. ^(e)
Odor	200	G only	Cool, 4°C	24 Hrs.
pH	25	P,G	Det on site	6 Hrs.
<u>Residue</u>				
Filterable	100	P,G	Cool, 4°C	7 Days
Non-Filterable	100	P,G	Cool, 4°C	7 Days
Total	100	P,G	Cool, 4°C	7 Days
Volatile	100	P,G	Cool, 4°C	7 Days
Settleable Matter	1000	P,G	None Req.	24 Hrs.
Temperature	1000	P,G	Det. on site	No Holding
Turbidity	100	P,G	Cool, 4°C	7 Days
<u>Metals</u>				
Dissolved	200	P,G	Filter on site HNO ₃ to pH<2	6 Mos. ^(e)
Suspended	200		Filter on site	6 Mos.
Total	100	P,G	HNO ₃ to pH<2	6 Mos. ^(e)

(continued)

TABLE 1. (continued)

Measurement	Vol. Req. (ml)	Container ^(b)	Preservative	Holding Time ^(c)
Mercury Dissolved	100	P,G	Filter on site HNO ₃ to pH<2	38 Days (Glass) 13 Days (Hard Plastic)
Total	100	P,G	HNO ₃ to pH<2	38 Days (Glass) 13 Days (Hard Plastic)
<u>Inorganics, Non-Metallics</u>				
Acidity	100	P,G	None Req.	24 Hrs.
Alkalinity	100	P,G	Cool, 4°C	24 Hrs.
Bromide	100	P,G	Cool, 4°C	24 Hrs.
Chloride	50	P,G	None Req.	7 Days
Chlorine	200	P,G	Det. on site	No Holding
Cyanides	500	P,G	Cool, 4°C NaOH to pH 12	24 Hrs.
Fluoride	300	P,G	None Req.	7 Days
Iodide	100	P,G	Cool, 4°C	24 Hrs.
Nitrogen				
Ammonia	400	P,G	Cool, 4°C H ₂ SO ₄ to pH<2	24 Hrs.
Kjeldahl, Total	500	P,G	Cool, 4°C H ₂ SO ₄ to pH<2	24 Hrs. ^(f)
Nitrate plus Nitrite	100	P,G	Cool, 4°C H ₂ SO ₄ to pH<2	24 Hrs. ^(f)
Nitrate	100	P,G	Cool, 4°C	24 Hrs.
Nitrite	50	P,G	Cool, 4°C	48 Hrs.

(continued)

TABLE 1. (continued)

Measurement	Vol. Req. (ml)	Container ^(b)	Preservative	Holding Time ^(c)
Dissolved Oxygen Probe	300	G only	Det. on site	No Holding
Winkler	300	G only	Fix on site	4-8 Hrs.
Phosphorus Ortho-phosphate, Dissolved	50	P,G	Filter on site Cool, 4°C	24 Hrs.
Hydrolyzable	50	P,G	Cool, 4°C H ₂ SO ₄ to pH<2	24 Hrs. ^(f)
Total	50	P,G	Cool, 4°C H ₂ SO ₄ to pH<2	24 Hrs. ^(f)
Total, Dissolved	50	P,G	Filter on site Cool, 4°C H ₂ SO ₄ to pH<2	24 Hrs. ^(f)
Silica	50	P only	Cool, 4°C	7 Days
Sulfate	50	P,G	Cool, 4°C	7 Days
Sulfide	500	P,G	2 ml zinc acetate	24 Hrs.
Sulfite	50	P,G	Det. on site	No Holding
<u>Routine Organics</u>				
BOD	1000	P,G	Cool, 4°C	24 Hrs.
COD	50	P,G	H ₂ SO ₄ to pH<2	7 Days ^(f)
Oil & Grease	1000	G only	Cool, 4°C H ₂ SO ₄ or HCL to pH<2	24 Hrs.
Organic Carbon	25	P,G	Cool, 4°C H ₂ SO ₄ or HCL to pH<2	24 Hrs.
Phenolics	500	G only	Cool, 4°C H ₃ PO ₄ to pH<4 1.0 g CuSO ₄ /l	24 Hrs.

(continued)

TABLE 1. (continued)

Measurement	Vol. Req. (ml)	Container ^(b)	Preservative	Holding Time ^(c)
MBAS	250	P,G	Cool, 4°C	24 Hrs.
NTA	50	P,G	Cool, 4°C	24 Hrs.

- a. A general discussion on sampling water and industrial wastewater may be found in ASTM, Part 31, p. 72-82 (1976) Method D-3370.
- b. Plastic (P) or Glass (G). For metals polyethylene with a polypropylene cap (no liner) is preferred.
- c. It should be pointed out that holding times listed above are recommended for properly preserved samples based on currently available data. It is recognized that for some sample types, extension of these times may be possible while for other types, these times may be too long. Where shipping regulations prevent the use of the proper preservation technique or the holding time is exceeded, such as the case of a 24-hour composite, the final reported data for these samples should indicate the specific variance.
- d. If the sample is stabilized by cooling, it should be warmed to 25°C for reading, or temperature correction made and results reported at 25°C.
- e. Where HNO₃ cannot be used because of shipping restrictions, the sample may be initially preserved by icing and immediately shipped to the laboratory. Upon receipt in the laboratory, the sample must be acidified to a pH < 2 with HNO₃ (normally 3 ml 1:1 HNO₃/liter is sufficient). At the time of analysis, the sample container should be thoroughly rinsed with 1:1 HNO₃ and the washings added to the sample (volume correction may be required).
- f. Data obtained from National Enforcement Investigations Center-Denver, Colorado, support a four-week holding time for this parameter in Sewerage Systems. (SIC 4952).

LETTER REPORT

TITLE: Review of "Downhole Geophysical Logging," Ann. Rev. Earth Planet. Sci. 13, 315-44, (1985), A. Timur and M. N. Toksoz

AUTHOR: J. G. Blencoe

PROJECT TITLE: Technical Assistance in Geochemistry

PROJECT MANAGER: Susan K. Whatley

ACTIVITY NUMBER: ORNL #41 37 54 92 4 (189 #B0287)/NRC #50 19 03 01

SUMMARY

This interesting and useful article describes the most common methods of, and recent developments in, borehole geophysical logging (well-logging technology). Borehole geophysical logging involves performing in situ geophysical measurements in boreholes, transmitting the signals to recording and processing equipment at the surface, and then analyzing the data to elucidate petrophysical properties of subsurface lithologies.

Timur and Toksöz emphasize that it is now possible to simultaneously measure several tens of petrophysical properties during a single excursion into a borehole. Typically, petrophysical properties are measured as a function of depth using a single downhole sensor (sonde) containing both source(s) and receiver(s). The source(s) and receiver(s) may be as little as 10 cm apart or as much as tens of meters apart. Measurements are usually repeated every few centimeters as the sonde is lowered or raised in the borehole: this strategy permits fine-scale spatial resolution of the geophysical properties of rock formations both adjacent to and beneath the borehole. It is also possible to conduct downhole measurements with the sonde in the borehole at depth and a source at the surface. In this kind of well logging, the source signal is repeated as the sonde is moved incrementally down or up the borehole.

The bulk of the Timur and Toksöz commentary is devoted to summarizing the most commonly used techniques of downhole geophysical logging. These techniques can be divided into three principal categories: electrical methods, nuclear methods, and acoustic methods. Of principal interest to geochemists concerned with radionuclide migration in rock/groundwater systems are the methods that provide information on primary and secondary (fracture) porosity in the rocks. The text below briefly describes these particular methods.

Electrical methods. Downhole electrical logging usually involves measuring resistivity or conductivity over a broad range of frequency. In practice, the measuring apparatus is arranged in such a way that a particular zone is investigated. The electrical method most commonly used to investigate the porosities of rocks is the nonfocused electric log technique.

Nuclear methods. These downhole techniques typically measure natural radioactivity (natural gamma-ray logs), gamma-ray scattering (gamma-gamma logs), neutron scattering/absorption (neutron and pulsed-neutron logs), or induced-gamma-ray spectra (pulsed-neutron logs). The methods most commonly used to investigate the porosities of rocks are the gamma-gamma, neutron-gamma, neutron-thermal neutron, and neutron-epithermal neutron techniques.

Acoustic (seismic) methods. These methods involve measuring the travel times and rates of attenuation of seismic waves (P- and S-waves) that propagate through — and are refracted by — nearby rock. In a typical arrangement, the sonde is hung in the center of the borehole and lowered or raised as logging proceeds. Apart from this usual strategy, however, methods of acoustic logging assume various forms. In particular, a major distinction between the various techniques concerns whether the sonde contains at least one source and at least one receiver, or whether it contains only one or more receivers. In the latter case, the source is at the surface (e.g., see Beydoun et al., 1985), and the method is called vertical seismic profiling (VSP). VSP can be used to locate and characterize fracture zones in rocks either adjacent to or below the borehole.

The acoustic methods most commonly used to investigate the porosities of rocks include the conventional acoustic and full-waveform acoustic techniques. In conventional acoustic logging, a sonde commonly contains one or two sources and a pair of receivers; in this method only the time delay of the compressional headwave is recorded. By contrast, with full-waveform acoustic sondes, the entire microseismogram is recorded digitally at each receiver. The full-waveform technique is particularly useful for detecting and characterizing fractures that intersect a borehole.

Still another, but very different, type of acoustic logging is borehole televising. This method, which is used in an open hole to locate fractures, bedding planes, and vuggy porosity, is especially advantageous in highly fractured rocks, because it provides data that no other combination of logs can produce. The technique involves using high-frequency acoustic waves to image the wall of a borehole. A single transducer rotates at constant speed, emitting acoustic pulses in the megahertz range while simultaneously receiving reflected waves from the borehole wall. In this fashion, the borehole televiewer produces a continuous acoustic "picture" of a borehole wall. Recently, image-enhancement techniques have been developed to improve the ability of televiewers to locate fractures in boreholes.

References

- W. B. Beydoun, C. H. Cheng, and M. N. Toksöz, "Detection of Open Fractures with Vertical Seismic Profiling," Jour. Geophys. Res. 90, No. B6, 4557-66, (1985).

LETTER REPORT

TITLE: Comments concerning S. L. Phillips' reply to LR-290-10,
March 28, 1985

AUTHOR: G. K. Jacobs

PROJECT TITLE: Technical Assistance in Geochemistry

PROJECT MANAGER: S. K. Whatley

ACTIVITY NUMBER: ORNL #41 37 54 92 6 (FIN No. B0287)
NRC #50 19 03 1

I spoke with S. L. Phillips by telephone to discuss his comments on my letter report (LR-290-10) concerning geochemical modeling and thermodynamic data. Sid correctly pointed out my inadvertant error of including the complex PuCO_3^{2+} in the list of species that have been identified as predominant species in some geochemical modeling calculations, yet no evidence is available to firmly support their actual existence. We also discussed some of the uranium-bearing solids for which there are no thermodynamic data (e.g., boltwoodite), yet these phases continue to be found precipitating in experiments. Sid suggested trying to model our experimental results using a surrogate phase (e.g., uranophane) for the boltwoodite that precipitates in our experiments. Sid and I also discussed some of the limitations in attempting to derive information on speciation from experiments designed to measure solubilities, such as those performed by Rai and Ryan (1985). It is often advantageous to design tests to specifically determine speciation and solubility using independent experimental strategies. This approach is especially desirable if one wishes to investigate the solubility of a solid phase having a low solubility, because the sensitivity of speciation determinations will be poor. Sid and I are in general agreement on the content of my original letter report and his reply. It is critical that accurate and internally consistent thermodynamic data become available before geochemical modeling of the solubility/speciation of radionuclides can be considered reliable.