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Ms. Susan K. Whatley
Oak Ridge National Laboratory
P.O Box X
Chemical Technology Division
Building 4500 N, MS 211
Oak Ridge, TN 37831

AUG 20 1985

Dear Ms. Whatley:

SUBJECT: REVIEW OF THE DRAFT 189 FOR B0290, "LABORATORY EVALUATION OF DOE RADIONUCLIDE SOLUBILITY DATA AND SELECTED RETARDATION PARAMETERS EXPERIMENTAL STRATEGIES, LABORATORY TECHNIQUES AND PROCEDURES"

I have reviewed the draft 189 for B0290 and found it to be acceptable. Enclosed is a mark-up suggesting only minor changes.

I suggest that, prior to starting any work under Task 3, a study should be initiated in B0287 to clarify the scope of this task. The scoping study should discuss probabilities of various release scenarios adopted by the DOE and sensitivity of solubility/sorption to variations in geochemical conditions.

The 189 does not contain a discussion of the termination of the contract. I suggest that a section be included in the text of the 189 that describes the year of contract termination and the final contract products.

I note that you plan to study Sr, Cs, Tc, Np, Eu, Am and Pu in FY 1986. This appears to be rather ambitious. Inasmuch as Am and Pu normally head the list of key radionuclides (total release/EPA limit), I strongly recommend that work begin in FY 86 on these two radionuclides. I will call you soon to discuss where I think the emphasis should be placed in B0290.

I consider the suggestions I have made to be only minor. Consequently, I do not envision a delay in the approval process of this revised 189.

Sincerely,

Original Signed By

John W. Bradbury
Geochemistry Section
Geotechnical Branch
Division of Waste Management
Office of Nuclear Material Safety
and Safeguards

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Information from all those sources will be utilized in planning for this work. The NRC/RES geochemical research activities are directly related to this work and will be a major source of information and technical input. Those activities include research on the geochemistry of waste, canister, backfill, and host rock, as well as assessment modeling and evaluation of natural analogs. NRC projects of special relevance to the activities described here include B3040 at LBL, which involves measurement of solubilities of pure actinide species in carbonate groundwaters, establishing an experimental setup to investigate solubilities at elevated temperatures, and investigations concerning experimental methods used to generate geochemical information. Project B0462 at ORNL is also of special relevance since it is concerned with researching valence effects on adsorption, and the conduct of this research involves determination of neptunium and technetium sorption and speciation effects at very low concentrations. The activities of this project will be coordinated with those in B3040 and B0462 since both of these projects concern closely-allied geochemical information and techniques. Additional NRC/RES research on near-field transport, far-field transport, and performance assessment are relevant to this work, and interaction will be maintained with these projects.

The DOE-supported activities for the three candidate sites (BWIP, NTS, and salt) by the site contractors and by other industrial and university contractors will, obviously, be another major area of interaction and information.

6. REPORTING SCHEDULE:

Previous Publications

1. Quarterly progress reports for the fiscal year 1985, Progress in Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Nuclear Waste Repository Site Projects: Volume 1, Report for October–December 1984, Volume 2, Report for January–March 1985, Volume 3, Report for April-June 1985, NUREG/CR-4136 (Vol. 1, 2, 3, 4), ORNL/TM-9526/V1, V2, V3, V4.

2. R. E. Meyer, W. D. Arnold, J. S. Johnson, Jr., A. D. Kelmers, J. H. Kessler, R. J. Clark, G. C. Young, F. I. Case, and C. G. Westmoreland, "Technetium and Neptunium Reactions in Basalt/Groundwater Systems," Scientific Basis for Nuclear Waste Management VIII, Mat. Research Soc., p. 333-42, Pittsburgh, PA, 1985.

3. Meeting report MR-5.4, "B0287 and B0290 Project Review."

4. Meeting report MR-290-1, "Trip Report on 1984 MRS Symposium."

5. Letter report LR-290-10, "Recommendations on Geochemical Modeling of Radionuclide Solubility/Speciation."

Expected Future Reports

Monthly management reports will be issued which will provide technical highlights.

Quarterly ORNL/TM progress reports will be issued. These will provide tabulations of results, evaluate the data and laboratory procedures, discuss the experimental design, and discuss uncertainties in the data and limitations in the precision and

accuracy. The quarterly progress reports will identify significant differences in the results between the NRC data and the DOE data, identify areas requiring additional attention by the DOE programs, and identify additional research needed by the NRC. Special attention will be paid to the applicability of results to the NRC HLW program and the NRC site-specific licensing (review) activities.

Topical reports will be issued as appropriate for the compilation and summation of major experimental areas, results, or issues.

Letter reports may be issued covering specific brief topics or issues.

Papers presented at technical meetings or submitted to scientific journals may also be issued as reports.

7. SUBCONTRACTOR INFORMATION:

Not applicable.

8. LIST NEW CAPITAL EQUIPMENT REQUIRED:

Not applicable.

9. DESCRIBE SPECIAL FACILITIES REQUIRED:

Not applicable.

10. CONFLICT OF INTEREST INFORMATION:

There are no known relationships between this organization or its employees with industries regulated by the NRC and suppliers thereof that might give rise to an apparent or actual conflict of interest regarding the work described in this proposal.

Draft (barely) work up B0290

Laboratory Evaluation of DOE Radionuclide Solubility Data and Selected Retardation Parameters, Experimental Strategies, Laboratory Techniques, and Procedures

1. OBJECTIVE:

The overall objective of this work is to supply the NRC with a selected independent laboratory-oriented evaluation of DOE's past, present, and proposed future geochemical data and data acquisition methods related to candidate high-level waste (HLW) repositories. The results of this work will allow the NRC to independently review and evaluate the key data values and data acquisition methods. The results will also help to define the uncertainties or bounding limits of the data and will be used to support NRC evaluations of site performance. This work will assure that the information available to the NRC to assess performance for licensing decisions is adequate and accurate. In addition, the work will identify areas requiring additional attention by the DOE program(s) and/or needing additional research by the NRC.

2. SUMMARY OF PRIOR EFFORTS:

Activities during FY 1985 have focused on evaluating key radionuclide values reported for the Basalt Waste Isolation Project (BWIP) candidate site in basalt. Batch contact experiments for 14 d and 50 d were performed under anoxic redox conditions (air excluded) on Tc, Np, and U at elevated temperatures (60°C). These experiments were with McCoy Canyon and Cohassett basalts using synthetic groundwater GR-2 and GR-4, respectively.

All currently planned work to evaluate the sorption/solubility behavior of technetium in basalt/groundwater systems has been completed. The following major conclusions were reached as a result of this work:

1. Significant sorption is not observed under oxic redox conditions.

2. Significant sorption is observed only if the basalt is crushed and stored in an inert atmosphere and stringent precautions are taken to exclude traces of air from the experiment; the test atmosphere must contain <1 ppm oxygen.

3. Sorption isotherms are linear at low technetium concentrations under anoxic redox conditions.

4. Technetium sorption ratios are higher for the Cohassett-basalt/synthetic-groundwater GR-4 system than for the McCoy Canyon-basalt/synthetic-groundwater GR-2 system.

5. The sorption ratios measured are not very sensitive to the particle size of the basalt used in the anoxic redox condition tests. This is in sharp contrast to the results we obtained earlier for neptunium sorption.

6. The solubility limit for reduced technetium species may be lower than the values of 10^{-5} and 10^{-6} mol/L which we previously reported. This is being explored further in work under a parallel NRC/Research contract.

7. Sorption of pertechnetate clearly involves reduction to a lower valence, but the reactions are complex and not clearly understood.

We conclude that our evaluation of both the experimental methodology and results reported by the BWIP to date for technetium sorption or solubility limits do not conclusively indicate that significant retardation may be provided by phases present in the basalts at the Hanford Site. Additional consideration of technetium sorption/solubility behavior may be necessary if the Hanford Site performance assessment strategy will give importance to retardation of technetium by site components.

Neptunium sorption information relative to the BWIP site in basalt was evaluated under both oxic and anoxic redox conditions. Sorption isotherms were constructed for neptunium(V) in synthetic groundwater with McCoy Canyon and Cohassett basalt samples. Under oxic conditions, steady-state was achieved in a few days, low sorption ratios were measured, and the isotherms were linear over several orders-of-magnitude neptunium concentration. The neptunium geochemistry was more complex under anoxic conditions. Sorption continued for longer periods of time, and the measured sorption ratio was sensitive to the basalt particle size used in the test. Much of the neptunium was reduced, presumably by iron(II) in the basalt, to Np(IV), while some still remained as Np(V) and a small amount of Np(VI) was generated, possibly by some disproportionation reaction. Much larger sorption ratio values were obtained under anoxic conditions. We were concerned that the BWIP apparently has not identified the valence of the neptunium involved in their experiments; thus extrapolation of their test results for repository modeling could be uncertain.

The uranium isotherms were completed under anoxic redox conditions. Sodium boltwoodite [a U(VI) silicate] was shown to be the U(VI)-containing solid phase which precipitates during the experiments. Schoepite is typically assumed to be the stable U(VI) solid phase under oxidizing conditions in geochemical modeling calculations, in part, due to the absence of thermodynamic data for sodium boltwoodite. The unexpected formation of boltwoodite shows the importance of identifying the solid phase present in experimental measurements and highlights the limitations of the existing thermodynamic data bases for compounds and conditions of interest to repository assessment.

An evaluation was made of the information developed by DOE on the native copper deposits of Michigan as a natural analog for the possible emplacement of copper canisters in a repository in basalt. We found that the similarity in bulk chemistry of the basalts, relied upon heavily by DOE in their analysis, cannot be used to unequivocally conclude that similar geochemical conditions, and particularly controls on the geochemical conditions, exist within the basalt/water systems at Michigan and at the Hanford Site. Significant differences exist in the mineralogy and texture of the two basalt occurrences. Better definition of the actual mechanisms involved in controlling the groundwater chemistry is required before a valid analogy can be demonstrated.

Results of the radionuclide solubility/speciation calculations, published by the NNWSI relevant to the Yucca Mountain site, were evaluated. The calculated solubility/speciation of several radionuclides appear to be reasonable for the assumptions

and thermodynamic data used. However, agreement between our results and those published by the NNWSI do little more than verify that the computer code used by NNWSI (EQ3/6) and that used by us (MINTEQ) solve thermodynamic relationships correctly and that the data bases are not inconsistent. Limitations of such calculations include: (1) the assumption of equilibrium, (2) missing or invalid data, (3) incomplete accounting of all geochemical processes, and (4) lack of experimental validation.

3. WORK TO BE PERFORMED AND EXPECTED RESULTS:

The work will be divided into three major tasks:

Task 1. Evaluation of the Solubilities of Selected Radionuclides in Basalt, Tuff, and Salt Environments. Under this task, selected solubility values for key radionuclides (with emphasis on the actinides and selected fission products) will be independently assessed under site-specific groundwater/backfill/host rock chemistry parameters.

Task 2. Examination of Selected Retardation Parameters and Test Methods Being Used in the Characterization of Site Geochemistry. Under this task, radionuclide (with emphasis on the actinides and selected fission products) retardation/migration parameters and mechanisms will be independently assessed. Emphasis will be given to ion exchange and surface adsorption phenomena, chemisorption and sorption/desorption kinetics, and multiple speciation effects under site-specific groundwater/host rock chemistry parameters.

Task 3. Evaluation of Geochemical Conditions in Basalt, Tuff, and Salt Environments. The geochemical conditions present at a given site will control, in part, the solubility and sorption behavior of radionuclides released from waste packages. Therefore, under this task, geochemical conditions important to the solubility and sorption processes in the engineered barrier system, disturbed zone, and the geologic setting will be evaluated using laboratory and calculational methods. This task will directly support Tasks 1 and 2 through evaluation of whether DOE-defined geochemical conditions and test conditions are sufficiently relevant and bounding for use as input to performance assessment analyses.

Task 4. Prediction and Modeling of Dominant Reactions and Stabilities of Both Solid Phases and Solution Species under Site Specific Conditions. Geochemical codes such as EQ3/EQ6, MINTEQ, PHREEQE and WATEQ will be utilized in conjunction with standard thermodynamic data bases to support the first two tasks through the calculation of estimated solubility for experimental confirmation and as a check on the DOE calculational methods and results.

Under Tasks 1, 2, and 3, the experimental results will be evaluated, including consideration of the experimental design and uncertainties in the data and limitations in the precision and accuracy, and the data and methods will be compared with those of DOE. Significant differences in results between the NRC data and the DOE data will be identified. Areas which may require additional attention by DOE programs and/or additional research by the NRC will be identified. It is recognized that the separation

between the tasks is to a degree arbitrary, and the work will be closely coordinated. For some of the experimental systems, it may be difficult to differentiate sorption from precipitation phenomena and, in such cases, the objectives of the experiments may be to evaluate the magnitude of the problem. Evaluation of the effect of laboratory experimental uncertainties on site radionuclide migration is one of the objectives of this work. The details of the experiments to be performed, including experimental setups, elements, rock types, groundwater compositions, and other aspects of the experimental protocol, will be established by mutual agreement between the ORNL and NRC project managers based on periodic updates to the work plan previously submitted to and agreed upon by the NRC.

Task 1 will involve the measurement of solubilities of selected radionuclides in site-specific groundwater/backfill/host rock environments. Temperatures, pressures, solution pH, valence of nuclides and the components controlling effective redox conditions, primary and secondary minerals and solid phases, and solution species to be encountered in the near field and far field environments will be considered. Emphasis will be given to the actinide elements. Tests will also be conducted with fission products selected for their importance to performance assessment considerations. Determinations relevant to basalt (BWIP), tuff (NNWSI), and salt [site(s) unspecified] will be conducted. The experimental design of the DOE test and other standard or innovative methods will be evaluated and considered in the selection of the test protocol(s). Careful attention will be given to analytical methods and their associated uncertainties.

In Task 2, tests of DOE procedures for selected retardation mechanisms will be conducted. These methods will include at least ion exchange and surface adsorption mechanisms as a function of oxidation state of the radionuclides. Selected measurements of site-specific materials including groundwater, backfill, and host rock will be performed. Careful attention will be given to the DOE experimental method(s) and to analytical procedures and uncertainties.

Task 3 will involve evaluations of geochemical conditions used by the DOE in their solubility/sorption testing programs. Laboratory and calculational methodologies will be utilized as deemed necessary. Typical parameters to be evaluated include: groundwater chemistry, redox conditions, pH, and the alteration of host rocks. Evaluation of possible bounding values for test methods and the implications on the resulting solubility and sorption information will be specifically addressed.

Task 4, which is related to and supportive of Tasks 1, 2, 3, involves the use of thermodynamic data in existing computer routines to predict and model dominant reactions and stabilities of both solid phases and solution species. Geochemical codes which are being used by the DOE repository projects (e.g., EQ3/EQ6, MINTEQ, PHREEQE, WATEQ) will be employed in this task. These codes will be evaluated on the basis of the extent to which they can be utilized to define expected geochemical conditions or waste element properties, such as oxidation states, speciation, and solubility. An interactive exchange will be established so that the thermodynamically-based predictions can be used to guide the experimental effort. Likewise, the experimental results from Tasks 1-3 will be used to help evaluate the precision and uncertainties in the thermodynamic data used by the codes. This information will help the NRC assess the adequacy and accuracy of the DOE thermodynamic data bases and the DOE performance assessment modeling for each candidate site. Areas which may need additional development by the DOE programs and/or NRC research will be identified.

FY 1986

During FY 1986, we plan to evaluate radionuclide sorption and solubility information and other geochemical information and calculational methodology relevant to the Yucca Mountain candidate site in tuff. All presently planned work relative to the Hanford candidate site in basalt was completed in FY 1985, and additional basalt work will not be initiated during FY 1986, except following consultation with the NRC Project Manager. Yucca Mountain tuff and groundwater materials were received from the NNWSI in FY 1985, and these will be utilized in experiments to evaluate the methodology employed by the NNWSI project.

A number of important methodology issues will be explored during FY 1986 including: (1) comparison of the applicability of sorption/solubility information obtained from batch contact vs column chromatographic vs autoradiographic studies to model engineered facility and repository behavior of radionuclides solubilized in migrating groundwater, (2) evaluation of radionuclide sorption/solubility information obtained with pure minerals representative of those in Yucca Mountain tuff vs information developed from crushed or whole tuff material to best model radionuclide migration conditions, (3) comparison of sorption/solubility information obtained by the use of actual J-13 well water vs synthetic well water (especially relative to biological activity in actual J-13 water and biological sorption of radionuclides and the composition of trace minerals), (4) evaluation of the effect of well water pH (the CO_2 content of well water in the tests will be maintained by a controlled atmosphere) on sorption/solubility information, and (5) consideration of the validity of the extrapolation of laboratory results with crushed or whole tuff to model radionuclide migration and engineered facility and repository retardation performance.

We plan to assess the degree of reproducibility and the sensitivity of the sorption/solubility measurements with regard to a number of parameters. The initial tests are planned to be run with Sr and Cs sorption from synthetic groundwater onto crushed tuff (the simplest and potentially most reproducible set of conditions and parameters). Then, the batch contact work will be expanded to include actual J-13 well water, other important parameters and conditions, and other key radionuclides such as Tc, Np, Eu (fission product proxy for Am), Am, and Pu.

This seems rather ambitious

Evaluation of possible methodologies employing column chromatographic and autoradiographic techniques will be initiated simultaneously with the batch contact work. Some tuff mineralogical characterization work, including various surface analytical techniques, will be used to support the autoradiographic investigations. As experience with the batch contact/column chromatographic/autoradiographic methodology evaluation develops, emphasis may be shifted during the year to maximize the attainment of evaluative information to support the NRC needs.

Geochemical modeling activities during FY 1986 will be concentrated in three areas: (1) implementation and testing of EQ3/6, (2) sensitivity analyses, and (3) analysis of geochemical scenarios. Emphasis will be given to Yucca Mountain, although calculations related to basalt and/or salt may be performed as needed.

EQ3/6 is currently on-line at ORNL. The software package needs to be rigorously tested with some site-relevant problems. It is anticipated that a revised version of EQ3/6 will be released by Lawrence Livermore National Laboratory by December 1985. This new package will have extensive new capabilities and a revised data base. The new version is to be FORTRAN-77 compatible and should be converted for use on the computers at ORNL with little difficulty.

Sensitivity analyses may include evaluations of the impact of varying geochemical conditions on the solubility/speciation and sorption of radionuclides relevant to a repository constructed at Yucca Mountain. The effects of waste package interactions on radionuclide solubility/speciation and thus, sorption, may also be investigated with geochemical models. One of the key issues for the Yucca Mountain site is what the range in water chemistry may be as a result of boiling and concentration of dissolved salts. Bounding values of geochemical parameters may be estimated for this scenario using EQ3/6. These bounding estimates will allow the test protocols being used by DOE to obtain information relevant to the Yucca Mountain candidate site to be evaluated. As experience is gained with EQ3/6, emphasis may be shifted as needed to provide timely evaluations of DOE information.

3. WORK TO BE PERFORMED AND EXPECTED RESULTS (continued):

FY 1987

The work will continue as an extension of FY 1986 work and results. During this period potential work areas include: (a) examination of solubility and sorption data for additional radionuclide elements, (b) evaluation of radionuclide retardation in flowing systems, and (c) examination of data under other parameters.

Beyond FY 1987 I suggest replacing this paragraph with a close-out statement.

The work will be a continuation and extension of the confirmation and analysis activities. Emphasis will be on areas selected from those listed above but not yet considered or in areas such as confirmation of the possible effects of colloids, particulate transport, and organic complexes on radionuclide migration. The work will continue to support the NRC needs for analysis and support in the licensing process and be subject to the approval of the NRC project managers.

4. DESCRIPTION OF ANY FOLLOW-ON EFFORTS:

Not applicable.

5. RELATIONSHIP TO OTHER PROJECTS:

This work will be closely coordinated with NRC contract B0287, "Technical Assistance in Geochemistry," being carried out by ORNL, which will compile existing geochemical information relevant to the candidate HLW sites, define issues, aid in the future analysis of the DOE site SCRs, and generally supply and support the NRC with geochemical expertise and analyses. Those activities, in conjunction with geochemical information and approach used by the DOE during the licensing process, will define the data, methods, analyses, and/or factors in the near-field and the far-field environments that are critical to the demonstration or modeling of satisfactory site performance.