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AUG 06 1985

426.1/B0287/DJB/85/08/06

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Ms. Susan K. Whatley, Manager
Engineering Analysis and Planning
Chemical Technology Division
Oak Ridge National Laboratory
P.O. Box X
Oak Ridge, TN 37830

WM-RES
WM Record File
B0287
ORNL

WM Project 10/11
Docket No. PDR
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(Return to WM, 623-33)

Dear Ms. Whatley:

SUBJECT: CONTRACT NO. NRC-50-19-03-01, FIN B-0287, ORNL NO. 41-37-54-92-4,
"TECHNICAL ASSISTANCE IN GEOCHEMISTRY," JUNE (1985) MONTHLY PROGRESS
REPORT

I have reviewed the June monthly progress report dated July 15, 1985. Based on my review, I have the following comments:

Task 1 - BWIP Technical Assistance

- Progress to date is satisfactory.
- Based on ORNL comments, and comments from the Repository Projects Branch, I have made several changes to the hydrazine STP. These changes have been marked for your review (Attachment 1). A mark-up or telephone response will be adequate. Please let me know when this can be completed.
- Attachment 2, "Chlorine Isotopes as Environmental Tracers in Columbia River Basalt Groundwater" needs review. Please comment on the uncertainties of the chlorine methodology, and the very old dates attributed to deep BWIP groundwaters.

Task 2 - NNWSI Geochemical Technical Assistance

- Progress to date is satisfactory.

Task 3 - Salt Site Geochemical Technical Assistance

- Progress to date is satisfactory.

Task 4 - Short-term Geochemical Technical Assistance

- Progress to date is satisfactory.

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NAME : DJBrooks;mt	:		:		:		:
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- o I have reviewed your proposal to delay the workshop on natural analogues. I agree with the delay and propose the following:
 1. As soon as practical, Doug Brookins should review and report on the status of his work on analogues. This would take place in Silver Spring and would include interested NRC staff.
 2. Upon completion of the Brookins work, we would hold an NRC/DOE meeting in Silver Spring. At this time Dr. Brookins would present his final results. I would anticipate that this meeting would be held sometime next spring.
- o As we discussed in July, a workshop on sorption testing and modeling should be considered. Such a workshop would fit into our plans for finalizing our technical position on sorption. Among other presentations, we would present and discuss our technical position. Please investigate the feasibility of holding such a workshop.

Task 5 - Project Management

- o Progress to date is satisfactory.
- o Plans should be made for having a contract review. This review should consist of:
 1. A presentation to NRC staff of FY 85 results, (this could include a presentation by Jim Blencoe on his solubility topical report and a demonstration of the data base retrieval system); and
 2. Discussions of FY 86 work plans.
- o Please send a printout of the current data base for BWIP, NTS and Salt.

The action taken by this letter is considered to be within the scope of the current contract NRC-50-19-03-01/FIN B-0287. No changes to cost or delivery of

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contracted products are authorized. Please notify me immediately if you believe that this letter would result in changes to cost or delivery of contracted products.

Sincerely,

David J. Brooks
Geochemistry Section
Geotechnical Branch
Division of Waste Management
Office of Nuclear Material Safety
and Safeguards

Enclosure:
As stated

DFC : WMG	:	:	:	:	:	:
NAME : DJBrooks,mt	:	:	:	:	:	:
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Attachment-1

Note: **DRAFT**
See end comment
on highlighted
portions.

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SITE TECHNICAL POSITION
DOE HIGH LEVEL WASTE REFERENCE REPOSITORY LOCATION
HANFORD SITE

Use Of Hydrazine To Experimentally Simulate
Expected Site Redox Conditions And Reactions

INTRODUCTION

The Department of Energy (DOE) is required by the Nuclear Waste Policy Act of 1982 (NWP) and by Nuclear Regulatory Commission (NRC) regulations (10 CFR 60) to conduct a program of site characterization prior to any site submitting a license application for NRC approval. In this regard the DOE/Hanford Staff is performing laboratory and field investigations to acquire data needed to address repository performance based on site geochemical conditions. The Nuclear Waste Policy Act (NWP) and Nuclear Regulatory Commission (NRC) regulations (10CFR60) and agreements governing licensing of a geologic repository provide for consultation between DOE and NRC staffs prior to formal licensing to assure that licensing information needs and requirements are identified at an early time.

The performance criteria of 10CFR60 include limits on the amount of radionuclides permitted to be released from a repository. In order to demonstrate compliance with these criteria, DOE/Hanford is identifying the particular aspects of site geochemistry that will be relied upon to retard radionuclide migration. Based on discussions presented by DOE in the Hanford

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Draft Site Characterization Report (DSCR), the Draft Environmental Assessment (DEA), and at site workshops, DOE/Hanford is taking the position that site redox conditions will maintain redox-sensitive radionuclides such as uranium, plutonium, technetium and neptunium, in their least mobile state, thus contributing to the control of the release of radionuclides from the repository (DOE, 1982, 1984, among others). Therefore, site redox conditions have been identified in NRC issues 3.1, 3.2 and 3.3 as a significant site condition that DOE/Hanford needs to address in order to characterize the Hanford site (NRC, 1984). This site technical position presents the major concerns of the NRC staff regarding the adequacy of DOE experimental results that make use of hydrazine to simulate expected redox conditions and reactions.

BACKGROUND

DOE/Hanford expects that post-closure redox conditions will reduce redox-sensitive radionuclides to their least mobile valence state. To support this expectation, a calculated groundwater Eh between -0.3 and -0.48 volts is frequently cited (Salter, 1981a and DOE 1982 and 1984a). Assuming that these expected repository conditions will be chemically reducing, DOE/Hanford adds 0.05 to 0.1 M hydrazine (as hydrazine hydrate, $N_2H_4 \cdot H_2O$) to synthetic groundwater solutions used in experiments, in order to simulate the expected site redox conditions and reactions (Barney 1982a, 1982b, and 1983; Salter 1981b, Salter 1981c, SCR 1982). They have identified these tests as "reducing condition" tests with basalt (Salter, 1981c), secondary minerals (Salter, 1981b), and interbed materials (Barney, 1982a and Barney, 1982b). Some of the advantages and disadvantages of using hydrazine are discussed by Barney (1983). According to DOE (1984), the validity of these experiments is being currently evaluated.

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Further, according to Kelmers et al. (1984), the chemistry of the basalt/groundwater system seems to be primarily dominated by the rock components of the system. Thus, reactions leading to radionuclide removal from solution by sorption or precipitation could involve heterogeneous reactions between basalt solid phases and radionuclide species in solution. Some of these reactions are likely to be slow. The addition of hydrazine, or any exogenous reducing chemical, may result in homogeneous solution reactions. These reactions have not been shown to model heterogeneous, in situ radionuclide reactions; and it seems unlikely that such test systems could be shown to be an accurate measure of the expected behavior of radionuclides. For example, the rate of reaction between hydrazine and technetium(VII) has only been studied at a pH of 11 and the reaction was reported to proceed more slowly or not at all at a higher or lower pH (Galateanu, 1977). The reaction products were not identified, but were assumed to be Tc(IV) compounds. To date, DOE/Hanford reports do not identify the products formed from the reaction of hydrazine with technetium (or any other radionuclide). Further, there is considerable uncertainty as to the reduced form of technetium produced by hydrazine. It has been reported that metallo-organic compounds containing a Tc-N bond are formed (the formal valence of the technetium was not established) (Baldas, 1982). The possible formation of at least transiently stable Tc(V) complexes cannot be ruled out (Davidson, 1982). Recent work has shown that a number of what were believed to be Tc(VI) organic compounds are actually Tc(III) compounds, and that Tc(III) is generally more stable in aqueous solutions than had been generally believed (Jones, 1982). Two different DOE/Hanford reports have suggested that the solid formed by the reaction of hydrazine with the pertechnetate anion are $TcO_2 \cdot 2H_2O$ (Barney, 1981) or $TcO_2 \cdot xH_2O$ (Barney, 1982b). According to Kelmers et al. (1984), a black solid is formed, presumably a hydrated Tc(IV) oxide, when hydrazine is added to pertechnetate solutions. The technetium solution species in equilibrium with

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this solid are undefined.

[REDACTED]

Finally, hydrazine is a very aggressive chemical and reacts with plastics. According to Kelmers et al. (1984), the rapid reaction of hydrazine visibly attacks polycarbonate test tubes, either causing them to crack with resulting loss of solution or causing etching of the tube and a brown discoloration of the groundwater solution. Further, Kelmers et al. (1984), reported a slight reaction with polypropylene. To date, all of the radionuclide sorption work performed by DOE/Hanford under hydrazine-induced reducing conditions have been conducted in polycarbonate tubes. While the details of the hydrazine-polycarbonate reaction are not known, it clearly represents a loss of hydrazine from solution. In addition, the formation of brown-colored groundwater solutions strongly suggests the presence of organic degradation products in the radionuclide sorption tests.

[REDACTED]

TECHNICAL POSITION

[REDACTED] the uncertainties associated with the data presented in the [REDACTED] and [REDACTED] that can be used to characterize radionuclide [REDACTED].

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This position is the result of NRC sponsored laboratory work which high-lighted a number of fundamental concerns about the use of hydrazine in experiments to poise the experimental system at some predetermined Eh or redox condition (Kelmers et al., 1984). These general concerns are:

1. Hydrazine can exhibit both reduction reactions and oxidation reactions which have widely different standard potentials. [REDACTED]
2. Hydrazine hydrate dissociates to release hydroxide ions. [REDACTED]
3. Hydrazine can react with the bicarbonate anion to form the carbamate anion. [REDACTED]
4. [REDACTED] disagrees [REDACTED] ons.
5. The chemistry of basalt rock/groundwater systems seems to be primarily dominated by the rock components. Therefore, reactions leading to radionuclide removal from solution by sorption or precipitation must involve heterogenous reactions between basalt solid surfaces and radionuclide species in solution. [REDACTED] any [REDACTED] conditions.

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6. Hydrazine is a very aggressive chemical and reacts with plastics in the experimental apparatus. Thus complicating the interpretation of experimental data to point that results may no longer represent site conditions or reactions.

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