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MEMORANDUM FOR: Hubert J. Miller, Chief, WMRP
 Joseph O. Bunting, Chief, WMPC
 John T. Greeves, Chief, WMEG

FROM: Malcolm R. Knapp, Chief, WMGT

SUBJECT: REVIEW OF DRAFT SITE TECHNICAL POSITION (STP) ON USING HYDRAZINE TO
 EXPERIMENTALLY SIMULATE EXPECTED HANFORD SITE REDOX REACTIONS AND
 CONDITIONS (O.P. RP 39/534231-3)

Attached is a draft site technical position concerning the use of hydrazine to experimentally simulate expected Hanford site redox reactions and conditions. This satisfies detailed Operating Plan Milestone RP 39/534231-3 (Geochemical Conditions/Hydrazine/Internal Draft).

The lead for this draft STP is David Brooks (Geochemistry Section). The draft has been reviewed by the Geology/Geophysics Section and the Hydrology Section. Please arrange to have this draft reviewed by someone in your Branch, and let me know who the reviewer(s) will be. Comments should be received by July 15, 1985. Once comments have been resolved, a final draft will be prepared. It is expected that the final draft will be ready by the end of August.

If you have any problems in meeting this schedule or any other questions, please refer them to David Brooks (74603) of the WMGT-Geochemistry Section.

Malcolm R. Knapp, Chief
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UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D. C. 20555

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JUN 23 1985

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HJM
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MR Knapp

Malcolm R. Knapp, Chief
WMGT

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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

D.J. Brooks, J.W. Bradbury, W.L. Dam,
K.C. Jackson, W.R. Kelly, L.A. Kovach,
NRC/NMSS/WMG/Geochemistry Section

INTRODUCTION

The Department of Energy (DOE) is required by the Nuclear Waste Policy Act of 1982 (NHPA) 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 (NHPA) 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.

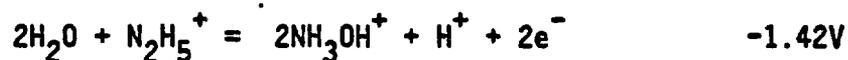
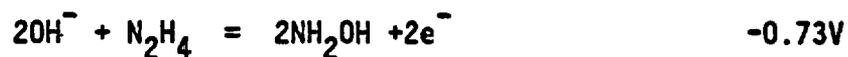
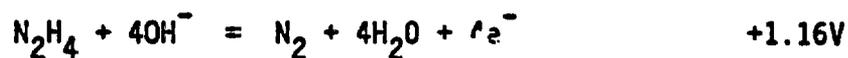
BACKGROUND

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.

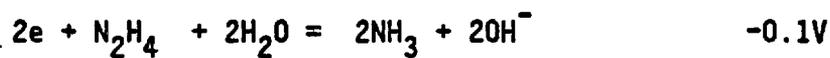
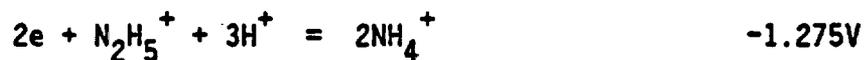
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Four completely different reactions with widely varying standard potentials are commonly cited for hydrazine reduction reactions (Kirk-Othmer, 1980). These are:



Hydrazine can also act as an oxidant in the same Eh potential range (Kirk-Othmer, 1980). For example:



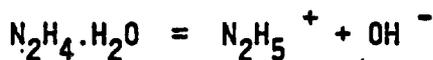
DOE/Hanford reports that the addition of hydrazine to experimental groundwater solutions results in experimental groundwater redox conditions of about -0.8 volts (Barney, 1982 (a), and 1983). However, as noted previously, expected site redox conditions are assumed to be -0.3 volts (Salter, 1981 a, DOE 1982 and 1984). In addition, according to Barney (1982, Figure-6) under site pH conditions, an Eh of -0.8 volts would result in the dissociation of water in the experiment as well as in the natural setting, indicating that an Eh other

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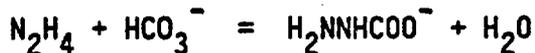
than -0.8 volts is actually achieved during the experiments. Thus, it would appear that site conditions are not simulated, and the experimental redox conditions in the experiments are unknown. Therefore, without knowledge of the specific reactions(s) occurring between hydrazine and the groundwater, it is impossible to ascertain that the reactions/results obtained are equivalent to reactions/results that can be expected in site groundwater without hydrazine.

Further, the dissociation of hydrazine is most likely the dominant influence on the experimental groundwater pH. For example, hydrazine in aqueous solution is present as the hydrate, which dissociates to generate hydroxide ions:



The dissociation constant is 1.7×10^{-6} (Audrieth, 1951). Since the hydrazine is added to the experiments at 0.05 to 0.1 M concentration, while the carbonate/bicarbonate concentration in the synthetic groundwater used is only about 0.001 M, it is probable that all of the synthetic groundwater samples containing hydrazine are buffered by the hydrazine rather than by the synthetic groundwater carbonate/bicarbonate solution components or by the basalt rock phases. Also, according to Kelmers et al. (1984), the addition of hydrazine is observed to raise the groundwater pH by about one-half to one unit. Thus, the pH conditions in the experiments are no longer representative of in situ pH conditions.

In addition, hydrazine can react with the bicarbonate anion to form the carbamate anion (Staal 1951):

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Little information is available in the literature concerning hydrazine carbamate chemistry. However, this reaction could deplete the groundwater bicarbonate concentration due to the large excess of hydrazine relative to bicarbonate in the synthetic groundwaters used in the experiments, and introduce a complexant (carbamate) not found in site groundwater. In any case, the solution would appear to be no longer representative of the in situ groundwater.

Also, hydrazine has been reported to interact with clay minerals in a number of ways. For example:

- (1) hydrazine may be preferentially adsorbed onto surface exchange sites and therefore compete with anticipated ion exchange sorption processes (Hayes, 1982). This potential problem has been recognized by DOE/Hanford (Ames, 1982). In addition, irreversible chemisorption of hydrazine also has been reported (Hayes, 1982).
- (2) Hydrazine apparently disrupts the silicate layering of clays and leads to mineral disaggregation (Bleakley, 1968, Huff, 1971 and El-Messide, 1977).

Such reactions between hydrazine in the synthetic groundwaters and basalt and/or secondary minerals could lead to significant alteration of the solids in the reducing condition tests, as well as alter the apparent radionuclide sorption behavior through sorption competition. The possibility of significant chemical reactions between hydrazine and the basalt or secondary minerals that would lead to alteration of the basalt phases/secondary minerals and/or surfaces, raises concerns about the use of hydrazine to simulate reducing conditions.

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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. Thus, the cumulative effect of uncertainties such as these result in concern that the application of results from these experiments may not adequately reflect site conditions or reactions.

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. This practical experimental problem would seem to render suspect all of the work for all radionuclides under hydrazine-induced reducing conditions. In fact, DOE suggests that results from these experiments are suspect (Barney (1982b)).

TECHNICAL POSITION

It is the position of the NRC that unless DOE can overcome the uncertainties associated with the use of hydrazine (such as those represented in the foregoing), the use of hydrazine to simulate Hanford site redox conditions and reactions will not provide defensible data that can be used to characterize radionuclide behavior.

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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. Thus experimental redox conditions may not reflect site redox conditions.
2. Hydrazine hydrate dissociates to release hydroxide ions. Thus experimental pH conditions may not reflect site pH conditions.
3. Hydrazine can react with the bicarbonate anion to form the carbamate anion. Thus the experimental groundwater may no longer be representative of site groundwater conditions.
4. Hydrazine is reported to disrupt the mineral structure of clays, and disaggregate rock. Thus the rock/mineral components of the experiments may no longer represent those found under site conditions.
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. Thus, the addition of hydrazine (or any exogenous reducing chemical) seems likely to result in homogeneous solution reactions involving radionuclides not expected under site 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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