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Mr. O. L. Olson, Director
 Basalt Waste Isolation Division
 U.S. Department of Energy
 Richland Operations Office
 P.O. Box 550
 Richland, WA 99342

Dear Mr. Olson:

During a recent NRC/DOE management meeting, the use of hydrazine to simulate redox conditions at the Hanford Site was brought up by the NRC as an example of a long-standing open item that needs to be pursued and resolved. Subsequent to the meeting DOE (R. Stein) requested that Dr. Panno of Roy F. Weston Inc. contact the NRC staff to further discuss the hydrazine concern.

A telephone conversation took place on August 22, 1986 between Dr. Panno and Mr. David Brooks of the Waste Management geochemistry staff. As a result of the conversation, it was agreed that the NRC would send Dr. Panno additional information relating to the hydrazine concern with a commitment to follow-up with further discussions on the subject. The transmittal letter sent with the additional information briefly describes the NRC staff concerns with the use of hydrazine, which have been previously brought to the attention of your staff. I have attached a copy of the letter and the draft site technical position related to the use of hydrazine for your information. Should you have any questions, please contact Paul Hildenbrand of my staff at FTS 427-4672 or David Brooks at FTS 427-4543.

Sincerely,

Original Signed By:

John J. Linehan, Acting Chief
 Repository Projects Branch
 Division of Waste Management

Enclosures:
 As stated

cc: R. Stein, DOE-HQ

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Dr. S. Panno
Roy F. Weston, Inc.
955 L'enfant Plaza, SW
8th Floor
Washington, DC 20024-2119

Dear Dr. Panno:

SUBJECT: USE OF HYDRAZINE TO SIMULATE HANFORD SITE REDOX CONDITIONS
AND REACTIONS

In response to our telephone conversation on Friday, August 22, 1986, I have attached a copy of our draft site technical position (DSTP) on the use of hydrazine by the Department of Energy/Rockwell Hanford Operations (DOE/RHO) to simulate expected conditions in a high-level waste repository in basalt, and a copy of NUPEG/CR-3851, Volume 1, entitled, "Progress in Evaluation of Radionuclide Geochemical Information" The technical basis for the STP is contained in the NUREG/CR (pp 18-22).

Recently, the DSTP was reevaluated in light of a recent publication on radionuclide sorption in bentonite packing material (Barney et al. 1985). In that report, hydrazine was added to accelerate radionuclide reduction and sorption reactions in some of the radionuclide - traced groundwater/packing material mixtures used in the sorption tests. Also, in this report, Barney et al. address the concerns that we raised in the DSTP.

In general, we still have serious reservations concerning the use of hydrazine. The DSTP raised six concerns. The details of our reevaluation follow:

DSTP Concern 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."

This is still an important concern for the NRC evaluation of geochemical work employing the addition of hydrazine to adjust test redox conditions. Considerable research has been conducted over the years to understand the oxidation and reduction reactions of hydrazine in aqueous solutions and pertinent review references are included in the draft STP. Unless the reaction products are identified, no formal Eh value or redox condition can be assigned to the hydrazine-containing systems. In fact, it is not even certain if the systems are more reducing or oxidizing after the addition of hydrazine. Hydrazine usually acts as a reductant (although the kinetics may be slow for some metal ions), but it can also act as an oxidant in some cases. Thus, while hydrazine could offer a means of accelerating repository-relevant reactions in laboratory experiments, the reaction products must be shown to be equivalent to those expected in the repository.

This concern is highly relevant to an evaluation of the work of Barney et al. (1985) because little work was done on the chemistry of the hydrazine-containing radionuclide-traced groundwater/basalt-bentonite mixtures. The only data collected was the measurement of the radionuclide sorption or desorption ratio after the batch contact. The reduced species of radionuclides believed to result from the addition of hydrazine were based on a few Russian references (Barney et al. (1985), Table 5). Even if those species are correct, which is uncertain (see discussion below), no evidence was presented to show that these species would be formed by the in situ reactions with basalt. This one concern, alone, seems sufficient

to question the application of the data to, and validity of the conclusions for, repository assessment purposes.

DSTP Concern 2. "Hydrazine hydrate dissociates to release hydroxide ions. Thus experimental conditions may not reflect site pH conditions."

This concern remains valid. However, it may be of secondary importance for NRC evaluation of geochemical work involving the addition of hydrazine as a solution of hydrazine hydrate to groundwaters. Hydrazine hydrate is a strong base. Some groundwaters are poorly buffered, and their pH may be easily changed by the addition of even small amounts of hydrazine hydrate. While hydrazine hydrate can be neutralized with acid, as was done by Barney et al. (1985), appreciable amounts of an anion will have been added to the groundwater. Thus, the use of hydrazine may be a "Catch 22" situation. For example, the groundwater pH may become significantly more basic if the hydrazine hydrate is not neutralized, but large amounts of additional anions are added to the groundwater if the hydrazine hydrate is neutralized. Either way, the hydrazine-treated groundwater may no longer be representative of repository conditions.

Barney et al. (1985) (Table 6) recognized this concern and used HCl to adjust the pH of the hydrazine-containing synthetic groundwater. However, as shown in their Table 6, the addition of 0.05 M hydrazine resulted in a large increase in the Cl^- concentration of the groundwater. Changes in Cl^- may not affect the sorption of some radionuclides, as suggested by Barney et al. (1985), with the exception of those which can form stable chloride complexes. Conversely, the increased ionic strength due to the added hydrazine chloride could affect the speciation of some elements.

DSTP Concern 3. "Hydrazine can react with bicarbonate anion to form carbamate anion. Thus the experimental groundwater may no longer be representative of site groundwater conditions."

This may be the weakest concern in the DSTP due to the sparsity of data. Barney et al. (1985) suggested that the formation of hydrazine carbamate is unlikely, but conducted no experiments to explore this reaction. We concur that little strong evidence exists to support the supposition that hydrazine carbamate would form in dilute solutions. This concern may be of minimal relevance to the radionuclide sorption/desorption tests and thus may be dropped from the final STP.

DSTP Concern 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."

This concern remains valid for the NRC evaluation of any radionuclide sorption or solubility work, or work conducted to poison rock/groundwater systems at some reducing redox condition, which employs the addition of hydrazine to site rocks or minerals. Hydrazine is a very aggressive chemical and good supporting references for this concern are cited in the DSTP.

This is an important concern relative to the work described in Barney et al. (1985). Their data for groundwater composition after contact with packing material at 90 C (Table 6) show a considerable difference in the concentration of many solution components between tests with or without added hydrazine. For example, sodium, potassium, calcium, and strontium

were increased by factors of about 1.5 to 3 by the addition of 0.05 M hydrazine. Barney et al. (1985) recognized this result, and suggested that cation exchange of $N_2H_5^+$ with packing components was responsible. It seems likely that ion exchange reactions of radionuclides with the $N_2H_5^+$ form of minerals could be different from the reactions with the native form (Ca^{2+} , Na^+ , H^+ , etc.), and sorption behavior could be quite different due to the addition of hydrazine. Extensive physicochemical analysis of the basalt and bentonite after hydrothermal alteration was conducted to characterize the altered mineral reaction products, however, this characterization work was limited to hydrazine-free conditions. It is unfortunate that parallel work was not done in the presence of hydrazine. An alternate explanation of the data in Table 6 is that hydrazine may be reacting with significant proportions of the basalt-bentonite mixture, and not only changing the groundwater composition but also the final nature of the minerals. The changes in groundwater composition are large enough to suggest that substantial reactions of some sort may be occurring between hydrazine and the packing materials. It seems possible that the radionuclide sorption results may reflect the unanticipated result of alteration of the nature of solids or solution component concentrations by hydrazine to conditions which are not representative of the repository.

DSTP Concern 5. "The chemistry of basalt rock/groundwater systems seems to be primarily dominated by rock components. Therefore, reactions leading to radionuclide removal from solution by sorption or precipitation must involve heterogeneous 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."

This concern remains valid for the NRC evaluation of any radionuclide sorption or solubility information obtained in the presence of hydrazine. The addition of hydrazine, or use of any other chemical or electrochemical means to attempt to poise the test system redox condition or accelerate radionuclide reduction reactions, can only be accepted as relevant for performance assessment purposes if the reactions produced by the exogenous means can be shown to be equivalent to those expected to occur in the repository.

This concern is not specifically addressed in Barney et al. (1985). In fact, they implicitly assume that radionuclide reduction reactions with basalt solid surfaces (possibly with Fe^{2+} sites) and with hydrazine in solution (present as N_2H_5^+ ions) are equivalent. Otherwise, the methodology selected would be invalid. According to work done at the Oak Ridge National Laboratory, 0.1 M hydrazine does not reduce neptunium (V) in groundwater in times of up to one week. However, they have observed rapid sorption (and presumed reduction) of neptunium when hydrazine is added to basalt/neptunium (V) - traced groundwater mixtures. Barney et al. (1985), in Table 13, report similar enhanced neptunium sorption in the presence of hydrazine. Clearly, understanding of the sorption reactions is necessary before the relevance of the hydrazine reaction results of Barney et al. (1985) can be related to repository performance of the packing.

DSTP Concern 6. "Hydrazine is a very aggressive chemical and reacts with plastics in the experimental apparatus. Thus complicating the interpretation of experimental data

to the point that results may no longer represent site conditions or reactions."

This concern is based on observations (contained in NUREG/CR-3851) of chemical reactions of hydrazine-containing groundwater with polypropylene or polycarbonate vials. Similar observations were reported by DOE/RHO back in 1982. Such vials, or tubing or other apparatus made of these materials, are commonly used in laboratory work. This is a valid concern which must be considered when the NRC evaluates any experimental data based on tests conducted in the presence of hydrazine.

The work described in Barney et al. (1985) was conducted using Teflon vials. Teflon is generally chemically unreactive, so it seems probable that reaction between hydrazine and the sample container was not a problem in their work. However, final characterization of both the liquid and solids are needed in order to determine that no reactions with sample containers are taking place.

In summary, DSTP concerns 1 and 5 remain major concerns relative to the use of hydrazine in laboratory experiments to simulate expected Hanford Site repository redox conditions or reactions. These two concerns will be emphasized in the final STP. These concerns clearly establish that understanding of both the expected repository conditions and reactions, and of the laboratory simulation of these conditions and reactions, is essential to demonstrating the relevance of the laboratory data for performance assessment purposes. Such understanding is necessary, to a degree, for any type of laboratory simulation, but is especially important when exogenous means, such as the addition of hydrazine, are employed in the tests. Concern 1 questions the redox reactions which may result from

the addition of hydrazine. Hydrazine can undergo a variety of reduction or oxidation reactions having widely different standard potentials. Clearly, the experimenter does not know what changes have been produced in the test system by the addition of hydrazine unless the reactions are understood. Concern 5 is broader in nature and explores the possible differences in the heterogeneous reactions of radionuclide species in solution with the basalt solid surfaces (repository situation) as compared to homogeneous solution reactions (hydrazine test situation). Not only the kinetics but also the reaction products may be different in these two situations. Again, the respective reactions must be understood before the test information may be acceptable for repository performance assessment purposes. In addition, DSTP concerns 2, 4, and 6 remain important concerns that question aspects of the experimental technique. They will also remain in the final STP. It is possible for experimenters to deal with the technical aspects of these concerns and show that they do not materially degrade the test information. The pH can be measured and adjusted (concern 2), the rock surface and mineral assemblage can be characterized after exposure to hydrazine (concern 4), and chemically inert apparatus can be employed (concern 6). Finally, draft STP concern 3 is based on minimal technical data and it is likely that it will be dropped from the final STP. Barney et al. (1985) may be correct when they suggest that the reaction of hydrazine hydrate with bicarbonate to form hydrazine carbamate will not proceed in dilute solutions.

I hope you find that this information provides useful insight into our concerns about using hydrazine to simulate site redox conditions and reactions. If you have any questions, please call me (427-4543). I will

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call you during the week of September 15 to talk to you further concerning this matter.

Original Signed By

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

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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

U. S. Nuclear Regulatory Commission
Division of Waste Management (WMGT)
Geochemistry Section

INTRODUCTION

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

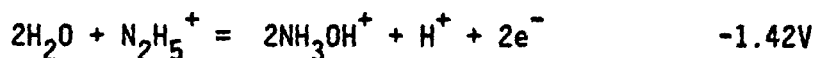
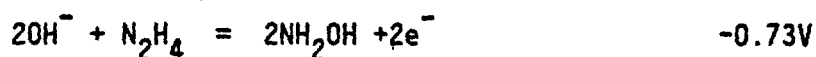
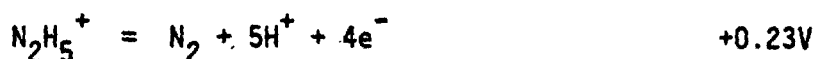
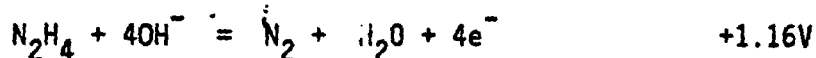
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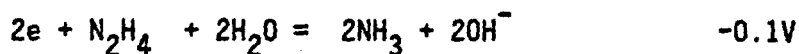
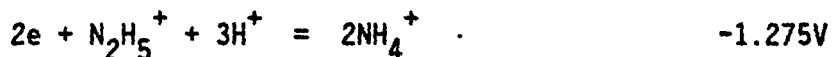
DISCUSSION

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

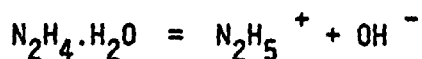
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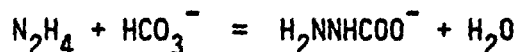
than -0.8 volts is actually achieved during the experiments. Thus, it would appear that site conditions are not simulated, and the experimental redox conditions in the experiments are unknown. Therefore, without knowledge of the specific reactions(s) occurring between hydrazine and the groundwater, it 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 $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ (Barney, 1981) or $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ (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 heterogeneous 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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