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Dr. S. Panno
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955 L'enfont Plaza, SW
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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 NUREG/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

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> 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

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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 poise 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

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> 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

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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
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