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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

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INTRODUCTION

The DOE/Hanford Staff performs laboratory and field investigations to acquire data needed to address repository performance based on site geochemical conditions. The Nuclear Waste Policy Act (NWPA) 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. This determination depends, in part, on whether the geochemical data being collected is adequate to characterize repository performance.

Technical criteria of 10CFR60.113, includes a limit on the amount of radionuclides permitted to be released from the engineered barrier system and to the accessible environment. In order to demonstrate compliance with this

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limit, DOE/Hanford must identify the particular barriers that will be relied upon to retard radionuclide migration. Based on discussions presented by DOE in the Hanford Draft Site Characterization Report (DSCR), the Draft Environmental Assessment (DEA), and at site workshops, DOE/Hanford is taking the position that under the anticipated site Eh of -0.3 volts (or lower), the reference repository location has chemically reducing conditions that will maintain redox-sensitive radionuclides such as uranium, plutonium and neptunium, in their least mobile state, thus contributing to the control of the release of radionuclides from the repository (DOE, 1982 and 1984). 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 anticipates that the redox condition in the undisturbed host rock and in the repository will chemically reduce redox-sensitive radionuclides to their least mobile state. To support this expectation, a calculated or proposed groundwater Eh as low as -0.48 volts is frequently cited (Salter,

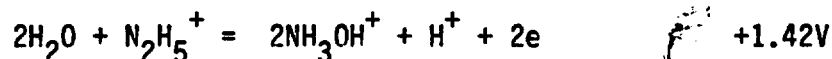
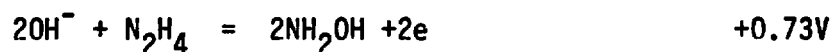
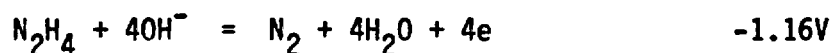
1981a). Assuming that these expected conditions are chemically reducing, DOE/Hanford adds 0.05 to 0.1 M hydrazine (as hydrazine hydrate, $N_2H_4 \cdot H_2O$) to synthetic groundwater solutions used in experiments, in order to simulate the expected site redox conditions and reactions. The justification for the use of hydrazine has never been well developed in DOE/Hanford reports which describe its application to sorption tests (Barney 1982a, Barney 1982b, Salter 1981b, Salter 1981c, SCR 1982). In order to confirm the validity of these experiments, DOE/Hanford is currently evaluating experimental results that use hydrazine to control radionuclide behavior (DOE, 1984).

TECHNICAL POSITION

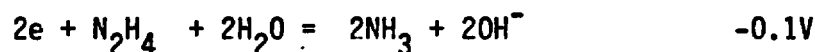
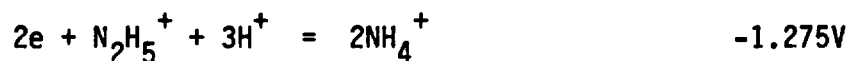
The effective solution redox conditions generated by hydrazine are strongly dependent upon the specific reduction reaction(s) involved. DOE/Hanford has not identified the reaction(s) occurring between hydrazine and any reducible radionuclide species in groundwater; thus, the effective Eh or redox conditions/reactions in these experiments must be considered to be unknown. Therefore, the NRC position is that the use of hydrazine to simulate Hanford site redox conditions and reactions will not provide defensible data that can be used to characterize expected radionuclide behavior.

DISCUSSION

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

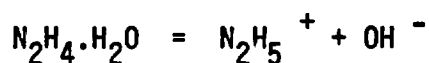


Hydrazine can also act as an oxidant in the same Eh potential range. For example:



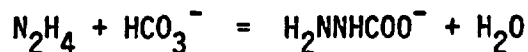
Thus, without knowledge of the specific reaction(s) occurring between hydrazine and the solute of interest, it is not possible to estimate what Eh value or redox condition is effective in experimental solutions.

Further, the dissociation of hydrazine hydrate 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 DOE/Hanford 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 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 synthetic groundwater/hydrazine mixture is no longer representative of in situ pH conditions.

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



This reaction could deplete the bicarbonate concentration due to the large excess of hydrazine relative to bicarbonate in the synthetic groundwaters used in the experiments. This could also affect the solution pH, in addition to hydrazine hydrate dissociation. In any case, the solution would no longer be representative of in situ groundwater conditions. Also, the carbamate anion could form complexes with transition elements or actinides similar to the well-known amine complexes (need ref.). Little information is available in the literature concerning hydrazine carbamate chemistry.

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 and leads to mineral disaggregation (Bleakley, 1968, and El-Messide, 1977). Further, the use of hydrazine hydrate solutions for chemical disaggregation of rock has been patented (Huff, 1971).

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 and/or surfaces, raises significant concerns about the use of hydrazine.

The chemistry of the basalt/groundwater system seems to be primarily dominated by the rock components. Thus, reactions leading to radionuclide removal from solution by sorption or precipitation must involve heterogeneous reactions between basalt solid phases and radionuclide species in solution. Some of these reactions are likely to be kinetically slow. The addition of hydrazine, or any exogenous reducing chemical, seems likely to result in rapid 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 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 this solid is undefined.

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 these experiments do need to be repeated Barney (1982b).

SUMMARY

In order to simulate expected redox conditions and reactions, DOE/Hanford has conducted much of their reported radionuclide sorption experimental work by adding 0.05 to 0.1 M hydrazine hydrate to the synthetic groundwater used in their experiments. 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). As a result of laboratory work, the NRC has 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 major concerns are:

1. Hydrazine can exhibit four different reduction reactions and two oxidation reactions which have widely different standard potentials.
2. Hydrazine hydrate dissociates to release hydroxide ions.
3. Hydrazine can react with the bicarbonate anion to form the carbamate anion.
4. Hydrazine has been reported to react with clay minerals and disaggregate the mineral structure.
5. The chemistry of basalt rock/groundwater systems seems to be primarily dominated by the rock components. Thus, reactions leading to radionuclide removal from solution by sorption or precipitation must involve heterogeneous reactions between basalt solid surfaces and radionuclide species in solution. The addition of hydrazine, or any exogenous reducing chemical, seems likely to result in rapid homogeneous solution reactions involving radionuclides.
6. Hydrazine is a very aggressive chemical and reacts with plastics in the experimental apparatus.

Therefore, it is the position of the NRC that 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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