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September 16, 1986

Dr. David J. Brooks
Geochemistry Section
Geotechnical Branch
Division of Waste Management
Office of Nuclear Material Safety and Safeguards
United States Nuclear Regulatory Commission
Washington, D.C. 20555

Dear Dr. Brooks:

Thank you for your very informative discussion of the issue concerning the use of hydrazine at the Hanford Site (August 22, 1986), and for the related materials that I received subsequent to our conversation (received September 15, 1986). As promised, I have enclosed a copy of my memo to Dr. Allen Jelacic on this subject.

Your suggestion of a DOE-NRC workshop on sorption, for the purpose of resolving the hydrazine and other related issues, was well taken by DOE-HQ and BWIP-RHO. The organization and implementation of the workshop will be coordinated by Dr. Cyrus Klingsburg of DOE-HQ. The date and location of this workshop have not been set at this time. I or Dr. Klingsburg will contact you concerning the planning of this meeting.

It should be noted that per a conversation with Dr. Scott Barney of BWIP-RHO, sorption experiments that incorporate hydrazine as a reducing agent are still being conducted at the Hanford site.

If you have any further questions concerning this or any other issue, please feel free to call me at (301) 646-6648.

Sincerely,

ROY F. WESTON, INC.

Samuel V. Panno

Samuel V. Panno

Enclosures

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WESTON
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inter-office memorandum

TO: R. E. Jackson

DATE: September 5, 1986

FROM: S. V. Panno SVP

SUBJECT: NRC's Renewed Interest in the use of Hydrazine at the Hanford Site (TDD # 3002-24-28-3050)

W. O. No.:

Introduction

Per a request by Dr. Allan Jelacic, I have investigated the NRC's renewed concern over the use of hydrazine in laboratory sorption experiments. A discussion of these concerns was conducted with Dr. David Brooks of the NRC on August 22, 1986. A brief description of the hydrazine issue and the results of my conversation with Dr. Brooks are presented below. Attached is a bulletized summary of the hydrazine issue.

Background

The chemical reducing agent hydrazine (N_2H_4) has been used for a number of years by investigators at the Hanford Site in order to create reducing conditions in laboratory sorption experiments comparable to those expected at the repository horizon (i.e.,-0.4V). The Basalt Waste Isolation Project (BWIP) first described the use of hydrazine in a report published in 1981. The report elicited concerns by the Nuclear Regulatory Commission (NRC) who subsequently solicited the aid of Dr. Donald Kelmers at Oak Ridge National Laboratory (ORNL) to conduct sorption experiments parallel to those of BWIP in order to evaluate the validity of using hydrazine. Results of these experiments by ORNL were presented in 1982, 1983, and 1984 as NUREG reports and at several DOE/NRC Geochemistry meetings and workshops. The concerns of NRC, which appeared in a number of these reports, are as follows:

1) The presence of hydrazine in a sorption experiment creates an unrealistic chemical environment that may not reflect the natural system. When hydrazine is added to the experimental system it is not clear what reactions are controlling the redox conditions. In some cases hydrazine acts as a strong reductant and in other cases it acts as an oxidant.

2) Hydrazine is a strong base and the resulting solution must be buffered (with HCl) in order to return to the proper pH conditions. The effects of the buffer on the sorption chemistry are unclear.

3) Hydrazine could react with bicarbonate in the water to form hydrazine carbonate. This in turn would remove a potential complexing agent, thereby keeping some portion of radionuclides in solution and resulting in unrealistically high sorption coefficients. (NRC is considering dropping this concern).

4) The reaction of hydrazine with the host rock and associated secondary minerals is unclear. That is, it is not known with certainty whether hydrazine "conditions" the water or the rock/mineral surfaces.

5) Polycarbonate reaction vessels used in the sorption experiments were attacked by the hydrazine and, in some cases, resulted in the destruction of the vessels. Postcharacterization of the reaction vessels must also be conducted in order to show that part of the equipment didn't participate in the sorption reactions.

6) Hydrazine may be too strong a reducing agent and could result in the formation of species of radionuclides that have a lower oxidation state than would be found under field conditions. The use of hydrazine to overcome kinetics problems may accelerate reactions that would never come to fruition under natural circumstances.

NRC feels that any or all of these potential problems could result in experimental data that would have so much associated uncertainty that the data might not be useable in a licensing process. Prior to the end of 1985, and because of the concerns expressed by NRC, BWIP appeared to have decided not to use hydrazine in sorption experiments because of potential licensing problems; NRC felt the issue had been laid to rest.

The Issue Reappears

An indication of the continued use of hydrazine at BWIP reappeared in a Rockwell report on sorption and desorption by Barney et al. (1985). Within this report is a point by point rebuttal of the NRC's (Kelmers et al., 1984) concerns on the use of hydrazine in the determination of sorption and desorption isotherms. NRC feels that BWIP is making a mistake by reconsidering the utility of hydrazine as a viable means of reproducing in-situ reducing conditions. It is felt that sorption data involving hydrazine will be of questionable validity if its use continues in BWIP's geochemical program. The potential for spending a significant amount of time and money in an attempt to prove that hydrazine-spiked experiments are valid while never satisfying the critics is extremely high. These concerns, as well as NRC's position on the use of hydrazine, will be presented in a forthcoming Site Technical Position on this subject.

BWIP's present position is to show that the data collected from experiments that involved the use of hydrazine are valid and may be used in licensing. BWIP maintains that hydrazine is a useful reducing agent that makes exceedingly difficult experiments possible. The shortcomings of the use of hydrazine have been pointed out many times and BWIP is aware of the strong criticism. However, experimental results suggest that hydrazine does not significantly interfere with the sorption behavior of redox-sensitive radionuclides. Further, limitations in available experimental procedures preclude the removal of oxygen in laboratory experiments comparable to levels found in the Grande Ronde Formation. For example, without the use of hydrazine (at 60 C, pH 8.0), the sorption behavior of Tc, Np, and Pu is the same as it would be in air-saturated ground water. Reduction of Np does occur at higher temperatures, but the rate of reduction is exceedingly slow. BWIP feels that hydrazine merely speeds up the inevitable process of reduction.

Current plans include further development of experimental techniques that would reduce the amount of oxygen in sorption experiments (without hydrazine) and, thereby, provide more reducing conditions that would be closer to those in the natural system. Data from these and other experiments will be compared to previous, sorption experiments in order to test the validity of using hydrazine.

Summary and Recommendations

The hydrazine issue is relatively important in that it bears heavily on the accurate specification of the retardation capabilities of the basalt and secondary minerals at Hanford Site. The characterization of the ability of basalt and associated secondary minerals to retard key radionuclides is an integral part of the performance of the site. BWIP believes that they can successfully show that hydrazine provides a true representation of deep in-situ conditions, while NRC feels that the uncertainties of the effects of hydrazine are high and that further use of hydrazine and/or a program carried out for the sole purpose of proving the reliability of hydrazine-spiked experiments could prove to be a drain on time and monetary resources resulting in inconclusive results.

Because of the potential for problems in the area of sorption of radionuclides, NRC suggested the possibility of a small workshop between the principals involved in order to resolve the hydrazine issue. It is recommended that DOE review NRC's Site Technical Position on hydrazine and plan an NRC-DOE meeting on the topic of sorption, as suggested by NRC. Some of the questions raised by NRC may have significant implications in the area of the retardation of radionuclides and licensing. It is further recommended that work at the Hanford Site on sorption continue since new techniques are being developed in order to conduct sorption experiments without hydrazine. Laboratory work should eventually be validated by in-situ tracer tests involving a redox-sensitive radionuclide (e.g., technetium) in order to validate in-situ redox conditions.

References

Barney, G.S., D.L. Lane, C.C. Allen, and T.E. Jones (1985). "Sorption and Desorption Reactions of Radionuclides with Crushed Basalt-Bentonite packing Material": Rockwell International Report, RH-BW-SA-416P.

Kelmers, A.D., J.H. Kessler, W.D. Arnold, R.E. Meyers, N.H. Cutshall, G.K. Jacobs and S.Y. Yee (1984). "Progress in Evaluation of Radionuclide Geochemical Information Developed by DOE High-Level Nuclear Waste Repository Site Projects-Report for October-December 1983": Oak Ridge National Laboratory, NUREG/CF-3851 V.1, ORNL/TM-9191/VI.