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Mr. Kien C. Chang  
Mail Stop 623-SS  
U.S. Nuclear Regulatory Commission  
Washington, D.C. 20555

Dear Mr. Chang:

GEOCHEMISTRY WORKSHOP TRIP REPORT

Attached is my trip report for the BWIP geochemistry workshop held in Richland, Washington January 9-12, 1984. As you suggested, I concentrated on items which have a bearing on our waste package work.

It appears that the BWIP people are moving forward with great intensity in their waste package performance assessment work, but have not openly discussed the details of their strategy. They apparently want to wait until the waste package workshop (last week in March) before discussing details of their work, even informally. Thus, we see the waste package workshop as being crucial in our understanding of the methods to be used by BWIP. I have read the January 5 list of waste package workshop items you and Everett Wick generated. I agree with all of them and suggest that we try to ensure that the following items are discussed. They arose during the geochemistry workshop.

1. Basis for De-emphasis of Leaching and Emphasis of Steady-State Concentration:

In the geochemistry workshop this was mentioned, but the rationale was not really explored. M. Wood, in his solubility presentation, presented a number of conclusions and indicated that the solubility limit/steady-state concentration approach is "testable and defensible". Thus, it is essential that the rationale be discussed in the waste package workshop.

2. Basis for D. Lane's Packing Conclusions (Presentation on Basalt/Water Interactions and Packing Stability):

The conclusions regarding retention of swelling capabilities should be discussed in relation to C. Claiborne's feeling that a 75%/25% basalt/bentonite ratio may not result in sufficient swelling.

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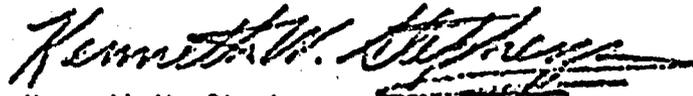
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3. Basis for Sorption/Desorption Conclusions:

In the sorption presentation by G.S. Barney and R.M. Smith, the conclusions dealt with items such as irreversibility of radionuclide sorption, and radionuclide-specific sorption rates. In addition, a list of priority radionuclides was presented. These issues should be explored in more detail.

Please call me if you have any questions.

Very truly yours,



Kenneth W. Stephens  
Manager, Technology Assessments  
Eastern Technical Division

KWS/gbf

Attachment

February 3, 1984

TRIP REPORT

K.W. STEPHENS

THE AEROSPACE CORPORATION  
(FIN A-4165-4)

BWIP/NRC WORKSHOP ON GEOCHEMISTRY  
Richland, Washington  
January 9-12, 1984

Summary

The Basalt Waste Isolation Project (BWIP) of the Department of Energy is investigating a potential high-level nuclear waste repository to be located on the Hanford site near Richland, Washington. The workshop was held to: (1) provide an overview of site characterization investigations related to geochemistry, and (2) discuss geochemistry concerns raised by NRC in the Draft Site Characterization Analysis of the BWIP Site Characterization Report (NUREG 0960).

The meeting resulted in frank and open discussion of the issues and provided valuable information to organizations such as Aerospace that are dealing with waste package issues influenced by the geochemistry. In anticipation of the BWIP Waste Package Workshop to be held the last week in March, certain waste package issues were briefly discussed.

At the end of the workshop, joint meeting notes were developed by BWIP and NRC and were subsequently distributed to the meeting attendees. Those notes summarize the issues and action items related to geochemistry. The information included below contains observations on the presentations, with emphasis on items which have an impact on our waste package work.

## General Observations

### Overview:

P.F. Salter of Rockwell Hanford (the prime BWIP contractor) presented an overview of how the geochemistry fits into the project as a whole. The BWIP project is organized such that groups deal with particular areas, such as engineered barriers and performance assessment. Concurrently, there is an integration effort to tie the pieces together.

During the presentation, it became clear that the key link between the geochemistry and the waste package performance relates to the issue of steady-state radionuclide concentration. The BWIP approach is based on the premise that there is some steady-state concentration that will be reached and that this concentration will control the quantity of radionuclides released. Accordingly, the geochemistry program is centered around being able to obtain the data necessary to model the steady-state concentration with confidence.

### Performance Assessment

P.F. Salter also presented a summary of performance assessment as it relates to geochemical modeling. In discussing the work on developing a waste package performance model, she said the model will cover, as a function of time: (1) physical-chemical (environmental) conditions, (2) the engineered barrier system and its degradation and failure modes, and (3) radionuclide release and transport through the waste package.

During the discussion of the model's general attributes, questions were asked related to the failure modes to be assumed. In response to this question and many other specifics regarding waste packages, the speaker deferred discussion until the waste package workshop. She did, however, show a slide which indicated that the approach to evaluating long-term performance of barrier materials is based on the belief that the stability of barrier materials is dominated by interaction with groundwater. In particular, the initial groundwater plus the barrier materials' initial unstable solid phases are expected to yield the final groundwater and secondary stable solid phases. Consequently, the solubility of the solid phase is believed to be directly related to its stability, i.e., the more stable the phase, the less soluble it is.

The waste package performance model is comprised of two sub-models: (1) a waste package degradation submodel to establish containment failure time, and (2) a waste package radionuclide transport/release submodel to establish radionuclide flux to the rock. The BWIP goal is to complete the waste package model by the end of FY 84.

## Basalt Characterization

P.E. Long and C.C. Allen of Rockwell Hanford discussed the mineralogy and petrology of the BWIP sites and the projects plans for characterization. The information presented appears to have little or no direct impact on our waste package work.

## Groundwater

T.E. Jones, D.L. Graham, and T.O. Early discussed groundwater sampling, chemical analyses, and interpretation of data. Of particular interest was the evidence that there are predominant water movement directions of deep groundwaters (to the southeast and vertically upward) at least in certain formations. This may affect the assumptions of the waste package performance analysis. The BWIP people are investigating the movement phenomena to determine whether the vertical direction is a result of diffusion, vertical head gradients, or some other mechanism. No information is available on the rates of upward movement.

An additional item of interest is that significant amounts of methane have been found during test drilling.

## Basalt/Water Interactions and Packing Material Stability

D. Lane of Rockwell Hanford presented material pertaining to the geochemical environment surrounding the waste package, as well as the stability of the montmorillonite in the packing material. He discussed the maximum expected conditions within the waste package (250°C to 300°C, 30 MPa), but emphasized that the actual temperature will be a function of the waste form and its age.

It is clear that BWIP is considering the changes that occur in groundwater as it interacts with waste package materials and will examine the resulting effects on barrier materials, package lifetime, and radionuclide release and sorption. BWIP is engaging in natural-analog work with basalt in geothermal fields in Iceland and believes that this work will be valuable in helping correlate models with actual observations.

In his conclusions, Lane said that preliminary autoclave flow-through tests indicate the presence of an alteration assemblage that decreases the permeability of the basalt. In addition, the steady-state in situ pH is alkaline (7.5) from 100°C to 300°C. Finally, he said that tests performed under elevated conditions (300°C) will be needed to accelerate reaction rates for predictive models.

In a discussion on the packing material, Lane said that the following functional requirements will be used to minimize corrosion of the metal barriers: (1) delay water contact with the canister, (2) minimize groundwater flux past the container, (3) buffer oxygen content near the container, and (4) localize corrosion products at the packing material/container interface. Packing material tests will be performed to determine the thermal stability of bentonite as well as the effects of hydrothermal conditions and the presence of basalt and groundwater on bentonite stability.

In the conclusions for the packing presentation, Lane said that the packing material retained its structural and swelling properties in a year-long experiment at 370°C, and that in a 300°C hydrothermal environment, steady state conditions are attained in a few months, but the mineral assemblage is metastable. Finally, he concluded that kinetics may be as important as thermodynamic stability in modeling mineralogical changes. Other tests are planned to study items such as the effects of long-term, low-temperature conditions on packing materials. (It is important that the waste package workshop include a discussion of Lane's conclusions and the bases for them.)

#### Eh - pH Analyses

J. Myers of Rockwell Hanford presented material on the expected Eh and pH conditions and the effects of Eh and pH on repository components. Eh can be used to predict the stability of solid phases and aqueous species, and can indicate the corrosion propensity. He presented results of studies relating Eh and pH to various parameters such as solubility. There was extensive discussion concerning the difficulties in measuring Eh accurately and the possible techniques for improvement. In conclusion, Myers said that speciation of radionuclides will depend not only on Eh, but also on the reactions involved with the oxidation of the radionuclides (or the lack thereof). Preliminary indications are that Eh values can be maintained low enough in basalt mixtures to control corrosion and other reaction processes.

#### Radiolysis

W.J. Gray of Battelle Pacific Northwest Laboratory presented information related to gamma radiolysis effects on basalt groundwater. After describing the experiments, he proposed a tentative description of the radiolytic reactions of water containing methane. His conclusions described the polymers (similar to polyethylene) generated in the reactions and the relative insensitivity of the results to a wide range of conditions. Future work will include waste package components (e.g., bentonite) in the tests, measure any interactions with radionuclides, and investigate the mobility of the polymers in the environment.

## Sorption.

G.S. Barney and R.M. Smith of Rockwell Hanford described the experimental studies of radionuclide sorption in packing material and basalt. One interesting slide showed the estimated environmental parameters (temperatures, pH, etc.) expected 1,000 years after emplacement.

There were some significant conclusions: (1) Desorption rates are much less than sorption rates (radionuclides are irreversibly sorbed), (2) Sorption rates for uranium, neptunium, lead, and technetium are greater under reducing conditions, and (3) Sorption rates for uranium, neptunium, and lead are similar for a given sorbent and oxidation state. Further work will examine sorption using batch measurements and flow-through tests. In addition, more work will be done on methods for controlling important parameters such as Eh.

Included in the presentation was the list of priority radionuclides BWIP is using in their repository analysis. The rationale behind the radionuclide choices and the bases for the conclusions given above should be discussed at the waste package workshop.

## Natural Analogs

J. Myers described the natural analog studies in some depth. The work will examine uranium ore bodies as an analog of uranium migration, copper deposits in basalt in northern Michigan as an analog for the stability of cupro-nickel canister material, natural alteration minerals at Hanford as an analog for the stability of near-field alteration minerals, and the Icelandic geothermal fields as an analog for hydrothermal conditions within a basalt repository. In Iceland, hydrothermal water/rock interactions have been occurring on a geologic time scale; the temperatures range up to 300°C.

## Solubility

M. Wood of Rockwell Hanford delivered a presentation on the solubility-related issues affecting repository performance. The presentation covered waste form release rates, the importance of waste form release rates vs steady-state solubility in controlling radionuclide releases from the engineered system, and a discussion of solubility issues identified in the NRC Site Characterization Analysis (SCA). Future experimental work will examine solubilities in terms of interactions among the radionuclides, the barrier materials, and the basalt.

There were several significant conclusions: (1) Leach rate data cannot be used to evaluate long term waste form performance because leaching is an initial, transitory phenomenon, (2) Solubility steady-state concentration limits, imposed by radionuclide-bearing solids, represent a testable and defensible approach to evaluating long-term waste form performance, and (3) Radionuclide release rates will be proportional to the product of steady-state concentration and groundwater flow rate except for the diffusion case, where the rates will be proportional to only the steady-state concentration. (These conclusions and their bases should be discussed at the waste package workshop.)

## Colloids

G.S. Barney of Rockwell Hanford discussed experimental studies related to the effects of colloids. He said that the total concentration of radionuclides in groundwater equals the solubility-limited concentration plus the effects of colloids minus the sorption of radionuclides. Research for BWIP will determine the radionuclide distribution among groundwater, colloids, and geologic solids, i.e., determine whether nuclides are sorbed on colloids and desorbed on packing material and rock. In addition, future work will examine transport of colloids within rock fractures and porous engineered materials.