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

Dear Mr. Chang:

REVIEW OF DRAFT BNL-NUREG-24297

As you requested, we have reviewed the February 1984 draft of BNL-NUREG-24297, "Determination of the Waste Package Environment for a Basalt Repository: Phase I - Gamma Irradiation Conditions in the Absence of Methane."

This document will be an important topic of discussion at the upcoming BWIP Waste Package Workshop, because the experimental results indicate that the BWIP contention of reducing conditions may be incorrect. Attached are the comments by Dr. Robert Moler of our staff. He examined the document along with the related material from the BWIP Site Characterization Report.

There are several important conclusions that can be drawn:

1. The BNL experiment apparently presumed that the packing/water mixture would have a substantial amount of dissolved oxygen. This seems reasonable in view of the activities necessary to emplace the packing.

2. The dissolved oxygen declined by an order of magnitude during this two-month experiment, but the system continued to be oxidizing.

3. There is no way to tell at this point whether the system would ultimately become reducing, and if so, how long it would take.

In summary, the BNL experiment indicates that the conditions in the repository may be oxidizing, but does not show that reducing conditions cannot occur. It would be productive to ask that BWIP be prepared to discuss their rationale at the Waste Package Workshop. Similarly, BNL should be asked to discuss whether they would expect the results to be different for a longer experiment, and why.

If you have any questions, please call me.

Very truly yours,

Kenneth W. Stephens

Kenneth W. Stephens
Manager, Technology Assessments
Eastern Technical Division

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Attachment

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INTEROFFICE CORRESPONDENCE

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TO [redacted] cc R. Johnson, S. Smith, B. Crane

DATE 15 March 1984

Robert B Moler

SUBJECT Review of Draft Report BNL-NUREG-24297

FROM R. B. Moler
BLDG WDC ROOM 4021
EXT 6088

The subject report describes an experiment designed to determine the chemical environment that may exist in the material surrounding a high-level waste package. The simulated environment was that of a basalt repository. A condensation of the conditions is listed below:

a. Temperature and pressure, 150°C, 1500 psi;

b. Low carbon 1020 steel container material;

c. Synthetic basaltic ground water, nearly saturated (8.3 ppm) with O_2 (initial pH ~8);

d. A bentonite clay/basalt mixture; and

e. Irradiation of 3.8×10^4 Rad/hr for 60 days.

Following the end of the experiment, the pH of the water had declined to about 6.88 and the dissolved oxygen had declined to about 0.6 ppm. These conditions would result in an oxidizing environment (Eh = +0.87V).

By contrast, report DOE/RL 82-3, "Site Characterization Report," in part 6.2.3.4, claims that the environment would be reducing, and estimates an Eh of -0.45 volts. The measured pH was ~8 in agreement with the pH of the mixture used in the BNL study. Although oxygen was measured in the groundwater samples in the Site Characterization Report (Section 6.2.4), it is attributed to contamination, on the basis that dissolved oxygen is not compatible with the measured Eh values. This is an unconvincing argument.

In the BNL study, the low carbon steel showed definite inductions of oxygen (a coating of grey iron oxide) and had suffered a 0.3-g weight loss. The total amount of oxygen present (3.2 mg, or 0.1 mmole) is insufficient to

account for the loss of this much iron (5 mmole); however, a significant quantity of H_2 was formed during irradiation, indicating that radiolysis of water had taken place. The oxygen so produced would be sufficient to account for the loss of iron.

Under prolonged irradiation in an oxidizing environment, one might expect the Fe^{+2} in ilmenite and pigeonite to undergo further oxidation to Fe^{+3}, thus consuming oxygen.

The dissolved oxygen content in this experiment declined by an order of magnitude during the experiment, but the system continued to be oxidizing. Whether the oxidation potential would continue to decline, ultimately becoming reducing, is an open question. If the system had reached equilibrium, a possibility, then the import of the results could be substantial. A second question is whether the oxidative potential in combination with the depolarization of the steel by the remaining oxygen and ions in solution would overcome the overvoltage of the iron.

BNL apparently presumed that the basalt/clay/water mixture used to seal the waste package would have a substantial quantity of dissolved oxygen. From the practical point of view, this appears intrinsically reasonable. The question of how long the environment would remain oxidizing is an open question. It would appear to depend on several factors, such as:

(1) Reducing nature of some components in the environment;

(2) Effect of irradiation in maintaining an oxidizing environment (H_2 and methane while reducing may actually be lost to the system insofar as their impact on the system oxidation/reduction potential is concerned);

(3) The rate of replacement of water may be important if the replacement brackish water can lead to accelerated corrosion; and

(4) The time history of the temperature and radiation flux will be very important if tests can demonstrate that the system makes sense.

Having written the above, I am more dubious than ever of the assumption that the environment around a waste

container will be reducing. It seems self-evident that the environment will not be the same as the undisturbed environment from which the statement of a reducing environment came. That seems an especially naive view, one which warrants much closer examination. At some time millenia after the container emplacement, the environment may be approaching its original quasi-equilibrium condition. Until then, quite different conditions might prevail.