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MEMORANDUM FOR: Kien Chang, WMEG, NMSS
FROM: Michael B. McNeill, WMB, RES
SUBJECT: GROUNDWATER CHEMISTRY AT BWIP

I have reviewed the draft NUREG-24297 (BNL), "Determination of the Waste Package Environment for a Basalt Repository," as well as Aerospace Corporation's comments on it. These documents contain considerable discussion of groundwater chemistry, especially oxygen concentration and Eh, and I would like to offer a brief review of the problem.

Rockwell (DOE/RL 82-3, "Site Characterization Report" part 6.2.3.4) makes claims (based on arguments from thermochemical models) that Eh is quite reducing. They admit that the Eh they claim is inconsistent with their experimental measurements of oxygen concentration, but explain this discrepancy as being due to careless experimental work (the experimental work, in fact, did leave a lot to be desired). However, their thermochemical modelling analysis also left a great deal to be desired. Their analysis is based in part on the CH₄/CO₂ reaction, which does not equilibrate under normal low temperature conditions, and in part on the thermochemistry of fresh basalt surfaces. Arguments based on the thermochemistry of fresh basalt surfaces are relevant to unoxidized surfaces (e.g. from samples prepared in a vacuum), but all basalt surfaces at BWIP will have been exposed to air or water and will be oxidized. The point is that Rockwell's claims, therefore, are unsupported at this time, and we must consider other sources of information on repository groundwater conditions.

It is reasonable to assume that (and frankly I can not think of any other possibility), on closure, all water present and all solid surfaces are equilibrated with atmospheric oxygen. After closure, corrosion and internal conversion reactions in the solids will consume some of the dissolved oxygen in the water. However, additional oxygen will be supplied by desorption, by transport in groundwater, and by radiolysis.

Unless the containers are very badly designed, failures should be very unlikely during the period in which desorption will be significant. Therefore, assuming desorption will not have a significant effect, to support claims in regard to waste package behavior, DOE will have to submit information on both the flow and oxygen content of groundwater, and the effect of radiolysis on the groundwater oxygen concentration near the waste package. These are not separable issues.

The effect of radiolysis on groundwater oxygen is a very complex subject. It is clear that the oxygen concentrations depend upon the concentrations of a number of chemical species in the groundwater corrosion produce system as well as radiolysis, in ways that in my opinion are at best partially understood and

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which have not been adequately explained in any of the DOE or NRC geochemistry documents I have seen. I believe that Dr. McVay at PNL is doing experimental work in this field with ONWI funding, but little information has yet become available from this project. As part of the Battelle Columbus program we are studying how the groundwater in the immediate vicinity of waste package interacts physically and chemically with the package during the corrosion process and we are providing you with our research results as they become available. The basic issue of groundwater chemistry as a function of time cannot be regarded as satisfactorily settled at present.

I believe that Dr. Stephens of Aerospace is quite correct when he says, "I am more dubious than ever of the assumption that the environment around a waste container will be reducing." What I would add to this is the statement that many of the potential redox reactions in the system (and I particularly refer to those involving gas molecules) may simply be irrelevant to the questions of corrosion and speciation. For example, I very much doubt that the presence or absence of CH_4 is relevant to the important question (for corrosion) of whether chlorine is present in oxidized states, because of slow kinetics. I agree with BNL and Aerospace that superficial reasoning such as that in the SCR is irrelevant where it is not misleading.



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