

LETTER REPORT

TITLE: Scoping Review of the Draft EA for the Yucca Mountain Site

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General Comments

Most of the discussions in the EA that relate directly to geochemistry appear on pp. 6-134 through 6-167. Consequently, the scoping review presented here is focused principally on the text that appears on these pages.

My overall opinion of the subject material is that it is poorly written, repetitious, and often vague. Hopefully, the text will be substantially rewritten and clarified for the final EA.

As part of my review and assessment of the subject material, I checked to make sure that the references that appear in the text are also present in the list of references. I was pleasantly surprised to find that all but one of the cited references can be found in the list of references. The single missing reference is "Bryant et al., 1984," which is cited on p. 6-135 of the draft EA. I'm not familiar with this reference, so I don't really know whether it's important or not. Also, I'm not really sure that it actually exists. It is possible that this reference is actually supposed to be "Bryant and Vaniman, 1984," which appears in the list of references.

Specific Comments

Discussion items presented on the attached sheets describe the specific concerns that I have regarding geochemical information presented in the draft EA.

ORNL SCOPING REVIEW COMMENTS

DRAFT ENVIRONMENTAL ASSESSMENT FOR THE YUCCA MOUNTAIN SITE REPOSITORY

COMMENT NOS. 1-2

Draft EA Section: 6.3.1.2 Geochemistry (10 CFR 960.4-2-2)

Draft EA Subsection: II. RELEVANT DATA

Comment #1

The following sentence appears on p. 6-136: "For discussion about precipitation and complex formation, equilibrium chemical behavior is assumed; this assumption is generally valid."

In my opinion, this statement is somewhat contentious because it is likely that many rock/water reactions in the tuff-groundwater systems at the Nevada Test Site (NTS) will be either controlled or influenced by kinetics. This point is tacitly acknowledged by NNWSI inasmuch as the draft EA contains lengthy discussions of the possible effects of kinetics on the stabilities of zeolites and clay minerals in NTS tuffs. Furthermore, it has been demonstrated that supersaturation and redox disequilibrium (RUNNELS 1984) can occur in many different types of rock/groundwater systems, including tuff-groundwater systems such as those at the NTS.

Comment #2

On p. 6-137 it is stated: "Finally, only liquid-borne radionuclide transport has been considered."

This statement prompts the question: Why hasn't vapor or aerosol transport been considered? This question is apropos, because DOE now proposes to locate the Yucca Mountain repository in the unsaturated zone beneath Yucca Mountain, so it is possible that some radionuclide transport from this repository will occur by vapor or aerosol transport.

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COMMENT NOS. 3-4

Draft EA Section: 6.3.1.2 Geochemistry (10 CFR 960.4-2-2)

Draft EA Subsection: IV. FAVORABLE CONDITIONS

(1) The nature and rates of the geochemical processes operating within the geologic setting during the Quaternary Period would, if continued into the future, not affect or would favorably affect the ability of the geologic repository to isolate the waste during the next 100,000 years.

Comment #3

On p. 6-140 it is stated: "Barring climatic changes that would significantly increase the ground-water recharge or raise the static water level at Yucca Mountain, zeolitization should be an inoperative or minor process during the next 100,000 years, although the effect on potential glass-to-zeolite reactions due to increased heat from waste emplacement can not yet be predicted."

Due to the fact that glass-to-zeolite reactions may result in significant changes in the physical and chemical integrity of NTS tuffs (e.g., zeolitization could produce important changes in the porosities, permeabilities, and sorptive properties of the tuffs), it is evident that there should be an improved understanding of the effects of temperature on the kinetics of zeolitization in NTS tuffs.

Comment #4

The following sentences appear on pp. 6-140 and 6-141 of the draft EA: "Although future zeolitic alteration of glasses is not likely, studies of mineral assemblage transitions associated with increasing depth and subsurface temperature suggest that recrystallization of clinoptilite-mordenite assemblages to analcime assemblages may have occurred during the Quaternary Period and may continue during the next 100,000 years. This recrystallization is of interest because it could reduce the amount of zeolites present and thus reduce the radionuclide sorptive capacity at Yucca Mountain (Daniels et al., 1982)."

These statements refer to the importance of understanding the natural evolution of zeolite mineralogy in the far field where heat liberated from the decay of radioactive waste will not be important. The text

that accompanies these sentences implies that little is known about the history of zeolite crystallization in NTS tuffs, and, therefore, the reader is left with the impression that it may be impossible to predict zeolite stability very far into the future. This predictive capability is important because, as stated in the second quoted sentence, zeolites are likely to sorb radionuclides and thus decrease the rates of radionuclide migration from the Yucca Mountain repository to the biosphere.

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COMMENT NOS. 5-7

Draft EA Section: 6.3.1.2 Geochemistry (10 CFR 960.4-2-2)

Draft EA Subsection: IV. FAVORABLE CONDITIONS

(2) Geochemical conditions that promote the precipitation, diffusion into the rock matrix, or sorption of radionuclides; inhibit the formation of particulates, colloids, inorganic complexes, or organic complexes that increase the mobility of radionuclides; or inhibit the transport of radionuclides by particulates, colloids, or complexes.

Comment #5

The following sentences appear on pp. 6-144 and 6-149 of the draft EA: "Sorption data for many of the elements studied can be correlated with mineralogy (Daniels et al., 1982). These results show that sorption of alkali metals (e.g., cesium) and alkaline earths (e.g., strontium, barium, and radium), which probably exist in ground water as uncomplexed ions and sorb by ion exchange, is directly correlated with the presence of clinoptilolite and the smectite clays that contain exchangeable cations. A correlation of sorption of cerium, europium, plutonium, and americium with mineralogy is also found, but the relation is not as clear as for the alkali metals."

These statements are not completely consistent with the following analysis presented by Kelmers (1984, p. 3-10): "For many radionuclides, sorption ratios with different tuff samples varied by at least three to four orders-of-magnitude. The sorption ratios for some radionuclides seem to be related to the tuff sample minerals and a correlation of Rd vs sorptive mineral content was developed (DANIELS 1982a, ERDAL 1983, and BISH 1983). Sorption ratios for a number of radionuclides were plotted vs. clinoptilolite contents (DANIELS 1982a). Strontium and barium showed a positive correlation. Cesium seemed to be more correlatable with the smectite content of the tuff sample. Other radionuclides showed little or no correlation with zeolite or clay content of the tuff sample, including technetium, cerium, europium, americium, neptunium, uranium, and plutonium." In view of this analysis by Kelmers, it is evident that the quoted EA statements are somewhat contentious.

Comment #6

The following sentences appear on p. 6-151 of the draft EA: "The natural particulate content of water at Yucca Mountain has not yet been characterized; thus, it is not possible to know whether particulates containing waste elements will form. Certain actinides (plutonium, for example) are known to form colloidal particles in dilute, near-neutral aqueous solutions (Rai and Swanson, 1981; Kim et al., 1983; Olofsson et al., 1983; Newton and Rundberg, 1983). There is not enough information available at this time to know whether geochemical conditions at Yucca Mountain will inhibit formation of these colloids."

These statements indicate that there is very little available information concerning how particulates and colloids might influence radionuclide transport in tuff-groundwater systems. This lack of information is unfortunate, because there is a distinct possibility that particulates and (especially) colloids may be very important vehicles of radionuclide transport in tuff-groundwater systems. The EA does not indicate what steps will be taken to rectify the present situation.

Comment #7

On p. 6-153 it is declared: "There are no unusual conditions that would promote the precipitation of waste element solids other than oxides and hydroxides, or that would inhibit the formation of aqueous inorganic complexes with waste elements."

This is a puzzling statement, because NNWSI is well aware that the groundwaters beneath Yucca Mountain are saturated with silica, and this condition should favor the precipitation of uranium- and zirconium-bearing silicates such as $USiO_4$ and $ZrSiO_4$.

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COMMENT NO. 8

Draft EA Section: 6.3.1.2 Geochemistry (10 CFR 960.4-2-2)

Draft EA Subsection: IV. FAVORABLE CONDITIONS

(3) Mineral assemblages that, when subjected to expected repository conditions, would remain unaltered or would alter to mineral assemblages with equal or increased capability to retard radionuclide transport.

Comment #8

On p. 6-153 it is stated: "Within less than 20 m (65 ft) of the repository where the temperature conditions exceed the boiling point of water, these clays could reversibly collapse but will probably regain their cation-exchanging ability when the temperature again drops below the boiling point (Allen et al., 1983). Below the boiling point of water, the clays should remain stable."

These statements refer to conditions in the repository during the period of peak thermal loading. Use of words such as "will probably" and "should" indicates a lack of data to support the arguments that are being made. It is almost certainly true that additional pertinent evidence regarding the stabilities of clays at 40 to 100°C is available, and if this is so, then this evidence should be discussed briefly at this juncture in the draft EA.

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COMMENT NO. 9

Draft EA Section: 6.3.1.2 Geochemistry (10 CFR 960.4-2-2)

Draft EA Subsection: IV. POTENTIALLY ADVERSE CONDITIONS

(4) A combination of expected geochemical conditions and a volumetric flow rate of water in the host rock that would allow less than 0.001 percent per year of the total radionuclide inventory in the repository at 1000 years to be dissolved.

Comment #9

On p. 6-156 it is stated: "Calculations were done for 10 waste elements that represent approximately 99 percent of the spent fuel activity 1000 years after permanent closure. Table 6.3.1.2-4 lists the elements and the solubilities used."

The significance of these sentences and accompanying commentary is that it is made clear to the reader that, to date, NNWSI staff members have only obtained calculated solubilities for radionuclides in tuff-groundwater systems. There are many geochemists, myself included, who do not believe that such solubilities should be given much credence in performance assessment analyses. Instead, experimentally determined solubilities should be used, because these solubilities are almost certainly more accurate. This point emphasizes an apparent weakness in the NNWSI project; namely that, at the present time, there is no indication of a focused NNWSI program for measuring the solubilities of radionuclides under geochemical conditions which simulate those that are expected to develop in and around a repository at the Yucca Mountain site.

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COMMENT NOS. 10-12

Draft EA Section: 6.3.1.2 Geochemistry (10 CFR 960.4-2-2)

Draft EA Subsection: IV. POTENTIALLY ADVERSE CONDITIONS (Note: this should be subsection V, it is incorrectly designated subsection IV.)

(1) Ground-water conditions in the host rock that could affect the solubility or the chemical reactivity of the engineered barrier system to the extent that expected repository performance could be compromised.

Comment #10

The following sentences appear on p. 6-160: "The pre-emplacement water chemistry in the host rock is not presently known because samples from the Topopah Spring Member where it is in the unsaturated zone have not yet been obtained. However, because water in the saturated zone includes former vadose water, its basic chemical character should be similar to that of vadose water."

The problem here is that it is not necessarily true that vadose-zone water will be "similar" chemically to the groundwater in the saturated zone. A sizable fraction of the latter groundwater may originate in regions far removed from Yucca Mountain, and thus may have a different chemical "signature." Furthermore, the rocks beneath the water table may be somewhat different from the rocks present in the vadose zone, and, therefore, different rock/water reactions in the two zones may result in groundwaters with different chemistries. Finally, due to its closer proximity to the surface, vadose zone water is more likely to be enriched in hydrocarbons dissolved from decaying organic matter in overlying soil zones.

Comment #11

On p. 6-161 it is stated: "Samples of vadose water from the unsaturated tuff are expected to be obtained when the exploratory shaft is constructed. The reference repository water composition could then be revised and the effects of any differences between the vadose water and J-13 water can be assessed."

The first quoted sentence prompts the question: Why can't samples of vadose-zone water be obtained prior to constructing an exploratory shaft? If this sampling is, in fact, impossible or very impractical, then reasons for this should be given. Secondly, the argument that "the effects of any differences between the vadose water and J-13 water can be assessed" may be misleading in the sense that it implies that

assessment of the differences between the groundwaters will be straightforward and easily accomplished. To the contrary, it may turn out to be difficult to predict the effects of differences in groundwater chemistry. For example, it is likely that the rates of certain sorption reactions in tuff-groundwater systems will be strongly affected by the concentration of NaCl in the groundwater. However, at the present time, there is insufficient data available to predict quantitatively how significant these effects will be.

Comment #12

These sentences appear on p. 6-163: "Testing of spent fuel has been completed only in deionized water to date. Tests using J-13 water will be initiated in the near future."

After reading these sentences, the question that came to my mind is: Why are there no stated plans to "test" spent fuel in the presence of both J-13 water and tuff? It is evident to me that, in order to properly test potential waste forms under repository-specific conditions, it is necessary to have both groundwater and rock present in the tests.

REFERENCES

APPS 1983. J. A. Apps, et al., Status of Geochemical Problems Relating to the Burial of High-Level Radioactive Waste, 1982, NUREG/CR-3062, LBL-15103, 1983.

BENSON 1983. L. V. Benson, J. H. Robinson, R. K. Blakennagel, and A. E. Ogard, Chemical Composition of Groundwater and the Locations of Permeable Zones in the Yucca Mountain Area, Nevada, USGS-OFR-83-854, 1983.

BENSON 1983. L. B. Benson, J. H. Robison, R. K. Blankennagel, and A. E. Ogard, Chemical Composition of Groundwater and the Location of Permeable Zones in the Yucca Mountain Area, Nevada, UGS-OFR-83-854, U. S. Geological Survey, Denver, Colorado, 1983.

BISH 1982. D. L. Bish, D. T. Vaniman, F. M. Byers, Jr., and D. E. Broxton, Summary of the Mineralogy-Petrology of Tuffs of Yucca Mountain and the Thermal Stability of Secondary Phases in Tuffs, LA-9321-MS, Los Alamos National Laboratory, Los Alamos, New Mexico, November 1982.

BYERS 1983. F. M. Byers and R. G. Warren, Revised Volcanic Stratigraphy of Drill Hole J-13, Fortymile Wash. Nevada, Based on Petrographic Modes and Chemistry of Phenocrysts, LA-9652-MS, 1983.

CAPORUSCIO 1982. F. A. Caporuscio, D. Vaniman, D. Bish, D. Broxton, B. Arney, G. Heiken, F. Byers, R. Gooley, and R. Semarge, Petrographic Studies of Core from Drill Hole USW-G2 and of the Lower Crater Flat Tuff in Core from Drill Hole NE25B-1H, Yucca Mountain, Nevada, LA-9255-MS, 1982.

DANIELS 1982. W. R. Daniels, et al., Summary Report on the Geochemistry of Yucca Mountain and Environs, LA-9328-MS, Los Alamos National Laboratory, Los Alamos, New Mexico, 1982.

DENBIGH 1968. K. Denbigh, The Principles of Chemical Equilibrium, Cambridge University Press, Cambridge, p. 494, 1968.

KERRISK 1982. J. F. Kerrisk, "Solubility of Plutonium(IV) in Natural Waters with Carbonate Present," Section III. B. (pp. 6-18) in W. R. Daniels, et al., Research and Development Related to the Nevada Nuclear Waste Storage Investigations April 1-June 30, 1982, LA-9484-PR, Los Alamos National Laboratory, Los Alamos, New Mexico, 1982.

KERRISK 1983. J. F. Kerrisk, Reaction-Path Calculations of Groundwater Chemistry and Mineral Formation at Rainier Mesa, Nevada, LA-9912-MS, Los Alamos National Laboratory, Los Alamos, New Mexico, 1983.

KERRISK 1984. J. F. Kerrisk, Solubility Limits on Radionuclide Dissolution at a Yucca Mountain Repository, LA-9995-MS, Los Alamos National Laboratory, Los Alamos, New Mexico, 1984.

LEVY 1984. S. S. Levy, "Studies of Altered Vitrophyre for the Prediction of Nuclear Waste Repository-Induced Thermal Alteration at Yucca Mountain, Nevada," Materials Research Society Symposia Proceedings v. 26, p. 959-966, 1984.

LINDBERG 1984. R. D. Lindberg and D. D. Runnells, "Ground Water Redox Reactions: An Analysis of Equilibrium State Applied to Eh Measurements and Geochemical Modeling," Science, Vol. 225, pp. 925-927, 1984.

OVERSBY 1983. V. M. Oversby and K. G. Knauss, Reaction of Bullfrog Tuff with J-13 Well Water at 90°C and 150°C, UCRL-53442, 1983.

REES 1984. T. F. Rees, J. M. Cleveland, and K. L. Nash, "The Effect of Composition of Selected Groundwaters from the Basin and Range Province on Plutonium, Neptunium, and Americium Speciation," Nuclear Technology, Vol. 65, April 1984.

SINNOCK 1982. S. Sinnock, Geology of the Nevada Test Site and Nearby Areas, Southern Nevada, SAND82-2207, 1982.

STUMM 1981. W. Stumm and J. J. Morgan, Aquatic Chemistry, John Wiley & Sons, New York, p. 780, 1981.

VANIMAN 1984. D. Vaniman, D. Bish, D. Broxton, F. Byers, G. Heiken, B. Carlos, E. Semarge, F. Caporuscio, and R. Gooley, Variations in Authigenic Mineralogy and Sorptive Zeolite Abundance at Yucca Mountain, Nevada, Based on Studies of Drill Cores USW GU-3 and G-3, LA-9707-MS, Los Alamos National Laboratory, Los Alamos, New Mexico, 1984.

WOLFSBERG 1983. K. Wolfsberg, D. T. Vaniman, and A. E. Ogard, Research and Development Related to the Nevada Nuclear Waste Storage Investigations, January 1-March 31, 1983, LA-9793-PR, Los Alamos National Laboratory, Los Alamos, New Mexico, 1983.