

LR-287-67

01/09/87

LETTER REPORT

Title: Review and Evaluation of Gamma and Alpha Radiation Levels in a Basalt High-Level Waste Repository: Potential Impact on Container Corrosion and Packing Properties, RHO-BW-SA-462 P, Sept., 1985, by Donald T. Reed, Scott D. Bonar, and Michael F. Weiner.

AUTHOR: J. G. Blencoe
Chemistry Division
Oak Ridge National Laboratory

PROJECT TITLE: Technical Assistance in Geochemistry

PROJECT MANAGER: G. K. Jacobs

ACTIVITY NUMBER: ORNL #41 88 54 92 4 (FIN No. B0287)
NRC #50 19 03 01

OVERVIEW

This report describes preliminary calculations of two key performance characteristics of basalt-hosted HLW waste packages: (1) the radiolytic yields of primary molecular products (hydrogen and hydrogen peroxide) during the containment period, and (2) the radiation levels associated with transport of radionuclides through the packing material during the controlled release period. The results presented are used to address two issues: the effect of gamma radiation on the corrosion of the waste canister during the containment period, and the effect of alpha radiation on the crystallinity of bentonite in the packing material during the controlled release period. Regarding the effects of radiolysis in the waste packages of a basalt-hosted HLW repository, the

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authors conclude that: (1) gamma radiolysis of groundwater will produce only small quantities of hydrogen and hydrogen peroxide, (2) the potential for radiolytic enhancement of canister corrosion has been overestimated in previous studies because the rapid attenuation of gamma radiation was not taken into account, and (3) it is highly unlikely that alpha radiation will have serious adverse effects on the performance of bentonite in basalt + bentonite packing material.

REVIEW

Introduction

This report describes preliminary calculations of two key performance characteristics of basalt-hosted HLW waste packages: (1) the radiolytic yields of primary molecular products (hydrogen and hydrogen peroxide) during the containment period, and (2) the radiation levels associated with transport of radionuclides through the packing material during the controlled release period. The authors begin their discussion by pointing out that ionizing radiation (gamma radiation at first, and later alpha radiation) will be present continuously in waste packages after repository closure. This observation is noteworthy because radiolytic products have been shown to affect the rate of canister corrosion (Nelson et al., 1984), the composition of dilute aqueous solutions near the waste canister (Draganic and Draganic, 1971), the polymerization of organic compounds in "basalt groundwater" (Gray, 1984), and the speciation of radionuclides (Newton, 1975).

Reed et al. also stress that, from a radiolytic standpoint, the history of a nuclear waste repository in basalt (NWRB) can be divided into three sequential periods. Chronologically, these are: (1) the saturation (of the packing) period, (2) the saturation (of the packing) period with containment, and (3) the controlled release period.

- The saturation (of the packing) period begins at the time waste canisters are emplaced and continues until waste packages are saturated with groundwater. It is expected that some boiling of groundwater will occur during this period. An important concern regarding waste package performance during this period is whether gamma-radiation-generated "gas-phase products" adversely affect canister durability and the stability of packing material.
- The saturation (of the packing) period with containment starts at the time the waste packages become saturated with groundwater and ends at the time when canisters are breached. As in the previous period, gamma radiation is the principal form of ionizing radiation in the waste packages, and the effect of this radiation on canister corrosion and the stability of packing material continue to be important performance considerations.
- The controlled release period begins when waste canisters are breached. During this period there is direct interaction between the waste form (spent fuel) and "basalt groundwater." Assuming that the containment period is at least 1,000 years, alpha radiation will be the principal type of ionizing radiation during the controlled release period. Important radiolytic considerations during the post-containment period are the effect of alpha radiation on bulk solution properties in the waste package, and the radiolytic oxidation/reduction of radionuclides as they are released from the waste form into the packing material.

Gamma Radiation Levels During the Containment Period

Gamma radiation levels during the containment period were calculated using the QAD-CG/MS shielding code (Chapman et al., 1982). These calculations are based on the DOE (1984) conceptual design of basalt-hosted waste packages. In this design, the waste package consists of four 10-year-old pressurized water-cooled reactor (PWR) spent fuel

assemblies (33,000 Mwd burnup) with a combined (bundle) radius of 16.8 cm and a total length of 385 cm, housed in an 8.3-cm-thick low-carbon steel canister, which in turn is surrounded by 16.2 cm of packing material consisting of 75% basalt and 25% bentonite. To simplify the calculations, it was assumed that (1) the packing material was dry, and (2) the spent fuel was distributed homogeneously inside the canister. The gamma dose rate was calculated as a function of distance (radially and axially) in the packing material.

The QAD-CG/MS code yielded the following calculational results.

1. At the time of waste emplacement, the expected incident gamma dose rate at the surface of the canister is approximately 250 rad/h.
2. The packing material absorbs more than 85% of the gamma radiation emitted from the canister.
3. The flux of gamma radiation decreases rapidly with time.
4. The energy from the gamma radiation is not absorbed homogeneously in the packing material. Absorbed doses are maximal - 66 Mrad - immediately adjacent to the canister, and decrease to 7 Mrad near the outer edge of the packing material.

Yield of Radiolytic Products in the Waste Package

In order to estimate the yield of "molecular products" (hydrogen and hydrogen peroxide) generated by gamma radiation during the containment period, Reed et al. calculated the total energy absorbed in the packing material as a function of time. These calculations are based on the following assumptions: (1) the dose rate at a given time is constant at all points on the outer surface of the canister, (2) the attenuation of gamma flux as a function of time and distance from the canister surface is adequately represented by a simple exponential decay function, (3)

the "effective" density of the groundwater in saturated packing material is 0.4 g/cm^3 , and (4) saturation of the waste package occurs immediately after emplacement. With these assumptions, the calculations performed by Reed et al. indicate that a total of 160 MJ of energy is absorbed by the groundwater in each waste package during the nominal 1,000-year containment period. The calculated total yield of molecular products during the containment period and the maximum yield per year are listed below.

Product	Total Yield (moles)	Maximum Yield/Year (moles)
Hydrogen	5.7	0.18
Hydrogen Peroxide	7.5	0.24

Radiation Levels During the Controlled Release Period

Reed et al. also calculated the levels of alpha radiation associated with the transport of radionuclides through the packing material. The authors state that, in order to calculate radiation dose rates in the packing material as a function of time and space during the controlled release period, it is necessary first to calculate the concentrations of mobilized radionuclides as a function of time and distance from the waste canister. These calculations were performed using the CHAINT transport code (Baca et al., 1984). This code assumes that, at the time of canister breaching, the canister disappears and all radionuclides instantly dissolve to their solubility limits. Thereafter, it is assumed that the concentrations of radionuclides remain fixed at the waste form-groundwater interface. Additional assumptions in the calculations included: a 0.4 "effective" porosity for packing material, canister failure at 1,000 years, and a diffusion constant of $10^{-6} \text{ cm}^2/\text{s}$ for each radionuclide. The code was run only for ^{241}Am , ^{243}Am , ^{239}Pu ,

^{240}Pu , and ^{99}Tc because these radionuclides represent 95% of the total activity of 1,000-year-old spent fuel. Sorption coefficients and solubilities for these radionuclides were obtained from Salter and Jacobs (1983). Therefore, the calculated dose levels are partly a function of the assumed solubility and sorption properties of the radionuclides.

The calculations yielded the dose rate of each radionuclide at 0, 7, and 19 cm from the canister wall as a function of time. At 0 cm, the packing material was saturated with radionuclides from the time of canister breaching. Therefore, the dose rate at 0 cm was not only constant, but also the maximum dose rate possible for the assumed radionuclide solubilities.

Reed et al. express the belief that the results obtained from the CHAINT code are conservative estimates of the dose rate and total absorbed dose in the packing material because (1) the radionuclide solubilities adopted for the calculations were significantly higher than expected solubilities, and (2) the transport model assumed a constant radionuclide concentration at the source (no inventory limit or time decay effect on the source concentration).

Discussion

Reed et al. claim that the results of their calculations serve to elucidate the potential impact of radiolytic processes on the performance of a basalt-hosted waste package. In particular, they believe that their calculations provide useful estimates of (1) the effect of gamma radiation on the rate of canister corrosion, and (2) the effect of alpha radiation on the crystallinity of bentonite in the packing material.

Regarding the potential effect of gamma radiation on canister corrosion, the authors state their belief that this effect has frequently been

overestimated in the past. This opinion is based on two observations. First, experiments designed to measure radiation enhancement factors have been performed at very high dose rates for relatively short periods of time. Reed et al. believe that use of high dose rates to "accelerate" radiolytic effects is only valid if it is first demonstrated that the processes being studied are not dose-rate dependent. Second, Reed et al. note that previous investigators have neglected the fact that the flux of gamma radiation will attenuate rapidly during the containment period. When this attenuation is taken into account, calculations indicate that only relatively small amounts of radiolytic products are generated.

Reed et al. also believe that alpha radiation will have a negligible effect on the crystallinity of bentonite in basalt-hosted waste packages. This issue has been raised in view of results obtained from radiolysis experiments performed by Haire and Beall (1979). In these experiments, samples of H₂O-saturated bentonite were spiked with varying quantities of ²⁵³Es. In a "high-dose," seven-day experiment, the concentration of ²⁵³Es was 3.33×10^{-5} mol/g of bentonite, and the total absorbed dose was 4.8×10^{11} rad (the maximum dose rate was 3.2×10^9 rad/h). Additional "low-dose" experiments were performed wherein the H₂O-saturated bentonite contained 1% and 0.1% of the amounts of ²⁵³Es used in the high-dose experiment. Damage to the bentonite was only reported in the high dose experiment; this damage was evidenced by a loss of crystallinity, a decrease in permeability, and greater expansivity of clayey material.

Reed et al. emphasize that the radiolytic conditions in the experiments performed by Haire and Beall (1979) differ markedly from the radiolytic conditions that are expected to develop in the packing material of waste packages in an NWRB. Comparing the total absorbed dose in the high-dose experiment performed by Haire and Beall with the calculated total absorbed dose in the packing material of basalt-hosted waste packages at distances of 0, 7, and 19 cm from the canister wall, it is discovered

that the experimental dose is, respectively, 35, 40, and 44 times larger than the calculated doses in the basalt-hosted waste packages.

Furthermore, even with conservative estimates of the solubilities of radionuclides in the packing material of basalt-hosted waste packages, the dose rates used in the ^{253}Es experiments were 10^7 times higher than the calculated dose rates. In view of the very high total doses and extremely high dose rates required to cause significant structural damage to bentonite, Reed et al. suggest that the experiments performed by Haire and Beall are of little relevance to the performance of bentonite in basalt-hosted waste packages.

Conclusions

From the results of their calculations and analyses of relevant work performed by previous investigators, Reed et al. reach the following conclusions regarding the effects of gamma and alpha radiation in the waste packages of a basalt-hosted HLW repository: (1) gamma radiation during the containment period will produce only small quantities of hydrogen and hydrogen peroxide, and these molecular products of radiolysis will have little effect on the rate of canister corrosion; and (2) alpha radiation will have no serious adverse effects on the performance of bentonite in basalt-hosted waste packages.

REFERENCES

- Baca, R. G., R. C. Arnett, and D. W. Langford, 1984, "Modeling Fluid Flow in Fractured Porous-Rock Masses by Finite-Element Techniques," International Journal for Numerical Methods in Fluids, 4:337-348.
- Chapman, C., W. H. Hagan, and G. L. Simmons, 1982, "QAD-CG/MS A Multiple Source, Combinatorial Geometry Version of QAD-P5A, A Point Kernel Shielding Code," Science Applications, La Jolla, California.
- DOE (U.S. Department of Energy), 1984, Draft Environmental Assessment, Reference Repository Location, Hanford Site, Washington, 1984, U.S. Department of Energy, DOE/RW-0017, Office of Civilian Radioactive Waste Management, Washington, D.C., p. 6-245.
- Draganic, I. G. and Z. D. Draganic, 1971, The Radiation Chemistry of Water, Academic Press, New York, New York.
- Gray, W. J., 1984, "Gamma Radiolysis Effects on Grande Ronde Basalt Groundwater," Scientific Basis for Nuclear Waste Management VII, G. L. McVay ed., Materials Research Society Symposia Proceedings, 26:147-152, Elsevier Science Publishing Co., New York, New York.
- Haire, R. G. and G. W. Beall, 1979, "Consequences of Radiation from Sorbed Transplutonium Elements on Clays Selected for Waste Isolation," ACS Symposium Series #100, ed. S. Fried, pp. 291-295.
- Nelson, J. L., R. E. Westerman, and F. S. Gerber, 1984, "Irradiation-Corrosion Evaluation of Metals for Nuclear Waste Package Applications in Grande Ronde Basalt Groundwater," Mat. Res. Soc. Symp., 26:121.

Newton, T. S., 1975, "The Kinetics of the Oxidation-Reduction Reactions of Uranium, Neptunium, Plutonium and Americium in Aqueous Solutions," Energy Research and Development Administration, TID-26506.

Salter, P. F. and G. K. Jacobs, 1983, BWIP Data Package for Reference Solubility and K_d Values, SD-BWI-DP-001, Rev A-0, Rockwell Hanford Operations, Richland, Washington.

EVALUATION

This report describes preliminary calculations of two key performance characteristics of basalt-hosted HLW waste packages: (1) the radiolytic yields of primary molecular products (hydrogen and hydrogen peroxide) during the containment period, and (2) the radiation levels associated with transport of radionuclides through the packing material during the controlled release period. The results presented are used to address two issues: the effect of gamma radiation on the corrosion of the waste canister during the containment period, and the effect of alpha radiation on the crystallinity of bentonite in the packing material during the controlled release period. Regarding the effects of radiolysis in the waste packages of a basalt-hosted HLW repository, the authors conclude that: (1) gamma radiolysis of groundwater will produce only small quantities of hydrogen and hydrogen peroxide, (2) the potential for radiolytic enhancement of canister corrosion has been overestimated in previous studies because the rapid attenuation of gamma radiation was not taken into account, and (3) it is highly unlikely that alpha radiation will have serious adverse effects on the performance of bentonite in basalt + bentonite packing material.

The calculational results presented in this report fully support the conclusions drawn by the authors. However, the sum total of pertinent evidence is less than satisfactory. In particular, it is unfortunate that there are no experimental data available to validate the authors' calculated yields of hydrogen and hydrogen peroxide during the containment period. Without these data it is impossible to demonstrate the validity of key simplifying assumptions made in these calculations. Additionally, there are good reasons to question the applicability of the conceptual model of waste package performance upon which the authors' calculations are based. This conceptual model is subject to criticism on the following grounds:

1. The effects of gamma radiolysis on packing material and groundwater during the early saturation (boiling) period are not taken into account.
2. Groundwater is treated as pure H₂O - that is, the effects of the presence of dissolved and suspended material in "basalt groundwater" are neglected.
3. The waste package is treated as if it were an isothermal chemical system and, therefore, the effects of variable temperature are unaddressed.
4. There is no accounting for the effects of hydrothermal alteration on the physicochemical characteristics of packing material. Therefore, the calculations performed by Reed et al. ignore the possibility that silicification and/or growth of secondary aluminosilicate minerals may alter the porosity and permeability of packing material.
5. It is assumed that radionuclide migration in the packing material occurs solely by diffusion. Consequently, there is no attempt made to address the potentially significant effects of advective transport of radionuclides in basalt-hosted waste packages.

This report is also severely limited in scope. The authors have chosen to focus their discussions on two key performance issues: (1) that gamma radiation may generate significant quantities of "corrosive" hydrogen and hydrogen peroxide, and (2) that bentonite may be damaged significantly by alpha radiation. Left completely unaddressed are two additional issues that probably merit equal attention; these are: the effects of gamma and alpha radiation on the durability of canister metal, and the possibility that alpha radiation may oxidize radionuclides to more mobile forms.

Finally, two additional minor criticisms of this report. First, there are several places in the text where assumptions are made without elaboration. For example, the authors selected 0.4 g/cm^3 as the "effective" density of the groundwater in saturated packing material, and the diffusion constant for radionuclide diffusion through packing material was assumed to be $10^{-6} \text{ cm}^2/\text{s}$ for each radionuclide. There is little doubt that these values were chosen for justifiable reasons, but these reasons are not stated. Finally, it is regrettable that several key equations in this report are presented without accompanying references to publications that explain how the equations were developed. This omission makes it unnecessarily difficult for a reader to locate additional articles and reports that shed further light on the mathematical methods employed in this report.