Title 40 CFR Part 191 Compliance Certification Application for the Waste Isolation Pilot Plant

Appendix BACK

United States Department of Energy
Waste Isolation Pilot Plant

Carlsbad Area Office
Carlsbad, New Mexico

Control of the Chemical Environment Through Implementation of an MgO Backfill Material

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BACK.1 Introduction

A backfill system has been designed that will control the chemical environment of the postclosure repository to a domain where the actinide solubility is within its lowest region. The actinide solubility is highly dependent on the chemical species that constitute the fluid, the resulting pH of the fluid, and the oxidation state of the actinide which is stable under the specific conditions. Within some scenarios of the Waste Isolation Pilot Plant (WIPP) performance assessment, there will be a significant quantity of carbon dioxide (CO_2) generated as a result of microbial degradation of carbon containing waste material (that is, cellulosics, plastics, and rubbers). The formation of CO_2 has a significant impact on the solubility of the actinides through the following processes:

(1) Upon contact with water, carbon dioxide reacts according to the equation,

$$CO_2(g) + H_2O \leftrightarrow H_2CO_3$$

forming carbonic acid. Carbonic acid, although a relatively weak acid, is capable of driving the pH of the repository into the acidic range where the solubility of the actinides is typically at its highest point.

(2) As the carbonic acid dissociates according to the equations

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

and

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$

carbonate species are generated. The carbonate ion is known to bind very strongly to the actinides, forming stable, relatively highly soluble species. The presence of carbonate in any significant quantity therefore drives the actinide solubility to much higher values because of both lowering pH and forming soluble actinide carbonate complexes.

To mitigate these two detrimental effects of CO_2 generation, a material was required that would prevent the decrease in pH of the brines and minimize the ability of the carbonate ion to remove CO_2 and thus participate in complexation reactions. The alkaline earth oxides (for example magnesium oxide [MgO]) were identified as fulfilling these two functions.

The alkaline earth oxides react with water according to the following equation:

$$MgO(s) + H_2O \leftrightarrow Mg(OH)_2(s).$$

The hydroxide thus formed is then available to react with carbonic acid,

$$Mg(OH)_2(s) + H_2CO_3 \leftrightarrow MgCO_3(s) + 2H_2O,$$

thus effectively removing the carbonate from the system due to $MgCO_3$ being quite insoluble. The mineralogy of the solid magnesium carbonate phase is being investigated, but will not impact the pH buffering capacity.

BACK.2 Description of the Backfill System

The backfill material will be emplaced as a dry granular or pelletized material in bags. The bags serve two purposes: (1) provide ease of handling during the operational phase, and (2) provide protection from premature exposure to atmospheric CO_2 during handling and prior to room closure. The bags may be made out of plastic or cellulose.

Granular or pelletized material is specified for several reasons:

- reduction of dusting potential in case of a premature bag rupture,
- ensuring that sufficient permeability is maintained to make the backfill material accessible to any brine flow,
- reduction of the probability of the backfill material being flushed out of the repository system by entrainment in an established brine flow field, and
- providing for a high enough material density so that sufficient backfill material can be emplaced without major operational difficulties.

For the backfill material to be effective, it must be emplaced such that it is available to react with any brine that may reach the repository and with any CO_2 that is generated as a result of microbial action. To accomplish this, a design has been developed that provides for the dispersal of the backfill material throughout the waste emplacement. The specifics of this design are being documented by Westinghouse Electric Corporation, Waste Isolation Division.

Many chemical forms of MgO are available, but to ensure sufficient reactivity, the form resulting from low-temperature dehydration of magnesium hydroxide is required. Other forms, such as that resulting from calcination of magnesium carbonate or dolomite $\{Ca/Mg(CO_3)_2\}$, may not demonstrate sufficient reactivity to ensure the desired chemical effects.

BACK.3 Impacts on Balance of System

BACK.3.1 Gas Generation

The addition of MgO as a backfill material will increase and maintain the solution pH of the repository in the basic region. There has been no identified dependence of the generation rate of CO_2 by microbial action as a function of solution pH. With respect to the corrosion of steels, a correlation has been identified between pH and corrosion rate, and thus hydrogen generation rate. However, the experiments used to determine the range of hydrogen generation rates utilized in performance assessment (Wang and Brush 1996) were performed at a pH of approximately 10, which approximates the pH region expected from the addition of an MgO backfill (Telander and Westerman 1993). Additionally, the range of gas generation rates provided to the performance assessment has already taken into account the potential for variations in rates due to pH effects (Wang and Brush 1996).

As previously discussed in Section BACK.1, no new gas generating reactions are introduced by the addition of MgO. Although the MgO could be postulated to have adsorbed some gases during handling and transportation, the potential for this is minimized by the bagging of the material. Even if there were to be adsorbed gases, desorption generally requires elevated temperatures to be effective. No elevated temperatures are anticipated in the repository.

The addition of MgO will, however, impact the total quantity of gas that may be present in the repository. As described in Section BACK.1, the MgO is being added to react with the CO_2 potentially being generated by microbial action. Therefore, there will be an overall decrease in the total quantity of gas that may be present in the repository for scenarios in which sufficient microbial gas generation is assumed. This decrease of gas quantity is not significant in comparison with the total quantity of gas that may be generated by all processes during the repository lifetime.

Since the MgO backfill is being added in large excess, any quantity of brine that may enter the repository will be saturated with respect to the appropriate MgO reaction products. Therefore, any chemical changes induced as a result of the addition of MgO as a backfill are independent of the degree of saturation of the repository.

BACK.3.2 Disposal Room

The backfill material will occupy what would have been void space within the previous project baseline. Filling of this space will therefore have an effect on the closure rate of the repository. As shown in Figure BACK-1, the rate of closure is dependent on the presence of a material filling the void space; in the previous case, salt was used as a comparison. The curve for salt backfill was developed using a salt backfill creep model to describe densification with time. Thus, the resulting closure curve was reflective of the salt achieving a permeability nearly equivalent to that of the surrounding halite.

Within the current backfill design, not all of the available void space will be filled. This is primarily due to the design requirement quantity not requiring all of the void space for the amount of backfill specified, and operational concerns regarding placement. The net effect of this quantity of backfill being added is that we will achieve a closure curve intermediate between the no backfill curve (that is, the current baseline) and the salt backfill included curve. The DOE believes that the effect of the closure rate arising from emplacement of the current backfill system will have minimal impact on the performance assessment calculations. Figure BACK-1 shows that most of the closure will be achieved early in the life of the repository and thus could only have any impact at all during the first several hundred years postclosure. Even during this time frame, the DOE feels that the impact will be within the expected variation of the calculations. Previous performance assessment calculations have shown that the porosity of backfills in the drifts, experimental region, and the shaft below the seal, and the volume fractions of materials that are expected to have an impact on the final room porosity are less important parameters to compliance (WIPP Performance Assessment Department 1993a, 1993b).

BACK.3.3 Culebra Transport

In the chemical model used for performance assessment calculations, the effects of adsorption of actinides on dolomite surfaces in the Culebra are represented by retardation coefficients calculated using linear distribution coefficients (K_d) determined mainly by batch sorption experiments with dolomite-rich Culebra rock. Although pH can have an impact on adsorption of dissolved actinides on dolomite, most of the experimental sorption work for actinides has been done at pH values representative of the Culebra. However, a mechanistic study was carried out to evaluate the effects of pH, CO_2 pressure, and brine ionic strength on actinide sorption on pure dolomite. The pH range extended from 3 or 4 to 9 or 10, which would include the pH values to be expected in a repository backfilled with MgO. Data from the mechanistic sorption study were used to extend the range of K_d values submitted to performance assessment for deep (Salado and Castile) brines, since the pH of these brines is expected to be affected strongly by the MgO backfill. However, for the Culebra brines, it was assumed that mixing in the Culebra would be sufficient to produce brines similar in composition to the natural Culebra brines. Thus, the K_d values submitted to performance assessment for the Culebra were determined under pH conditions representative of the Culebra.

BACK.3.4 Colloidal Actinide Source Term

The colloidal actinide source term is sensitive to the chemical conditions in the repository. For example, the concentration of actinide intrinsic colloids is dependent on the pH of the fluid. At extremely low pH values (that is, high acidic solutions), actinide intrinsic colloid formation is inhibited (Cleveland 1979). At all of the pH values that could be possible within the repository, both with and without backfill material, actinide intrinsic colloids may be formed. However, the residual concentration of kinetically stable actinide intrinsic colloids

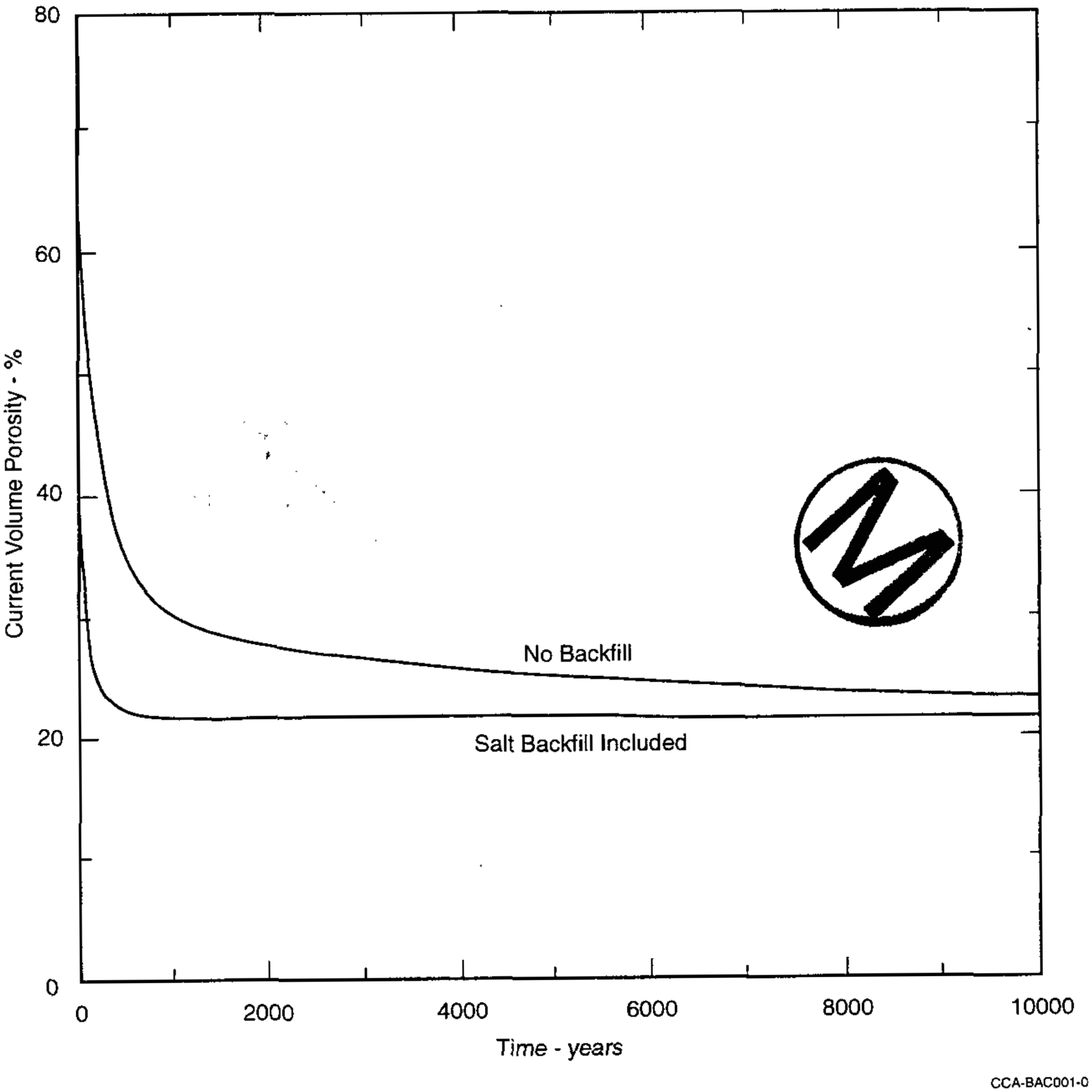

Figure BACK-1. **Comparison of the Closure Curve Used for the 12/92 Comparison Calculations with CCA Curves Which are Based on the Assumption of No Backfill and No Gas Generation**

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is dependent on the pH. Experiments within the colloidal actinide source term program have measured the residual concentration of actinide intrinsic colloids as a function of pH and the effects are thus accounted for.

The formation of actinide-bearing humic colloids is also impacted by the introduction of MgO backfill. Humic substances are known to complex with metal cations, including actinides (Choppin 1988). This complexation is typically through hydroxyl or carboxylic acid functionalities and is therefore pH dependent to some degree. Humic substances also will complex with non-actinide metal cations, such as magnesium. The magnesium added in the backfill competes with the actinides for complexation with the humics, resulting in a reduced contribution to the mobile actinide concentration from the humic substances.

REFERENCES

Choppin, G.R. 1988. "Humics and Radionuclide Migration," *Radiochemica Acta.* Vol. 44/55, pt. 1, 23–28.

Cleveland, J. 1979. *The Chemistry of Plutonium.* American Nuclear Society, La Grange Park, IL.

Telander, M.R. and Westerman, R.E. 1993. *Hydrogen Generation by Metal Corrosion in Simulated Waste Isolation Pilot Plant Environments, Progress Report for the Period November 1989 Through December 1992.* SAND92-7347, Sandia National Laboratories, Albuquerque, NM. WPO 23456.

Wang, Y. and Brush, L. 1996. "Estimates of Gas-Generation Parameters for the Long-Term WIPP Performance Assessment." Memo to Martin S. Tierney, 1/26/96. WPO 31943.

WIPP Performance Assessment Department. 1993a. *Preliminary Performance Assessment for the Waste Isolation Pilot Plant, December 1992. Volume 4; Uncertainty and Sensitivity Analysis for 40 CFR 191, Subpart B.* SAND92-0700/4. Sandia National Laboratories, Albuquerque, NM.

WIPP Performance Assessment Department. 1993b. *Preliminary Performance Assessment for the Waste Isolation Pilot Plant, December 1992. Volume 5; Uncertainty and Sensitivity Analysis of Gas and Brine Migration for Undisturbed Performance.* SAND92-0700/5. Sandia National Laboratories, Albuquerque, NM.