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PRELIMINARY MODEL OF REPOSITORY CHEMISTRY FOR THE WASTE ISOLATION PILOT PLANT[1]

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ABSTRACT

The design-basis, defense-related, transuranic (TRU) waste to be emplaced in the Waste Isolation Pilot Plant (WIPP) could, if sufficient H_2O and nutrients were present, produce as much as 1,500 moles of gas per drum of waste. Gas production could pressurize the repository to 150 atm (lithostatic pressure) and perhaps higher.

Anoxic corrosion of Fe and Fe-base alloys and microbial degradation of cellulosics are the processes of greatest concern, but radiolysis of brine could also be important. The proposed backfill additives $CaCO_3$, CaO, $CuSO_4$, KOH, and NaOH may remove or prevent the production of some of the expected gases.

Because of the heterogeneous nature of design-basis waste, the Eh and pH of any brine present in WIPP disposal rooms could vary significantly over short distances after reacting with the waste.

The WIPP Project is investigating the consequences of gas production and considering engineered alternatives, including reprocessing the waste, to reduce gas production rates or potentials. Reprocessing would also reduce the range of Eh and pH expected for the repository.

ANOXIC CORROSION

Lappin et al. (1989) estimated that, if sufficient brine were present and the concentration of O_2 were low, anoxic corrosion of all of the steel containers (drums and boxes) and Fe and Fe-base alloys in the design-basis TRU waste to be emplaced in WIPP disposal rooms would produce about 2 moles of H_2 per equivalent drum of waste per year for 400 to 500 years, or a total of 900 moles per drum. (There will be about 6,800 equivalent drums of waste per 3,640-m^3 room; each room will contain about 2,260 m^3 of void volume immediately after emplacement of the drums and crushed-salt or crushed-salt-and-bentonite backfill.) Anoxic corrosion of steel containers would produce

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600 moles of H_2 per drum; anoxic corrosion of Fe and Fe-base alloys in the waste would produce 300 moles of H_2 per drum. These estimates do not include H_2 from anoxic corrosion of Al and Al-base alloys in the waste because there was no reliable estimate of the quantity of these metals in the WIPP inventory at that time. Anoxic corrosion is the process of greatest concern from the standpoint of the gas budget of the repository.

Lappin et al. (1989) also noted that anoxic corrosion could consume significant quantities of brine. The quantity consumed will depend on the extent to which metals corrode and the H_2O content of the solid corrosion products, but may be as much as 200 m^3 per room. This estimate does not include the consumption of brine by anoxic corrosion of Al and Al-base alloys.

Because anoxic corrosion would consume brine, the quantity of H_2O in the disturbed rock zone (DRZ) available for transport to the waste, either by brine inflow or diffusion of H_2O vapor through the gaseous phase, may, in the absence of transport from the undisturbed (far-field) salt surrounding the repository, be insufficient for the production of 900 moles of H_2 per drum. An integrated model of the effects of gas pressurization, room closure, brine inflow and outflow, and vapor-phase transport of H_2O is still at an early stage of development. However, preliminary calculations suggest that absorption of H_2O by crushed salt and any bentonite in the backfill and the possible consumption of H_2O by microbial degradation of cellulosics (see below) may limit the extent of anoxic corrosion of metals.

Based on thermodynamic calculations and a review of previous kinetic data, Brush (1990) concluded that, in the absence of microbially produced CO_2 and H_2S, anoxic corrosion of Fe and Fe-base alloys by WIPP brines at 30°C would probably produce Fe_3O_4 (magnetite) or $(Fe,Mg,Mn)(OH)_2$ (amakinite) by the reactions:

$$3\ Fe + 4\ H_2O = Fe_3O_4 + 4\ H_2; \qquad (1)$$

$$Fe + 2\ H_2O = Fe(OH)_2 + H_2. \qquad (2)$$

He calculated equilibrium H_2 fugacities of about 400 and 60 atm for these reactions, respectively. These thermodynamic calculations imply that, if sufficient quantities of Fe and H_2O were present and O_2 were absent from WIPP disposal rooms, anoxic corrosion would produce significant H_2 pressures. The activity of H_2O vapor in equilibrium with brine from the Salado Fm. at or near the stratigraphic horizon of the WIPP is equal to the activity of H_2O in the brine, about 0.7. Therefore, the thermodynamic calculations described above apply to H_2O vapor as well as to brine. Significant anoxic corrosion would thus be possible if there were sufficient H_2O vapor present.

These calculations also illustrate the sensitivity of the equilibrium H_2 fugacity to the identity of the solid corrosion product. Assuming sufficient Fe and H_2O, anoxic corrosion would reach equilibrium at an H_2 fugacity of 60 atm if $Fe(OH)_2$ were the corrosion product, but would continue to an H_2

fugacity of 400 atm if Fe_3O_4 were formed. Because the former value is well below lithostatic pressure at the repository horizon (about 150 atm) and the latter well above it, the identity of the corrosion product formed would appear to affect the extent of pressurization significantly.

However, pure $Fe(OH)_2$ is unstable with respect to Fe_3O_4. The reaction for the conversion of $Fe(OH)_2$ to Fe_3O_4 is:

$$3\ Fe(OH)_2 = Fe_3O_4 + 2\ H_2O + H_2. \tag{3}$$

Brush (1990) calculated an equilibrium H_2 fugacity of 100,000 atm for this reaction. Clearly, the formation of $Fe(OH)_2$ would not constrain the H_2 fugacity to 60 atm if Fe_3O_4 nucleates and replaces $Fe(OH)_2$. Haberman and Frydrych (1988) observed both Fe_3O_4 and $Fe(OH)_2$ in their study of corrosion of steel by Permian Basin brines at 90, 150, and 200°C.

Previously obtained kinetic data (see, for example, Braithwaite and Larson, 1978; Haberman and Frydrych, 1988; Simpson and Schenk, 1989) imply that reactions 1 and 2 could, if sufficient brine were present, consume all of the Fe and Fe-base alloys in WIPP disposal rooms in 400 to 500 years. Brush (1990) found no data relevant to the corrosion of Fe and Fe-base alloys by H_2O vapor under conditions similar to those expected for the repository.

In the presence of microbially produced CO_2 or H_2S, anoxic corrosion of Fe or Fe-base alloys would produce $FeCO_3$ (siderite) or FeS_2 (pyrite), respectively. Although these reactions could consume all of these microbially produced gases, they could still produce large quantities of H_2. Brush (1990) found no kinetic data for these reactions under expected repository conditions.

We are carrying out or planning gravimetric (weight-loss) and electrochemical studies to: (1) quantify anoxic corrosion of low- and medium-C steels by WIPP brine (referred to as inundated conditions), H_2O vapor in equilibrium with WIPP brine (humid conditions), and H_2O absorbed by backfill materials, especially bentonite, at low pressures with N_2 and CO_2; (2) quantify anoxic corrosion of these steels at high H_2 pressures; (3) determine the effects of other factors, such as basic conditions and O_2 concentration on anoxic corrosion of steels; (4) quantify anoxic corrosion of other metals, especially Al and Al-base alloys. Brush (1990) described these studies in detail.

MICROBIAL ACTIVITY

Lappin et al. (1989) also estimated that, if sufficient brine and nutrients were present in WIPP disposal rooms, microbial degradation of cellulosics (mainly paper, treated and untreated lumber, and plywood) in TRU waste would produce about 1 mole of various gases per equivalent drum of waste per year for 600 years, or a total of 600 moles per drum. These gases could include CH_4, CO_2, H_2S, N_2, and NH_3, but the relative proportions are unknown at any given time and as a function of time. Microbial activity is the process of second greatest concern from the standpoint of the gas budget of the repository.

Because microbial activity may consume more H_2O than it produces, the quantity of H_2O in the DRZ available for transport to the waste, either by brine inflow or diffusion of H_2O vapor, may be insufficient for the production of 600 moles of gas per drum. The quantities of nutrients in WIPP brines and the waste may also limit microbial activity.

Conceptual models for the sequential use of electron acceptors by microorganisms in natural systems (see, for example, Froelich et al., 1979; Berner, 1980) and estimates of the quantities of electron acceptors that will be present in WIPP disposal rooms imply that the microbial processes denitrification, SO_4^{2-} reduction, and methanogenesis could affect the gas and H_2O budgets of the repository significantly. Aerobic respiration, reduction of Mn(IV) oxides and hydroxides, and reduction of Fe(III) oxides and hydroxides, on the other hand, would probably be insignificant.

Geochemists have described these microbial processes by writing overall reactions representative of each process (Froelich et al., 1979; Berner, 1980). They use formulas such as $(CH_2O)_{106}\cdot(NH_3)_{16}\cdot(H_3PO_4)$ (the Redfield ratio) or CH_2O (a simplified formula for glucose) to represent the substrate but rarely include synthesis of cellular material (biomass). Environmental microbiologists, on the other hand, usually include synthesis of biomass. To illustrate the effects of including biomass on the gas and H_2O budgets of WIPP disposal rooms, we present both types of reactions for the potentially significant microbial processes identified above. For the first reaction describing each process, we neglect synthesis of biomass and use the reaction of Berner (1980); for the second, we include synthesis of biomass according to McCarty (1969):

$$CH_2O + 0.8\ NO_3^- = 0.6\ H_2O + 0.8\ HCO_3^- + 0.2\ CO_2 + 0.4\ N_2; \tag{4a}$$

$$\begin{aligned} &CH_2O + 0.46\ H^+ + 0.46\ NO_3^- \\ &\quad = 0.076\ C_5H_7O_2N + 0.96\ H_2O + 0.624\ CO_2 + 0.192\ N_2; \end{aligned} \tag{4b}$$

$$CH_2O + 0.5\ SO_4^{2-} = 0.5\ H_2S + HCO_3^-; \tag{5a}$$

$$\begin{aligned} &CH_2O + 0.58\ H^+ + 0.04\ NO_3^- + 0.34\ SO_4^{2-} \\ &\quad = 0.04\ C_5H_7O_2N + 0.88\ H_2O + 0.18\ H_2S + 0.18\ HS^- + 0.4\ CO_2; \end{aligned} \tag{5b}$$

$$2\ CH_2O \rightarrow CH_4 + CO_2; \qquad (6a)$$

$$CH_2O + 0.04\ H^+ + 0.04\ NO_3^-$$
$$\rightarrow 0.04\ C_5H_7O_2N + 0.16\ H_2O + 0.26\ CH_4 + 0.44\ CO_2. \qquad (6b)$$

Microbial activity in WIPP disposal rooms would probably proceed according to the overall reactions written by microbiologists, at least initially. However, microbial degradation of previously synthesized biomass would decrease the ratio of existing biomass to the cumulative mass of substrate degraded, especially if the quantity of nutrients in brines and the waste limits biomass. Therefore, microbial activity could eventually approach the reactions written by geochemists.

These overall equations imply that all or most of the microbially produced CH_4, CO_2, H_2S, and N_2 would remain in the gaseous phase. It is also possible, however, to write these equations such that all or most of the CO_2 and H_2S dissolve in the aqueous phase. Significant quantities of CO_2 and H_2S would dissolve if enough brine were present and the pH of the brine were basic.

We are conducting or planning laboratory studies to: (1) determine which of the potentially significant microbial processes listed above occur under overtest conditions; (2) quantify the effects of those potentially significant processes that occur on the gas and H_2O budgets of WIPP disposal rooms under realistic conditions, both humid and inundated; (3) quantify the effects of pressure, if necessary, on any significant processes; (4) quantify the effects of potentially significant processes on the chemical behavior of the important radionuclides in the waste under realistic conditions; (5) determine whether or not the microorganisms responsible for any significant processes are likely to survive for periods sufficient to affect the long-term performance of the repository. As inocula, we are using various nonhalophilic microorganisms to simulate those present in the waste and halophilic microorganisms enriched from the WIPP Site and vicinity. Brush (1990) discussed these studies in detail.

RADIOLYSIS

Most of the data reviewed by Molecke (1979) imply that the radiolytic gas production rate for TRU waste in WIPP disposal rooms will be significantly lower than estimates by Lappin et al. (1989) of the gas production rates from anoxic corrosion or microbial activity.

However, estimates of the microbial gas production potential, and hence the total gas production potential, are very sensitive to assumptions of the extent to which microorganisms will degrade cellulosics and plastics in the waste to be emplaced in the WIPP. Lappin et al. (1989) estimated a microbial gas production potential of 600 moles per drum by assuming that microorganisms convert 100% of the cellulosics, 50% of the rubbers, but none of the plastics in the WIPP inventory to gas. Their estimate would have been much higher if they had assumed that microorganisms will degrade plastics significantly. The microbial gas production potential is much less sensitive to the conversion of rubbers because there is much less rubber than plastic in the inventory.

Microorganisms will almost certainly consume cellulosics in preference to plastics and rubbers. However, irradiation of plastics could cause scission, decreased saturation, and changes in the chemical composition of these materials such as uptake of N_2, O_2, and S, which could in turn make them more biodegradable (see Brush, 1990).

Compaction of previously or newly generated waste prior to emplacement and of emplaced waste during closure of WIPP disposal rooms may increase the radiolytic gas production rate by increasing the density of the waste and the extent to which α particles interact with it.

Inundation of the waste with brine may also increase the radiolytic gas production rate. The highest radiolytic gas production rates reviewed by Molecke (1979) occurred in sludges, and resulted from the high H_2O contents of the sludges. Furthermore, Gray and Simonson (1985) carried out an experimental and modeling study of α and γ radiolysis of brines at very high dose rates of 0.3 to 5 Mrad per hour. Their results suggest an equilibrium H_2 pressure of about 300 atm at an absorbed α dose of 2,000 Mrad. Because their dose rates were so much higher than those expected for brine in WIPP disposal rooms, the relevance of these results to the WIPP is unknown.

We are carrying out or planning laboratory studies to: (1) quantify the effects of α radiolysis on the biodegradability of polyethylene and polyvinyl chloride, the most important plastics in the WIPP inventory, under humid and inundated conditions; (2) determine the effects of waste compaction or inundation on the radiolytic gas production rate. Brush (1990) described these studies in detail.

PROPOSED BACKFILL ADDITIVES

Several proposed backfill additives could remove or prevent the production of some of the gases expected in WIPP disposal rooms (see Brush, 1990). $CuSO_4$ would, if brine were present, oxidize Fe and Fe-base alloys without producing H_2 by the reaction:

$$Fe + Cu^{2+} + SO_4^{2-} = Cu + Fe^{2+} + SO_4^{2-}. \tag{7}$$

$CaCO_3$, CaO, $Ca(OH)_2$, KOH, and NaOH would remove microbially or radiolytically produced CO_2 with and in some cases without brine present by reactions such as:

$$CaCO_3 + H_2O + CO_2 = Ca^{2+} + 2\ HCO_3^-; \tag{8}$$

$$CaO + CO_2 = CaCO_3; \qquad (9)$$

$$Ca(OH)_2 + 2\ CO_2 = Ca^{2+} + 2\ HCO_3^-; \qquad (10)$$

$$KOH + CO_2 = K^+ + HCO_3^-; \qquad (11)$$

$$NaOH + CO_2 = Na^+ + HCO_3^-. \qquad (12)$$

CaO, $Ca(OH)_2$, KOH, and NaOH would increase the pH of any brine present significantly. This could in turn affect the rate of anoxic corrosion of metals, the rate of microbial degradation of cellulosics, and the chemical behavior of radionuclides. Furthermore, the large quantities of these backfill additives that could be required would inhibit the closure of WIPP disposal rooms by increasing the strength of the materials in the repository. Whether the advantages of these backfill additives outweigh their disadvantages is still unknown.

There are no known backfill additives to remove CH_4, H_2, N_2, NH_3, or H_2S, or prevent the production of CH_4, N_2, NH_3 at reasonable cost. Fe, Fe-base alloys, or their corrosion products would remove H_2S, but the concomitant formation of FeS_2 would release large quantities of H_2.

Brush (1990) describes studies under way to: (1) determine whether or not the backfill additives $CaCO_3$, CaO, $CuSO_4$, KOH, and NaOH remove CO_2 or prevent the production of H_2 effectively; (2) quantify their effects on repository chemistry.

EFFECTS OF ANOXIC CORROSION, MICROBIAL ACTIVITY, RADIOLYSIS, AND BACKFILL ADDITIVES ON REPOSITORY CHEMISTRY

Because of the heterogeneous nature of design-basis TRU waste, the Eh and pH of any brine present in WIPP disposal rooms could vary significantly over short distances, perhaps just a few centimeters, after reacting with the waste. Oxidizing conditions, for example, could persist for lengthy periods near large, radionuclide-bearing particles because of continuous radiolytic production of O_2 and other oxidizing species from brine or sludges. Simultaneously, adjacent microenvironments devoid of radionuclides but with large quantities of metals and significant anoxic corrosion or organic matter and anaerobic microbial activity could rapidly become reducing. The pH could vary from acidic values in microenvironments containing microbially produced CO_2 to basic values near cements, grouts, and the proposed backfill additives CaO, $Ca(OH)_2$, KOH, and NaOH. Therefore, it is necessary to quantify the chemical behavior of Pu, Am. U, and Th under a wide range of conditions to define the source term for radionuclide-transport calculations.

CONCLUSIONS

Several chemical and microbial processes could affect the gas and H_2O budgets of WIPP disposal rooms significantly. We are carrying out the laboratory studies listed above to quantify these processes. The WIPP Project is also planning bin-scale and alcove tests to quantify these processes with actual contact-handled TRU waste (see Molecke, 1990a; 1990b).

The WIPP Project is investigating the consequences of gas production, especially its effects on room closure and possible release of radionuclides in the event of human intrusion. It is also considering engineered alternatives, including reprocessing the waste, to reduce the rate of or potential for gas production. Reprocessing options such as shredding, compacting, or grouting the waste could reduce the gas-production rate, but not necessarily the long-term gas-production potential. Incineration and vitrification would reduce the gas-production potential. Furthermore, reprocessing would reduce the range of Eh and pH expected for the repository. However, reprocessing would also result in near-term health risks for workers involved in waste treatment.

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